

# Solvent Engineering of Ionic Liquids for Stable and Efficient Perovskite Solar Cells

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Solution-processed perovskite solar cells (PSCs) are widely and dramatically developed with certificated record efficiency up to 25.7%, which have been regarded as the most promising candidates for next-generation photovoltaic devices. However, the current decent devices are dominantly fabricated based on traditional toxic organic solvents such as *N,N*-dimethylformamide and dimethyl sulfoxide, which inevitably leads to environmental damage and potential safety accidents. As green and nontoxic molten salts at room temperature, ionic liquids (ILs) as promising alternatives for traditional toxic organic solvents have attracted intensive research interest worldwide in the field of perovskite photovoltaics with encouraging development. Herein, especially concentrating on ILs solvent engineering rather than additive or post-treatment, discussion and summarization upon the recent progress on perovskite photovoltaics including both 3D and 2D-based PSCs is systematically carried out. An in-depth understanding regarding the interactions between IL molecules and perovskite precursor materials is thoroughly explored and summarized. Moreover, the detailed influence of ILs as solvent(s) on the aspects of perovskite material crystallization regulation, surface defect passivation, and performance improvement of resultant device is comprehensively overviewed and discussed. Finally, prospects of the application of ILs in the PSCs through solvent engineering are provided for further developments.

fabrication and decent PCE have enabled PSCs to be considered as one of the most potential candidates for next-generation solar cells.<sup>[5–7]</sup> In contrast to other deposition methods such as vapor-based one, solution processing approaches have attracted growing research attention worldwide since they can be compatible with roll-to-roll continuous manufacturing in industry and well matches the original motivation of low-cost characteristic of PSCs.<sup>[8,9]</sup> Intensive effort has been made in the solution-processed PSC with significant and promising progress.<sup>[10–12]</sup> Up to date, the majority of the reported decent PSCs are dominantly manufactured via solution processing from either one-step or two-step sequential deposition methods.

Encouraged by the highly efficient PSCs, huge research interests have been concentrated on device durability with multifarious approaches, including composition modification,<sup>[13,14]</sup> mixed-dimensional engineering,<sup>[13–16]</sup> grain-boundary passivation,<sup>[17,18]</sup> additive engineering,<sup>[19]</sup> transport layer engineering,<sup>[20,21]</sup> encapsulation engineering,<sup>[22]</sup> and so on. Li and

colleagues added an organic semiconductor material, 4,4'-(4,8-bis(5-(trimethylsilyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) (BDT-Si) into the conventional hole-transport layer (HTL), poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) through transport layer engineering.<sup>[23]</sup> Taking the advantages of excellent stability of the

## 1. Introduction

The rapid development of the field of perovskite solar cells (PSCs) has been witnessed in recent years since the first report in 2009 and the record power conversion efficiency (PCE) of single junction PSCs has already skyrocketed to 25.7%.<sup>[1–4]</sup> Low-cost

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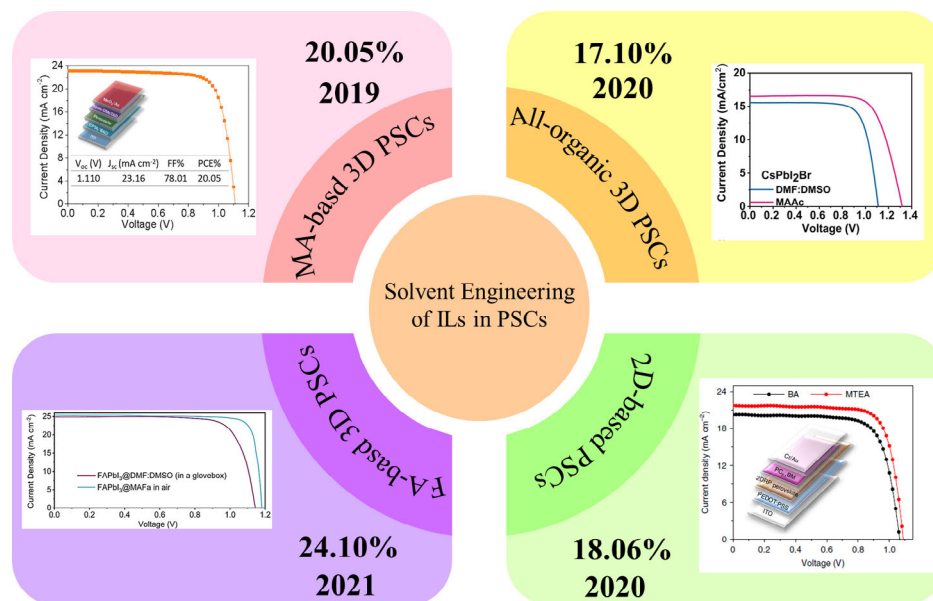
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PTAA:BDT-Si HTL film and the increased quality of the perovskite film, the corresponding PSCs exhibit robust operating stability. It leads to significant progress in the device stability, severely urging the scaling-up fabrication of PSCs for further massive manufacturing, such as blade coating,<sup>[10,24]</sup> inkjet printing,<sup>[25–27]</sup> magnetron sputtering,<sup>[28]</sup> slot-die coating,<sup>[29,30]</sup> and spray coating.<sup>[31,32]</sup> In all these processes, the selection of solvents plays a critical role in the dissolution of perovskite precursors and the formation of perovskite films.<sup>[33,34]</sup> Therefore, it is of great interest and necessity to systematically study the physical and chemical properties (boiling point, volatility, solubility) of solvents used in perovskite precursors, exploring more suitable candidates.<sup>[35]</sup> At present, organic solvents as the most widely used solvents in the preparation of perovskite films include *N,N*-dimethylformamide (DMF),<sup>[10]</sup> *N,N*-dimethylacetamide (DMAc),<sup>[36]</sup> dimethyl sulfoxide (DMSO),<sup>[37]</sup> *N*-methyl-2-pyrrolidone (NMP)<sup>[38]</sup> and  $\gamma$ -butyrolactone.<sup>[39,40]</sup> Recently, Huang et al.<sup>[41]</sup> reported a lead halide-template crystallization strategy to obtain high-quality films and air-printed high-performance PSCs through solvent optimization. The introduced NMP solvent can effectively inhibit the formation of solvent-coordinated perovskite intermediate complex and reduce the form energy of  $\alpha$ -phase perovskite. Although after optimization, the relevant PSCs possess outstanding performance of efficiency and stability. However, environmental friendliness and toxicity concerns have been considered one of the most urgent challenges for the further development of solution-processed PSCs toward massive production. To address this issue, acetonitrile,<sup>[42]</sup> water,<sup>[43]</sup> ethanol<sup>[44]</sup> have been adopted as the substitute for these toxic organic solvents in the preparation process of perovskite films.<sup>[45]</sup> But the relatively complex fabrication process and the unsatisfactory situation in the inferior performance of solar cells based on these solvents did not bring a promising result.

Therefore, searching out a suitable green solvent to replace the traditional toxic organic solvents without sacrificing the device performance in both photovoltaic and stability is the critical challenge researchers are working on.

In recent years, ionic liquids (ILs) have gradually entered into the sight of researchers because of their characteristics of environmentally friendly, wide liquid range, high carrier mobility, thermal and electrochemical stability and are widely used in flexible electronic devices,<sup>[46]</sup> intelligent materials,<sup>[47]</sup> energy devices,<sup>[48]</sup> and so on. The exciting thing is that equally effective applications of ILs occur in the perovskite field, including PSCs,<sup>[49,50]</sup> perovskite light-emitting diodes,<sup>[51]</sup> and perovskite photodetectors.<sup>[51]</sup> In particular, the additive engineering,<sup>[52–54]</sup> interface engineering,<sup>[55,56]</sup> and stability engineering<sup>[57,58]</sup> of ILs in PSCs have significantly promoted the development of high-efficiency devices. Unlike organic ferroelectric materials,<sup>[59]</sup> 2D materials,<sup>[60]</sup> organic semiconductors,<sup>[61]</sup> and organic salt<sup>[62]</sup> are applied singularly in interfacial or additive engineering for regulating the crystallization of perovskite film, the designability of chemical structures of ILs and the existence of hydrogen bonds as well as electrostatic network provided by cation and anion in ILs have prompted the same attention to ILs in solvent engineering to replace the toxic ones for improving the crystallization process with high quality perovskite film. It has also been reported that ILs can contribute to both the dissolution and stability of perovskite precursors solutions.<sup>[63,64]</sup> With those unique advantages, ILs have been considered as one of the most potential green solvent candidates for massive manufacturing high-quality perovskite films for PSCs.

In this review, we mainly focus on ILs as pure solvents for the preparation of high-quality perovskite films and corresponding high-performance PSCs as shown in **Figure 1**. The effects of



**Figure 1.** An overview of representative power conversion efficiency (PCE) of perovskite solar cells (PSCs) with different components based on solvent engineering of ionic liquids (ILs). Images for “MA-based 3D PSCs”: Reproduced with permission.<sup>[66]</sup> Copyright 2019, Elsevier Inc. Images for “FA-based 3D PSCs”: Reproduced with permission.<sup>[83]</sup> Copyright 2021, American Association for the Advancement of Science. Images for “All-organic 3D PSCs”: Reproduced with permission.<sup>[78]</sup> Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Images for “2D-based PSCs”: Reproduced with permission.<sup>[94]</sup> Copyright 2020, Springer Nature Limited.

ILs as pure solvents on the perovskite crystallization kinetics, morphology, and defect passivation as well as its influence on the photovoltaic property improvement of methylamine-based (MA-based), formamidine-based (FA-based), and all inorganic 3D perovskite films are systematically discussed and summarized. Moreover, the recent progress of the applications of ILs as pure solvents in 2D perovskite devices have also been over-viewed and analyzed. Finally, the challenges and prospects of ILs as single solvents in PSCs are provided for further research.

## 2. Solvent Engineering of ILs for 3D-Based PSCs

### 2.1. MA-Based PSCs

MA-based perovskite materials as one of the earliest studied perovskite with the traditional structure of  $ABX_3$ ,  $MA^+$  occupies the A position and the B position is usually composed of  $Pb^{2+}$  and  $Sn^{2+}$ , X position is halide ions ( $Cl^-$ ,  $Br^-$ ,  $I^-$ ).<sup>[65]</sup> Optimization of the device structure, perovskite composition, and fabrication conditions have enabled the MA-based perovskite devices with an efficiency of more than 23%.<sup>[66]</sup> However, at present, the reported MA-based perovskite films for high-efficient PSCs strongly rely on traditional organic solvents such as DMF or DMSO.<sup>[34,67]</sup> The toxicity and volatility of these organic solvents limit the massive fabrication conditions and further application of PSCs as discussed earlier.<sup>[68]</sup> Meanwhile, there also exists the dilemma on the instability of the device in the ambient environment through the processing of devices by current solvents although high PCE is delivered, resulting in the obstruction of commercialization.<sup>[69,70]</sup> To handle the aforementioned problems and obtain both efficient and stable MA-based PSCs, the optimization of pure solvent engineering is worth more research efforts.

ILs as green solvents were selected as a substitute for traditional organic solvents in PSCs (Table 1) and for the first time to dissolve perovskite precursor materials in 2015 by Moore and coworkers.<sup>[71]</sup> The employment of IL methylammonium formate (MAFa) to control the MA-based perovskite crystal growth to form high-quality  $MAPbI_3$  film has been systematically

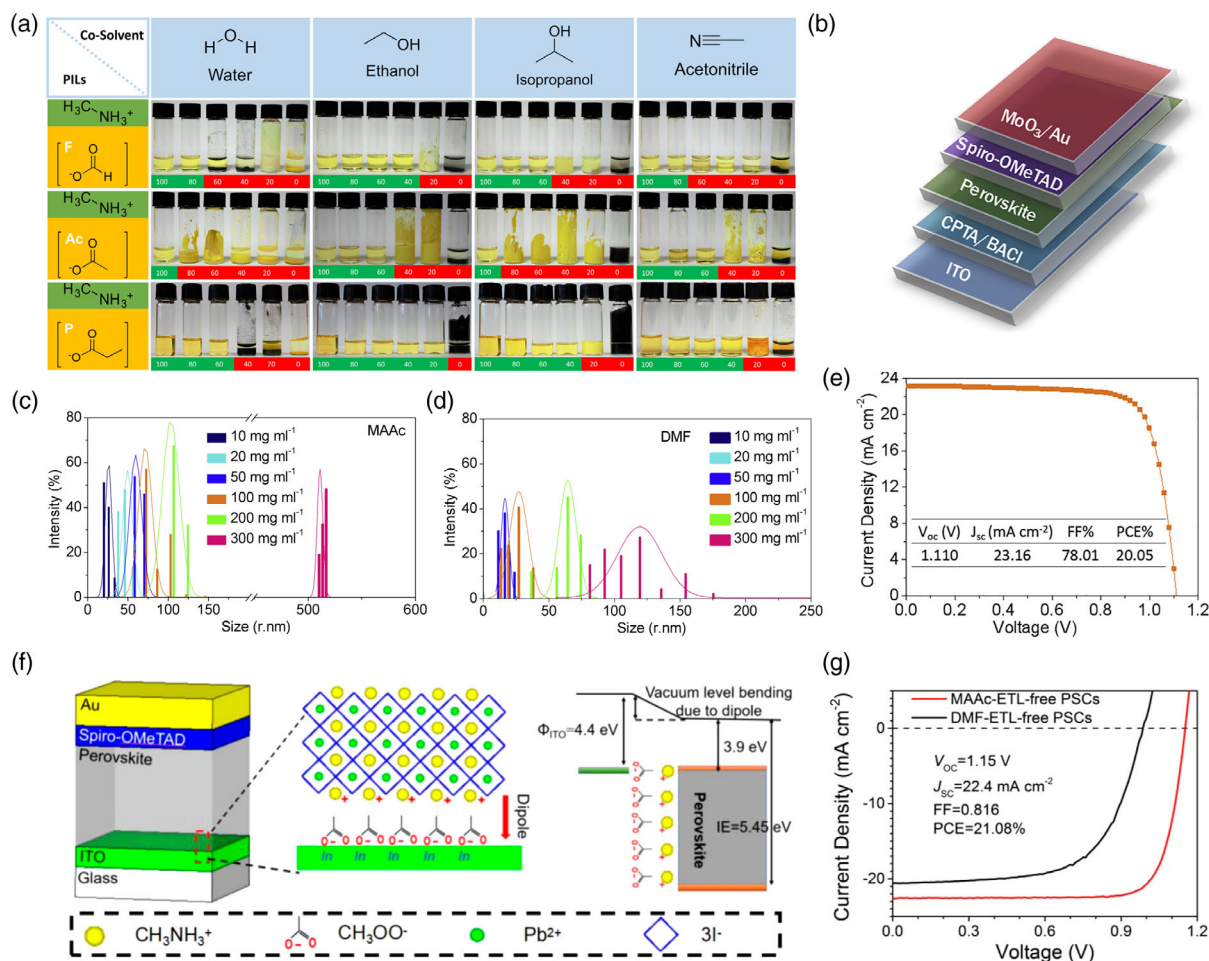
investigated. Another IL methylammonium acetate (MAAc) has been reported by Zhang et al.<sup>[72]</sup> to completely replace the toxic organic solvents (DMSO or DMF) system for the fabrication of high-quality  $MAPbBr_3$  film through a one-step process under ambient conditions. The formed strong  $NH^+ \cdots X^-$  hydrogen bonds between IL molecules and perovskite precursors in the MAAc solvent system have fundamentally contributed to the dissolution of perovskite precursors. Although the initial results showed that IL MAFa and MAAc possessed satisfactory solvability to  $PbX_2$  and MAX and IL can effectively improve the orientation of perovskite grains, the attention only stayed on perovskite thin film solidification process and the corresponding MA-based PSCs had not been involved yet. In 2018, Mathur and colleagues systematically investigated the solubility of MA-based perovskite precursors through ILs (MAFa, MAAc, and methylammonium propionate (MAPa)) as single solvent and co-solvents (Figure 2a).<sup>[45]</sup> Highly oriented  $CH_3NH_3PbI_3$  single crystals with an average size of around  $50 \mu m$  were formed through the dissolution of  $PbI_2$  in IL MAPa. However, the insurmountable dilemma still exists in the preparation of high-quality perovskite film at ambient temperature when IL as single solvent due to the viscosity of ILs-perovskite precursor inks. Ultimately, MA-based PSCs with the ILs MAPa as co-solvent in MAPa/acetonitrile/DMSO solvent system achieve a PCE of 15.46%.

In 2019, Chao and coworkers first proposed a strategy of IL as a single solvent for processing efficient and stable  $CH_3NH_3PbI_3$ -based PSCs under ambient air conditions (Figure 2b).<sup>[73]</sup> The nonuniform distribution of micelle size in DMF solvent has led to the formation of different sizes of perovskite crystal nuclei and eventually cause a rough surface of perovskite thin film. In contrast, the perovskite precursor in IL MAAc solvent system formed micelles with uniform size and ended up with a much smoother film. More importantly, a higher total colloid concentration showed up in the MAAc solvent system compared to the counterpart of the DMF system even with the same concentration of perovskite precursor solution (Figure 2c,d). The increased colloid concentration mainly originated from the formation of strong  $H^+ \cdots O=C$  hydrogen bonds in the IL MAAc solvent system after the addition of the perovskite precursor component ( $PbI_2$  and  $MAI$ ). The increased colloid concentration in MAAc solvent system can regulate the perovskite crystallization process to form a dense and pinhole-free perovskite film. Based on the high-quality perovskite thin film, the corresponding MAAc-PSCs delivered a maximum PCE of 20.05%, a short-circuit current density ( $J_{sc}$ ) of  $23.16 \text{ mA cm}^{-2}$ , open-circuit voltage ( $V_{oc}$ ) of 1.11 V, and a fill factor of 78.01% (Figure 2e). Meanwhile, the resulting unpackaged devices exhibited excellent stability with 93% of initial device efficiency in air after 1000 h under the humidity ranges from 30% to 80%. The application of MAAc as a single solvent for the acquisition of electron-transport-layer-free (ETL-free) PSCs in another interesting research was reported by Huang and colleagues (Figure 2f).<sup>[74]</sup> To process the perovskite photoactive layer for the ETL-free PSCs, the dissolved perovskite precursor in IL MAAc was directly spin-coated on top of the ITO substrate to fabricate  $MAPbI_3$  perovskite films without any anti-solvent treatment. Considering the existence of IL MAAc at the interface of the ITO/perovskite layer due to the high boiling point and low vapor pressure, MAAc can act as an interface modifier to promote charge collection and suppress interfacial charge

**Table 1.** Summary of the photovoltaic parameters of PSCs with solvent engineering of ILs.

Perovskite	ILs	$J_{sc}$ [ $\text{mA cm}^{-2}$ ]	$V_{oc}$ [V]	FF [%]	PCE [%]	References
$MAPbI_3$	MAFa	NA	NA	NA	NA	[71]
$MAPbI_3$	MAFa	NA	NA	NA	NA	[45]
$MAPbI_3$	MAFa	NA	NA	NA	NA	[77]
$MAPbBr_3$	MAAc	NA	NA	NA	NA	[72]
$MAPbI_{3-x}Cl_x$	MAAc	23.16	1.110	78.01	20.05	[73]
$MAPbI_3$	MAAc	22.40	1.150	81.60	21.08	[74]
$MASn_{0.3}Pb_{0.7}I_3$	MAAc	25.30	0.850	71.70	15.42	[75]
$FAPbI_3$	MAFa	25.34	1.170	81.36	24.10	[83]
$FA_xMA_{1-x}PbI_3Br_{3-x}$	MAAc	24.39	1.173	76.87	22.00	[76]
$CsPbI_{2.5}Br_{0.5}MAAc$	MAAc	17.67	1.300	74.18	17.10	[78]
$(MTEA)_2(MA)_4Pb_5I_{16}$	MAAc	21.77	1.088	76.27	18.06	[94]
$BA_2MA_{n-1}Pb_nI_{3n+1}$	BAAc	16.75	1.310	74.07	16.25	[93]





**Figure 2.** a) The picture of perovskite ink systems with IL methylammonium formate (MAFa), methylammonium acetate (MAAc), and methylammonium propionate (MAPa) as single solvent and co-solvent. Green indicates soluble and red indicates separation or formation of solids. Reproduced with permission.<sup>[41]</sup> Copyright 2018, Published by Elsevier Ltd. b) Schematic diagram of the device structure of planar MAAc-PSCs. c,d) Dynamic light scattering (DLS) spectra of perovskite precursor solution with different concentrations from 10 to 300 mg mL<sup>-1</sup> based on: c) MAAc and d) N,N-dimethylformamide (DMF) as a solvent, respectively. e) J-V curves of MAAc-PSCs measured under 100 mW cm<sup>-2</sup> AM1.5 G illumination. Reproduced with permission.<sup>[66]</sup> Copyright 2019, Elsevier Inc. f) Schematic diagram of electron transport layer (ETL)-free perovskite solar device structure and energy levels. g) J-V curves of ETL-free perovskite solar device. Reproduced with permission.<sup>[67]</sup> Copyright 2020, American Chemical Society.

recombination. As a result, the corresponding ETL-free MA-based PSCs exhibit a champion PCE of 21.08% (Figure 2g). Moreover, IL MAAc has also been employed as a pure solvent to fabricate Sn–Pb perovskite devices with the highest PCE of 15.42% through a one-step antisolvent-free method by Chen et al.<sup>[75]</sup> Notably, it was the first reported work that IL MAAc has been applied as a green solvent to fabricate Sn–Pb perovskite devices. As the Pb in perovskite material, considered with toxic concerns, has been partially replaced by Sn, it made one more step further to reduce the impact of perovskite devices on the environment, shed light on the bright future of “green” perovskite photovoltaic technology.

The principle of IL as a pure solvent to obtain efficient and stable devices has been systematically investigated by Huang and colleagues.<sup>[76]</sup> A full series of ILs, namely, MAFa, MAAc, MAPa, ethylammonium acetate (EAAc), propylammonium acetate (PAAC), and butylammonium acetate (BAAC) were first selected to perform as a solvent for the fabrication of

perovskite precursor solution. Then, the chemical interactions between ILs and perovskite precursor materials have been deeply investigated. The identical phenomenon in these different ILs systems was observed that all precursor solvents were colorless due to the strong chelation and hydrogen bonding interaction in the perovskite precursor solution, leading to the high saturation concentration of the perovskite precursor of 4 M in ILs systems.<sup>[76]</sup> The homologous dissolution phenomenon has also been reported in the research by Cho and colleagues for the preparation of large-area MAPbI<sub>3</sub> perovskite films.<sup>[77]</sup> More importantly, IL molecules as the pure solvent can effectively regulate the perovskite crystallization process and we take the MAAc–MAPbI<sub>3</sub> system as an example to better illustrate. PbI<sub>2</sub> and MAI were first dissolved in MAAc solvent to form a weak electrolyte due to the interaction of CH<sub>3</sub>COO<sup>-</sup> (Ac<sup>-</sup>) and Pb<sup>2+</sup>. The further reaction of heat-labile Pb(Ac)<sub>2</sub> with MAI transformed into MAPbI<sub>3</sub> under heating conditions. In contrast to the traditional organic solvent systems, the crystallization process of

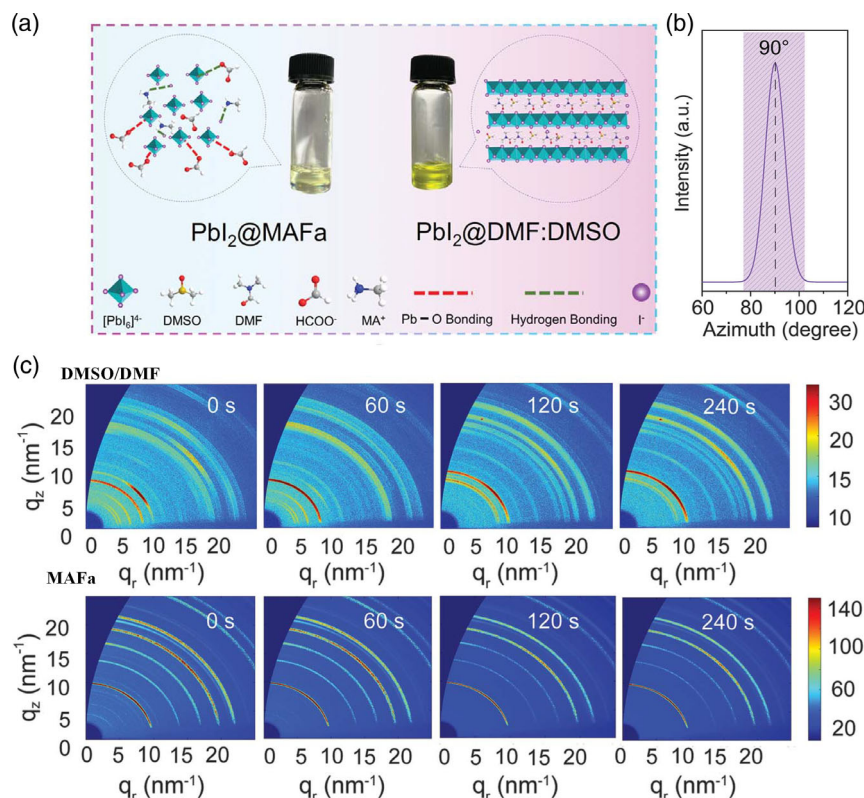
perovskite in the MAAC system has skipped the formation of multiple intermediate phases, which can cause unnecessary defects in perovskite film due to the incomplete phase-transition process, leading to the formation of high-quality perovskite films with fewer trap states. In addition to effect the dissolution of precursor materials and the crystallization process of perovskite, MAAC possessed the capability to passivate perovskite film by virtue of anchoring perovskite octahedrons through Pb–O interaction.<sup>[78]</sup>

## 2.2. FA-Based PSCs

As typical MA-based PSCs, the PCE of MAPbI<sub>3</sub> PSCs has been limited by the relatively larger bandgap and low charge-carrier mobility, due to the limited photo-current and photo-voltage of the devices.<sup>[13,41]</sup> After a few years of exploration, an FA cation-based FAPbI<sub>3</sub> perovskite material is proposed as an alternative to overcome the drawbacks of the MAPbI<sub>3</sub> counterpart.<sup>[79]</sup> However, tendentious transformation always happens from the perovskite phase ( $\alpha$ -FAPbI<sub>3</sub>) to the wide-bandgap yellow non-perovskite phase ( $\delta$ -FAPbI<sub>3</sub>) under the stimulus of the environment due to the temperature sensitivity of  $\alpha$ -FAPbI<sub>3</sub>, severely deteriorated device performance.<sup>[80]</sup> Some approaches mix alternative cations or anions to form hybrid formamidinium perovskites to stabilize  $\alpha$ -FAPbI<sub>3</sub>.<sup>[81,82]</sup> By doing so, great

breakthroughs of FA-based PSCs with satisfying efficiency and service life were realized, but these efficient and stable devices are still based on traditional toxic organic solvents.

Recently, Chen et al.<sup>[83]</sup> proposed a new strategy of synthesizing stable  $\alpha$ -FAPbI<sub>3</sub> under humidity and temperature by employing the IL MAFa as a solvent in two-step method. The lead iodide (PbI<sub>2</sub>) powder was dissolved in MAFa (Figure 3a) to obtain vertically aligned PbI<sub>2</sub> film, interpreting as the formation of strong interactions of C=O...Pb chelation and N–H...I hydrogen bonds in MAFa solvent with PbI<sub>2</sub> to promote the vertical growth (Figure 3b). Thus, MAFa as a substitute for organic solvents (DMSO or DMF) significantly improved the crystallization processes of PbI<sub>2</sub> to form full coverage of pinhole-free PbI<sub>2</sub> film. In addition, taking advantage of the strong interaction of chelation and hydrogen bond between residual MAFa and the PbI<sub>2</sub> framework, the MAFa-PbI<sub>2</sub> films exhibited better stability under high humidity conditions than the counterpart of DMF: DMSO-PbI<sub>2</sub>. More importantly, the formation of ion channels in MAFa system has promoted the entry of formamidinium iodide (FAI) into PbI<sub>2</sub> thin films, which remarkably reduced the formation energy barriers to suppress the transformation of PbI<sub>2</sub> to  $\delta$ -phase perovskite (Figure 3c). As a result, the corresponding PSCs based on MAFa-FAPbI<sub>3</sub> perovskite thin films achieved a PCE of 24.1% with the  $J_{sc}$  of 25.34 mA cm<sup>-2</sup>,  $V_{oc}$  of 1.17 V and FF of 81.36%, fabricated at the RH of 80%. The reduced tensile stress on the surface, low defect state density, and high crystalline



**Figure 3.** a) Schematic diagram of interactions in PbI<sub>2</sub>@MAFa and PbI<sub>2</sub>@DMF:DMSO solutions. b) Azimuth integration at  $q \approx 9.25 \text{ nm}^{-1}$  for PbI<sub>2</sub>@MAFa thin films from in situ grazing incidence wide-angle X-ray scattering (GIWAXS) spectra. c) In situ GIWAXS spectra of DMF:DMSO-FAPbI<sub>3</sub> perovskite and MAFa-FAPbI<sub>3</sub> perovskite thin films under different annealing times. Reproduced with permission.<sup>[83]</sup> Copyright 2021, American Association for the Advancement of Science.

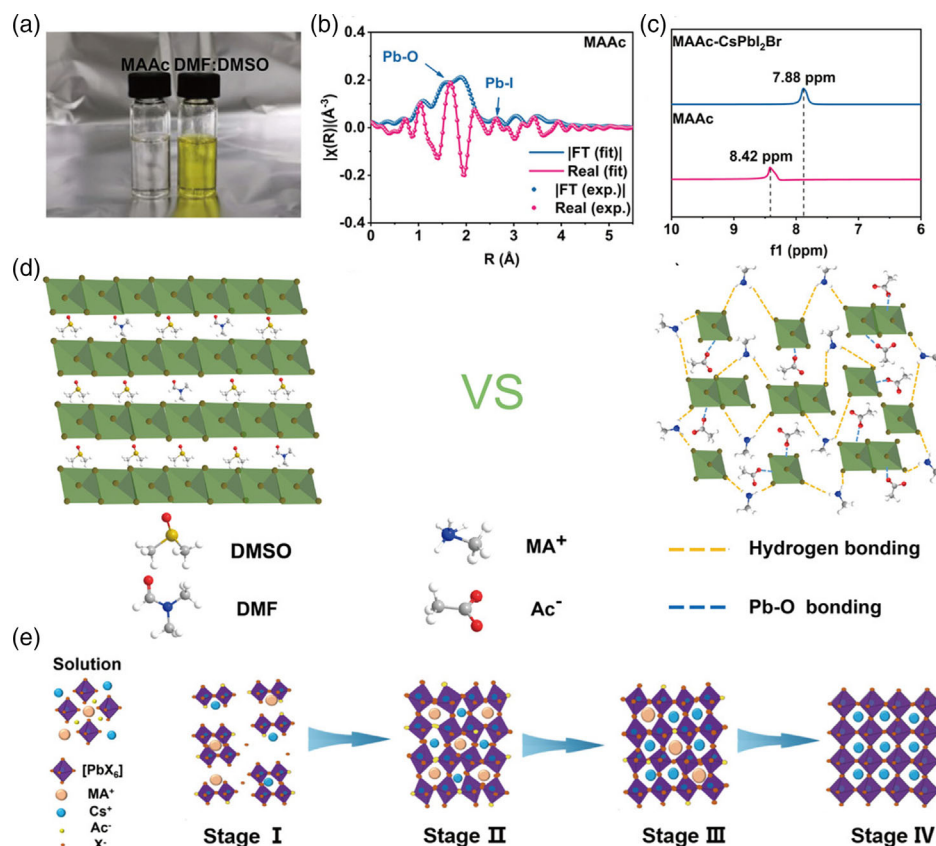
quality also endowed relevant PSCs with outstanding stability. The MAFA-devices maintained 93% of their initial PCE in the  $N_2$ -filled glove box after storage for 5000 h and retained 80% of its initial PCE at 85 °C in an  $N_2$ -filled glove box after 500 h. Huang and colleagues employed IL MAAC as a single solvent to obtain FA-based devices with a PCE of 22% through a one-step method in air.<sup>[76]</sup> Notably, the one-step preparation method based on IL as solvent simplified the traditional one-step process with an antisolvent and effectively optimized the operation steps to improve the repeatability without the dripping of the antisolvent. These breakthrough effects of these ILs as solvents in FA-based devices not only promoted the development of efficient and stable devices with processing conditions in air, but also improved the repeatability of the green and nontoxic solution preparation process.

### 2.3. All Inorganic-Based PSCs

Despite the breakthrough of organic–inorganic hybrid PSCs in efficiency, their long-term thermal stability still need to withstand the ordeals to meet commercialization.<sup>[84]</sup> Inorganic cesium cation ( $Cs^+$ ) was selected to substitute organic components to constitute all inorganic PSCs with superior thermal stability.<sup>[85,86]</sup>

Up to date, the reported all inorganic perovskite layer can maintain its absorbance after 100 h at 85 °C under ambient air conditions, and the corresponding all-inorganic devices achieve a PCE of 20.37%.<sup>[87]</sup> However, the present strategies principally concentrate on interface engineering,<sup>[88]</sup> additive engineering,<sup>[89]</sup> and component engineering<sup>[90]</sup> for the fabrication of efficient all-inorganic PSCs with long-term stability. Regarding green solvent engineering, the research on replacing generally accepted toxic organic solvents system (DMF and DMSO) are rarely mentioned.

Wang and coworkers proposed a solvent engineering strategy of employing the MAAC as a single solvent in the process of all-inorganic  $CsPbI_{3-x}Br_x$  PSCs.<sup>[78]</sup> Perovskite precursor solution appeared colorless in the MAAC system, while a clear yellow solution was observed in DMF:DMSO system (Figure 4a). The significantly different phenomenon has been interpreted as the existence of discriminating interactions between perovskite precursor materials and solvent. Specifically, the Pb–I bonds (yellow) were partially or totally superseded by Pb–O bonds (colorless) due to the stronger Pb–O interaction in the MAAC system (Figure 4b,c). Moreover, the formation of strong Pb–O interaction and N–H...I hydrogen bonds in the MAAC system (Figure 4d) promoted the dissolution of perovskite precursor materials and improved the crystallization process of all-inorganic



**Figure 4.** a) Photograph of MAAC and DMF:DMSO perovskite precursor solutions. b) Extended X-Ray absorption fine structure (EXAFS) spectra and fits in R-space at the Pb L3-edge of MAAC with the magnitude (blue line) and real components (pink line) of the Fourier transforms (FT). c)  $^1H$  Nuclear magnetic resonance ( $^1H$  NMR) spectra of MAAC solvent and MAAC perovskite precursor solution. d) Schematic diagram of interactions in DMF: DMSO and MAAC perovskite precursor solution. e) Schematic diagram of  $CsPbI_2Br$  film crystallization kinetics from stages I–IV with different annealing temperatures of 80, 100, 120, and 150 °C. Reproduced with permission.<sup>[78]</sup> Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

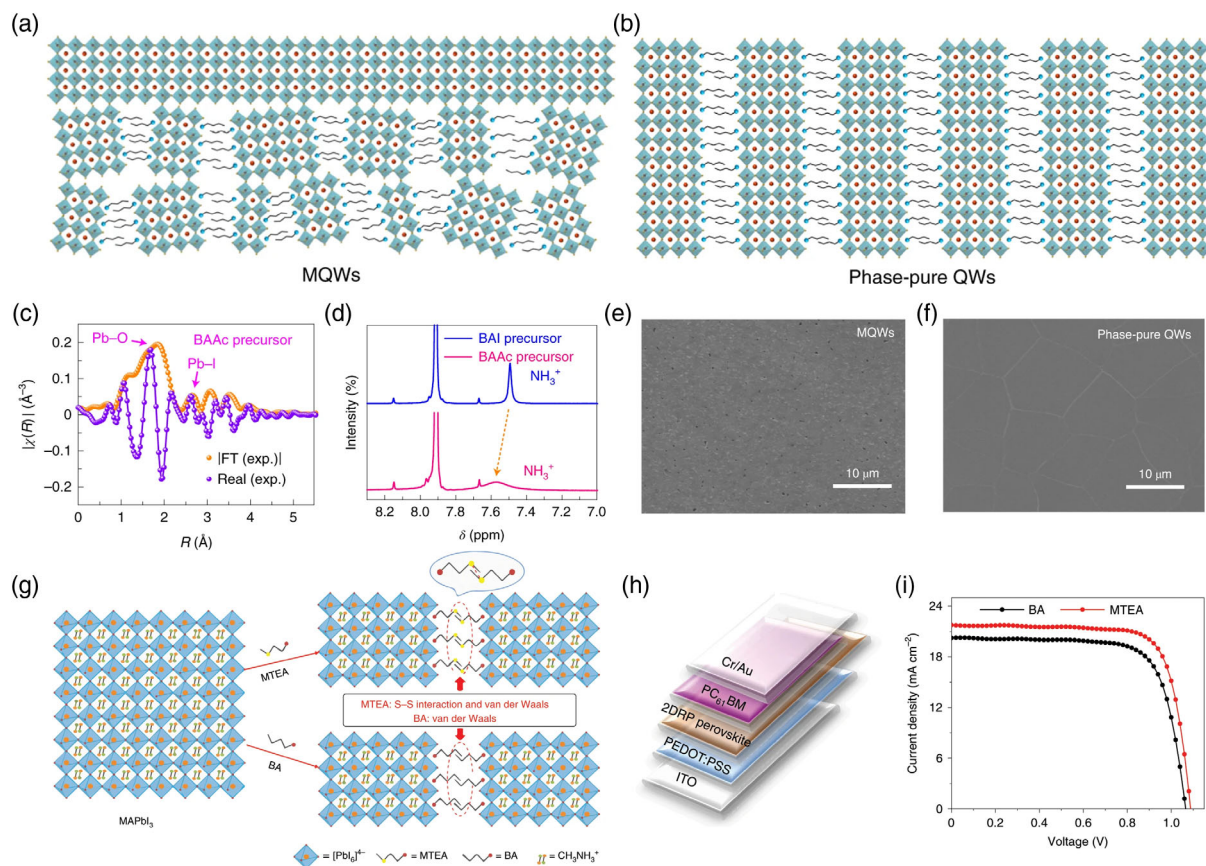


perovskite film. The formation of MAAC-CsPbI<sub>2</sub>Br films was divided into four stages as shown in Figure 4e. In stage 1, the nonvolatile MAAC induced the formation of intermediate perovskite phase Cs<sub>1-x</sub>MA<sub>x</sub>PbAc<sub>x</sub>I<sub>2-x</sub>Br after spin-coating and before the annealing stage. In stages II and III, Cs<sub>1-x</sub>MA<sub>x</sub>PbAc<sub>x</sub>I<sub>2-x</sub>Br gradually transformed into another intermediate phase CsPbI<sub>3-2t</sub>Br<sub>2t</sub> with the evaporation of MAAC. Subsequently, CsPbI<sub>2</sub>Br perovskite phase came into forming accompanied by the gradual disappearance of the two intermediate phases CsPbI<sub>3-2t</sub>Br<sub>2t</sub> and Cs<sub>1-x</sub>MA<sub>x</sub>PbAc<sub>x</sub>I<sub>2-x</sub>Br. The existence of these intermediate phases also effectively delayed the crystallization of the CsPbI<sub>2</sub>Br crystal films, leading to form the of high-quality film with a smoother morphology and large crystals in the MAAC system. Finally, in stage IV, MAAC was completely evaporated and the intermediate phase disappeared completely. Consequently, all-inorganic CsPbI<sub>2.5</sub>Br<sub>0.5</sub> devices achieved a PCE of 17.10% with V<sub>oc</sub> of 1.30, J<sub>sc</sub> of 17.67, and FF of 74.1%. Considering the complicated effect of the design of ILs and the interaction between ILs and perovskite precursor materials on the crystallization process

of all inorganic perovskite film and device performance, there are relatively few researches on the application of ILs as a single solvent in the field of all inorganic perovskite devices.

### 3. Solvent Engineering of ILs for 2D-Based PSCs

The application of ILs is not only limited to 3D PSCs, but also be extended to the field of 2D perovskite.<sup>[91]</sup> Currently, the obtained 2D-layered perovskites through solution methods easily produce a mixture of multiple quantum wells (MQWs) with a random well width distribution, which impedes the development of 2D-based PSCs.<sup>[92]</sup> Liang and colleagues introduced IL BAAC as spacer to replace the traditional halide spacer n-butylamine iodide (BAI) to acquire phase-pure quantum wells in 2D Ruddlesden-Popper layered PSCs.<sup>[93]</sup> In the traditional BAI system, thin and thick QWs (including the 3D phase) were distributed at the substrate and top respectively, which was prejudiced to the stability of the film (Figure 5a). A distinct phenomenon occurred



**Figure 5.** Structure diagram of: a) the multiple quantum well (MQW) film and b) the phase-pure QW film. c) Extended X-Ray absorption fine structure (EXAFS) spectra in R-space collected at the Pb L3 edge for the precursor solution prepared with BAAC. d) <sup>1</sup>H NMR spectra of the precursor solution prepared with BAAC in DMSO-d<sub>6</sub> at 295 K. A strong upfield chemical shift in the resonance signal of -NH<sub>3</sub><sup>+</sup> protons in BAAC precursor solution, compared to BAI precursor solution. Scanning electron microscopy (SEM) image of: e) the MQW film (<n> = 4) and f) phase-pure QW film (<n> = 4). Reproduced with permission.<sup>[93]</sup> Copyright 2020, Springer Nature Limited. g) Structure diagram of the 2DRP perovskites (BA)<sub>2</sub>(MA)<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> and (MTEA)<sub>2</sub>(MA)<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> and schematic diagram of van der Waals interactions and S-S interaction. h) Structure diagram of 2DRP PSCs with the structure of ITO/PEDOT:PSS/2DRP perovskite/PC61BM/Cr/Au. i) J-V curves of (MTEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> and (BA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> 2DRP perovskites devices under an AM1.5G solar simulator. Reproduced with permission.<sup>[94]</sup> Copyright 2020, Springer Nature Limited.

in the BAAC system, the formation of phase-pure QW films with a continuous phase distribution, leading to enhanced stability and efficient carrier transport in the vertical direction (Figure 5b). By analyzing the formation mechanism, the formed strong chelation and hydrogen bonding through introducing BAAC promoted the formation of phase-pure QW films (Figure 5c,d). In the perovskite precursor solution prepared with BAAC, the formative particles with a narrow size distribution of 0.6 nm, originating from strong chelation and hydrogen bonding for the suppression of the aggregation of colloids, which resulted to form the phase-pure QW films. Based on the uniformly distributed particle size in the perovskite precursor solution, the phase-pure QW films exhibited a smooth surface with a larger grain size than the MQWs film in the BAI system (Figure 5e,f). A device with the structure of layers of ITO/SnO<sub>2</sub>/perovskite QWs/spiro-OMeTAD (2,2',7,7'-tetrakis (*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene)/MoO<sub>3</sub>/Au achieved the champion PCE of 16.25% with a high  $V_{oc}$  of 1.31 V,  $J_{sc}$  of 16.75 mA cm<sup>-2</sup> and an FF of 74.07%. Moreover, the improved stability of devices based on phase-pure QW films was found through a uniformly protected function of the spacer layers on the inorganic slabs. The phase-pure QW solar cells maintained 93.8% of their initial PCE under 65 ± 10% relative humidity after 4680 h and 95.7% of their initial original PCE under heating at 85 °C after 558 h. Huang and coworkers reported a new bulky alkylammonium, 2-(methylthio)ethylamine hydrochloride (MTEACl) which contained S atoms as a spacer to fabricate 2D Ruddlesden–Popper phase (2DRP) perovskites film through employing MAAC as solvent.<sup>[94]</sup> In addition to the traditional van der Waals interactions, the involvement of the larger S atoms in MTEACl promoted the formation of S–S interaction in the 2DRP perovskites (MTEA)<sub>2</sub>(MA)<sub>*n*-1</sub>Pb<sub>*n*</sub>I<sub>3*n*+1</sub> (Figure 5g). Moreover, compared to the BA-based and 3D perovskite films, the phenomenon of much sharper and more discrete Bragg spots was found in the MTEA-based perovskite films from the results of grazing incidence wide-angle X-ray scattering (GIWAXS), which indicated highly oriented growth of 2DRP perovskites. The improved crystallinity and oriented growth in MTEACl-based 2DRP perovskites film facilitated efficient charge transport and extraction through continuous charge transport channels. Consequently, the (MTEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> PSCs with the structure of ITO/PEDOT: PSS/2DRP perovskite/PC61BM/Cr/Au achieved the champion PCE of 18.06% (17.8% certified) with  $J_{sc}$  of 21.77 mA cm<sup>-2</sup>,  $V_{oc}$  of 1.088 V, and an FF of 76.27% (Figure 5h,i). More importantly, the enhanced stability of (MTEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films under a constant temperature of 85 °C and 85% humidity in the air was induced by the existence of the S–S interaction to fastening framework of 2DRP perovskites. The device based on (MTEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films maintained 87.1% of its original PCE after the maximum power point (MPP) for 1000 h.

## 4. Summary and Prospects

In this review, we provide a comprehensive overview of the recent application and progress of solvents engineering of ILs in efficient and stable PSCs. Specifically, circumstantial description and summarization mainly concentrate on the aspects of familiar types of 3D-based PSCs and 2D-based

PSCs. Considering the characteristics of solution processability of perovskite film, we first discuss the dissolution principle of ILs as solvents for perovskite precursor materials and analyzed the interactions of between ILs and perovskite precursor materials in 3D-based PSCs. Upon the solubility of perovskite precursor materials in selected ILs, the latest evolution of employing solvents engineering of ILs for the fabrication of different types of 3D-based PSCs, including MA-based PSCs, FA-based PSCs, and all-inorganic-based PSCs are summarized, respectively. After that, we systematically summarize the function of solvent engineering of ILs in 2D-based PSCs. The summary of the solvent engineering of ILs will contribute to the acceleration of further development of devices and direct future correlative research efforts.

Notably, the solvents engineering of ILs endowed the current PSCs with a champion PCE of 24.1%, which is an approach to obtain devices through traditional organic solvent processing. More importantly, these ILs-devices are based on simplifying the environmental conditions requirements during the processing of devices. The processing conditions are extended into air or at a humidity of 80% instead of depending on the nitrogen environment. Even though these breakthroughs of solvents engineering of ILs have been reported in the territory of PSCs, the further development of ILs-device is still facing the following challenges: 1) A more comprehensive understanding of the effects of the chemical structure and physical properties of ILs on perovskite crystallization process is necessary and urgent to be delivered, which can provide clear guidance for the structural design of ILs for efficient PSCs with long service life. 2) The exploration of late-model type of ILs, which is appropriate for solvent engineering of PSCs needs to continue with practicability and commercial factors under consideration. 3) The expansion of ILs as solvents in large-area preparation process and the research of large-area devices based on ILs are worth focusing on. ILs will also be employed as potential materials to promote the commercialization of perovskite devices.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

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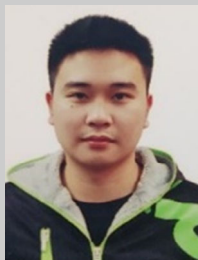


- [1] S. Y. Park, K. Zhu, *Adv. Mater.* **2022**, *34*, 2110438.
- [2] J. Jeong, M. Kim, J. Seo, H. Lu, P. Ahlawat, A. Mishra, Y. Yang, M. A. Hope, F. T. Eickemeyer, M. Kim, Y. J. Yoon, I. W. Choi, B. P. Darwich, S. J. Choi, Y. Jo, J. H. Lee, B. Walker, S. M. Zakeeruddin, L. Emsley, U. Rothlisberger, A. Hagfeldt, D. S. Kim, M. Grätzel, J. Y. Kim, *Nature* **2021**, *592*, 381.
- [3] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050.
- [4] M. A. Green, A. Ho-Baillie, H. J. Snaith, *Nat. Photonics* **2014**, *8*, 506.
- [5] H. Min, D. Y. Lee, J. Kim, G. Kim, K. S. Lee, J. Kim, M. J. Paik, Y. K. Kim, K. S. Kim, M. G. Kim, T. J. Shin, S. Il Seok, *Nature* **2021**, *598*, 444.
- [6] A. Zheng, M. Ren, Y. Zhang, Y. Cai, J. Zhang, Y. Yuan, M. Lei, P. Wang, *ACS Mater. Lett.* **2020**, *2*, 691.
- [7] Z. Qin, Y. Chen, K. Zhu, Y. Zhao, *ACS Mater. Lett.* **2021**, *3*, 1402.
- [8] Z. Saki, M. M. Byrannvand, N. Taghavinia, M. Kedia, M. Saliba, *Energy Environ. Sci.* **2021**, *14*, 5690.
- [9] X. Liang, X. Zhou, C. Ge, H. Lin, S. Satapathi, Q. Zhu, H. Hu, *Org. Electron.* **2022**, *106*, 106546.
- [10] H. Hu, M. Qin, P. W. K. Fong, Z. Ren, X. Wan, M. Singh, C. J. Su, U. S. Jeng, L. Li, J. Zhu, M. Yuan, X. Lu, C. W. Chu, G. Li, *Adv. Mater.* **2021**, *33*, 2006238.
- [11] H. Hu, Z. Ren, P. W. K. Fong, M. Qin, D. Liu, D. Lei, X. Lu, G. Li, *Adv. Funct. Mater.* **2019**, *29*, 1900092.
- [12] N. Xu, Y. Zhang, L. Fang, T. Li, X. Xie, J. Zhang, P. Wang, *ACS Mater. Lett.* **2022**, *4*, 11.
- [13] N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, S. Il Seok, *Nature* **2015**, *517*, 476.
- [14] K. Zou, Q. Li, J. Fan, H. Tang, L. Chen, S. Tao, T. Xu, W. Huang, *ACS Mater. Lett.* **2022**, *4*, 1101.
- [15] C. Ge, J. F. Lu, M. Singh, A. Ng, W. Yu, H. Lin, S. Satapathi, H. Hu, *Sol. RRL* **2021**, *6*, 2100879.
- [16] G. Uzurano, N. Kuwahara, T. Saito, A. Fujii, M. Ozaki, *ACS Mater. Lett.* **2022**, *4*, 378.
- [17] X. Zhu, S. Yang, Y. Cao, L. Duan, M. Du, J. Feng, Y. Jiao, X. Jiang, Y. Sun, H. Wang, S. Zuo, Y. Liu, S. Liu, *Adv. Energy Mater.* **2022**, *12*, 2103491.
- [18] Q. Jiang, Y. Zhao, X. Zhang, X. Yang, Y. Chen, Z. Chu, Q. Ye, X. Li, Z. Yin, J. You, *Nat. Photonics* **2019**, *13*, 460.
- [19] J. Zhu, D. H. Kim, J. D. Kim, D. G. Lee, W. Bin Kim, S. W. Chen, J. Y. Kim, J. M. Lee, H. Lee, G. S. Han, T. K. Ahn, H. S. Jung, *ACS Energy Lett.* **2021**, *3425*.
- [20] H. Yang, Y. Shen, R. Zhang, Y. Wu, W. Chen, F. Yang, Q. Cheng, H. Chen, X. Ou, H. Yang, F. Gao, Y. Li, Y. Li, *Adv. Energy Mater.* **2022**, 2202207.
- [21] Q. Cheng, H. Chen, F. Yang, Z. Chen, W. Chen, H. Yang, Y. Shen, X. M. Ou, Y. Wu, Y. Li, Y. Li, *Angew. Chemie - Int. Ed.* **2022**, *61*, e202210613, <https://doi.org/10.1002/anie.202210613>.
- [22] Z. Fu, M. Xu, Y. Sheng, Z. Yan, J. Meng, C. Tong, D. Li, Z. Wan, Y. Ming, A. Mei, Y. Hu, Y. Rong, H. Han, *Adv. Funct. Mater.* **2019**, *29*, 1809129.
- [23] G. Xu, R. Xue, S. J. Stuard, H. Ade, C. Zhang, J. Yao, Y. Li, Y. Li, *Adv. Mater.* **2021**, *33*, 2006753.
- [24] W. Q. Wu, P. N. Rudd, Q. Wang, Z. Yang, J. Huang, *Adv. Mater.* **2020**, *32*, 2000995.
- [25] Z. Wei, H. Chen, K. Yan, S. Yang, *Angew. Chem. Int. Ed.* **2014**, *53*, 13239.
- [26] P. Li, C. Liang, B. Bao, Y. Li, X. Hu, Y. Wang, Y. Zhang, F. Li, G. Shao, Y. Song, *Nano Energy* **2018**, *46*, 203.
- [27] S. K. Karunakaran, G. M. Arumugam, W. Yang, S. Ge, S. N. Khan, X. Lin, G. Yang, *J. Mater. Chem. A* **2019**, *7*, 13873.
- [28] B. Gao, J. Hu, S. Tang, X. Xiao, H. Chen, Z. Zuo, Q. Qi, Z. Peng, J. Wen, D. Zou, *Adv. Sci.* **2021**, *8*, 2102081.
- [29] F. Xu, J. Liu, A. S. Subbiah, W. Liu, J. Kang, G. T. Harrison, X. Yang, F. H. Isikgor, E. Aydin, M. De Bastiani, S. De Wolf, *Small Sci.* **2021**, *1*, 2000044.
- [30] Z. Yang, W. Zhang, S. Wu, H. Zhu, Z. Liu, Z. Liu, Z. Jiang, R. Chen, J. Zhou, Q. Lu, Z. Xiao, L. Shi, H. Chen, L. K. Ono, S. Zhang, Y. Zhang, Y. Qi, L. Han, W. Chen, *Sci. Adv.* **2021**, *7*, eabg3749.
- [31] J. E. Bishop, J. A. Smith, D. G. Lidzey, *ACS Appl. Mater. Interfaces* **2020**, *12*, 48237.
- [32] W. J. Scheideler, N. Rolston, O. Zhao, J. Zhang, R. H. Dauskardt, *Adv. Energy Mater.* **2019**, *9*, 1803600.
- [33] Q. Liang, K. Liu, M. Sun, Z. Ren, P. W. K. Fong, J. Huang, M. Qin, Z. Wu, D. Shen, C. Lee, J. Hao, X. Lu, *Adv. Mater.* **2022**, 2200276.
- [34] N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, S. Il Seok, *Nat. Mater.* **2014**, *13*, 897.
- [35] L. Chao, T. Niu, W. Gao, C. Ran, L. Song, Y. Chen, W. Huang, *Adv. Mater.* **2021**, *33*, 2005410.
- [36] J. Qiu, Y. Zheng, Y. Xia, L. Chao, Y. Chen, W. Huang, *Adv. Funct. Mater.* **2019**, *29*, 1806831.
- [37] N. Li, X. Niu, L. Li, H. Wang, Z. Huang, Y. Zhang, Y. Chen, X. Zhang, C. Zhu, H. Zai, Y. Bai, S. Ma, H. Liu, X. Liu, Z. Guo, G. Liu, R. Fan, H. Chen, J. Wang, Y. Lun, X. Wang, J. Hong, H. Xie, D. S. Jakob, X. G. Xu, Q. Chen, H. Zhou, *Science* **2021**, *373*, 561.
- [38] F. Yang, L. Dong, D. Jang, B. Saparov, K. C. Tam, K. Zhang, N. Li, C. J. Brabec, H. J. Egelhaaf, *Adv. Energy Mater.* **2021**, *11*, 2101219.
- [39] C. O. Ramírez Quiroz, I. Levchuk, C. Bronnbauer, M. Salvador, K. Forberich, T. Heumüller, Y. Hou, P. Schweizer, E. Spiecker, C. J. Brabec, *J. Mater. Chem. A* **2015**, *3*, 24071.
- [40] E. Rezaee, W. Zhang, S. R. P. Silva, *Small* **2021**, *17*, 2008145.
- [41] T. Bu, J. Li, H. Li, C. Tian, J. Su, G. Tong, L. K. Ono, C. Wang, Z. Lin, N. Chai, X. L. Zhang, J. Chang, J. Lu, J. Zhong, W. Huang, Y. Qi, Y. B. Cheng, F. Huang, *Science* **2021**, *372*, 1327.
- [42] R. Li, H. Zhang, M. Zhang, M. Guo, *Appl. Surf. Sci.* **2018**, *458*, 172.
- [43] X. Gong, M. Li, X. B. Shi, H. Ma, Z. K. Wang, L. S. Liao, *Adv. Funct. Mater.* **2015**, *25*, 6671.
- [44] P. Mao, Q. Zhou, Z. Jin, H. Li, J. Wang, *ACS Appl. Mater. Interfaces* **2016**, *8*, 23837.
- [45] S. Öz, J. Burschka, E. Jung, R. Bhattacharjee, T. Fischer, A. Mettenböcker, H. Wang, S. Mathur, *Nano Energy* **2018**, *51*, 632.
- [46] P. R. Pudasaini, J. H. Noh, A. T. Wong, O. S. Ovchinnikova, A. V. Haglund, S. Dai, T. Z. Ward, D. Mandrus, P. D. Rack, *Adv. Funct. Mater.* **2016**, *26*, 2820.
- [47] L. Chang, H. Liu, Y. Ding, J. Zhang, L. Li, X. Zhang, M. Liu, L. Jiang, *Nanoscale* **2017**, *9*, 5822.
- [48] M. Watanabe, M. L. Thomas, S. Zhang, K. Ueno, T. Yasuda, K. Dokko, *Chem. Rev.* **2017**, *117*, 7190.
- [49] A. Wang, X. Deng, J. Wang, S. Wang, X. Niu, F. Hao, L. Ding, *Nano Energy* **2021**, *81*, 105631.
- [50] Y. H. Lin, N. Sakai, P. Da, J. Wu, H. C. Sansom, A. J. Ramadan, S. Mahesh, J. Liu, R. D. J. Oliver, J. Lim, L. Aspitarte, K. Sharma, P. K. Madhu, A. B. Morales-Vilches, P. K. Nayak, S. Bai, F. Gao, C. R. M. Grovenor, M. B. Johnston, J. G. Labram, J. R. Durrant, J. M. Ball, B. Wenger, B. Stannowski, H. J. Snaith, *Science* **2020**, *369*, 96.
- [51] X. Peng, X. Yang, D. Liu, T. Zhang, Y. Yang, C. Qin, F. Wang, L. Chen, S. Li, *ACS Energy Lett.* **2021**, *6*, 4187.
- [52] J. Y. Seo, T. Matsui, J. Luo, J. P. Correa-Baena, F. Giordano, M. Saliba, K. Schenk, A. Ummadisingu, K. Domanski, M. Hadadian, A. Hagfeldt, S. M. Zakeeruddin, U. Steiner, M. Grätzel, A. Abate, *Adv. Energy Mater.* **2016**, *6*, 1600767.
- [53] S. Wang, B. Yang, J. Han, Z. He, T. Li, Q. Cao, J. Yang, J. Suo, X. Li, Z. Liu, S. (Frank) Liu, C. Tang, A. Hagfeldt, *Energy Environ. Sci.* **2020**, *13*, 5068.

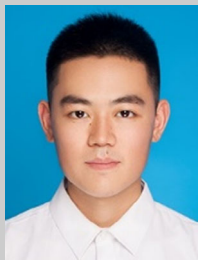
- [54] F. Wang, P. Wai-Keung Fong, Z. Ren, H.-L. Xia, K. Zhou, K. Wang, J. Zhu, X. Huang, X.-Y. Liu, H. Wang, Y. Shi, H. Lin, Q. Zhu, G. Li, H. Hu, *J. Energy Chem.* **2022**, *73*, 599.
- [55] X. Deng, L. Xie, S. Wang, C. Li, A. Wang, Y. Yuan, Z. Cao, *Chem. Eng. J.* **2020**, *398*, 125594.
- [56] F. Wang, D. Duan, M. Singh, C. M. Sutter-Fella, H. Lin, L. Li, P. Naumov, H. Hu, *Energy Environ. Mater.* **2022**, e12435, <https://doi.org/10.1002/eem.12435>.
- [57] E. Y. Muslih, A. K. M. Hasan, L. Wang, *Chem. Eng. J.* **2021**, *411*, 128461.
- [58] F. Wang, C. Ge, D. Duan, H. Lin, L. Li, P. Naumov, H. Hu, *Small Struct.* **2022**, *3*, 2200048.
- [59] W. Chen, S. Liu, Q. Li, Q. Cheng, B. He, Z. Hu, Y. Shen, H. Chen, G. Xu, X. M. Ou, H. Yang, J. Xi, Y. Li, Y. Li, *Adv. Mater.* **2022**, *34*, 2110482.
- [60] P. You, G. Tang, F. Yan, *Mater. Today Energy* **2019**, *11*, 128.
- [61] H. Chen, Q. Cheng, H. Liu, S. Cheng, S. Wang, W. Chen, Y. Shen, X. Li, H. Yang, H. Yang, J. Xi, Z. Chen, X. Lu, H. Lin, Y. Li, Y. Li, *Sci. Bull.* **2022**, *67*, 1243.
- [62] Y. Zhan, F. Yang, W. Chen, H. Chen, Y. Shen, Y. Li, Y. Li, *Adv. Mater.* **2021**, *33*, 2105170.
- [63] T. Niu, L. Chao, W. Gao, C. Ran, L. Song, Y. Chen, L. Fu, W. Huang, *ACS Energy Lett.* **2021**, *6*, 1453.
- [64] H. Gu, T. Niu, S. Zuo, Y. Cai, L. Chao, P. Müller-Buschbaum, Y. Xia, J. Zhang, G. Xing, Y. Chen, *CCS Chem.* **2022**, *4*, 3264.
- [65] J. Y. Kim, J. W. Lee, H. S. Jung, H. Shin, N. G. Park, *Chem. Rev.* **2020**, *120*, 7867.
- [66] K. Wang, C. Wu, Y. Hou, D. Yang, T. Ye, J. Yoon, M. Sanghadasa, S. Priya, *Energy Environ. Sci.* **2020**, *13*, 3412.
- [67] J. A. Christians, P. A. Miranda Herrera, P. V. Kamat, *J. Am. Chem. Soc.* **2015**, *137*, 1530.
- [68] Z. Arain, C. Liu, Y. Yang, M. Mateen, Y. Ren, Y. Ding, X. Liu, Z. Ali, M. Kumar, S. Dai, *Sci. China Mater.* **2019**, *62*, 161.
- [69] L. Meng, J. You, Y. Yang, *Nat. Commun.* **2018**, *9*, 5265.
- [70] N. Li, X. Niu, Q. Chen, H. Zhou, *Chem. Soc. Rev.* **2020**, *49*, 8235.
- [71] D. T. Moore, K. W. Tan, H. Sai, K. P. Barteau, U. Wiesner, L. A. Estroff, *Chem. Mater.* **2015**, *27*, 3197.
- [72] Z. Wang, M. Luo, Y. Liu, M. Li, M. Pi, J. Yang, Y. Chen, Z. Zhang, J. Du, D. Zhang, Z. Liu, S. Chen, *Small* **2021**, *17*, 2101107.
- [73] L. Chao, Y. Xia, B. Li, G. Xing, Y. Chen, W. Huang, *Chem* **2019**, *5*, 995.
- [74] D. Li, L. Chao, C. Chen, X. Ran, Y. Wang, T. Niu, S. Lv, H. Wu, Y. Xia, C. Ran, L. Song, S. Chen, Y. Chen, W. Huang, *Nano Lett.* **2020**, *20*, 5799.
- [75] S. Lv, W. Gao, C. Ran, D. Li, L. Chao, X. Wang, L. Song, Z. Lin, L. Fu, Y. Chen, *Sol. RRL* **2021**, *5*, 2100675.
- [76] L. Chao, T. Niu, H. Gu, Y. Yang, Q. Wei, Y. Xia, W. Hui, S. Zuo, Z. Zhu, C. Pei, X. Li, J. Zhang, J. Fang, G. Xing, H. Li, X. Huang, X. Gao, C. Ran, L. Song, L. Fu, Y. Chen, W. Huang, *Research* **2020**, *2020*, 2616345.
- [77] N. Cho, F. Li, B. Turedi, L. Sinatra, S. P. Sarmah, M. R. Parida, M. I. Saidaminov, B. Murali, V. M. Burlakov, A. Goriely, O. F. Mohammed, T. Wu, O. M. Bakr, *Nat. Commun.* **2016**, *7*, 13407.
- [78] X. Wang, X. Ran, X. Liu, H. Gu, S. Zuo, W. Hui, H. Lu, B. Sun, X. Gao, J. Zhang, Y. Xia, Y. Chen, W. Huang, *Angew. Chem. Int. Ed.* **2020**, *59*, 13354.
- [79] S. Akin, E. Akman, S. Sonmezoglu, *Adv. Funct. Mater.* **2020**, *30*, 2002964.
- [80] T. A. Berhe, W. Su, C. Chen, C. Pan, J. Cheng, H. Chen, M. Tsai, L. Chen, A. A. Dubale, B. Hwang, *Energy Environ. Sci.* **2016**, *9*, 323.
- [81] M. Qin, H. Xue, H. Zhang, H. Hu, K. Liu, Y. Li, Z. Qin, J. Ma, H. Zhu, K. Yan, G. Fang, G. Li, U.-S. Jeng, G. Brocks, S. Tao, X. Lu, *Adv. Mater.* **2020**, *32*, 2004630.
- [82] J. P. Correa-Baena, M. Saliba, T. Buonassisi, M. Grätzel, A. Abate, W. Tress, A. Hagfeldt, *Science* **2017**, *358*, 739.
- [83] W. Hui, L. Chao, H. Lu, F. Xia, Q. Wei, Z. Su, T. Niu, L. Tao, B. Du, D. Li, Y. Wang, H. Dong, S. Zuo, B. Li, W. Shi, X. Ran, P. Li, H. Zhang, Z. Wu, C. Ran, L. Song, G. Xing, X. Gao, J. Zhang, Y. Xia, Y. Chen, W. Huang, *Science* **2021**, *371*, 1359.
- [84] W. Zhang, H. Liu, X. Qi, Y. Yu, Y. Zhou, Y. Xia, J. Cui, Y. Shi, R. Chen, H. L. Wang, *Adv. Sci.* **2022**, 2106054.
- [85] M. B. Faheem, B. Khan, C. Feng, M. U. Farooq, F. Raziq, Y. Xiao, Y. Li, *ACS Energy Lett.* **2020**, *5*, 290.
- [86] Q. Tai, K. C. Tang, F. Yan, *Energy Environ. Sci.* **2019**, *12*, 2375.
- [87] S. M. Yoon, H. Min, J. B. Kim, G. Kim, K. S. Lee, S. Il Seok, *Joule* **2021**, *5*, 183.
- [88] X. Gu, W. Xiang, Q. Tian, S. Liu, *Angew. Chem. Int. Ed.* **2021**, *60*, 23164.
- [89] Y. Chen, X. Liu, Y. Zhao, *Angew. Chem. Int. Ed.* **2022**, *61*, e202110603.
- [90] S. Yuan, Y. Xian, Y. Long, A. Cabot, W. Li, J. Fan, *Adv. Funct. Mater.* **2021**, *31*, 2106233.
- [91] L. Chao, T. Niu, Y. Xia, Y. Chen, W. Huang, *Acc. Mater. Res.* **2021**, *2*, 1059.
- [92] H. Tsai, W. Nie, J. C. Blancon, C. C. Stoumpos, R. Asadpour, B. Harutyunyan, A. J. Neukirch, R. Verduzco, J. J. Crochet, S. Tretiak, L. Pedesseau, J. Even, M. A. Alam, G. Gupta, J. Lou, P. M. Ajayan, M. J. Bedzyk, M. G. Kanatzidis, A. D. Mohite, *Nature* **2016**, *536*, 312.
- [93] C. Liang, H. Gu, Y. Xia, Z. Wang, X. Liu, J. Xia, S. Zuo, Y. Hu, X. Gao, W. Hui, L. Chao, T. Niu, M. Fang, H. Lu, H. Dong, H. Yu, S. Chen, X. Ran, L. Song, B. Li, J. Zhang, Y. Peng, G. Shao, J. Wang, Y. Chen, G. Xing, W. Huang, *Nat. Energy* **2021**, *6*, 38.
- [94] H. Ren, S. Yu, L. Chao, Y. Xia, Y. Sun, S. Zuo, F. Li, T. Niu, Y. Yang, H. Ju, B. Li, H. Du, X. Gao, J. Zhang, J. Wang, L. Zhang, Y. Chen, W. Huang, *Nat. Photonics* **2020**, *14*, 154.



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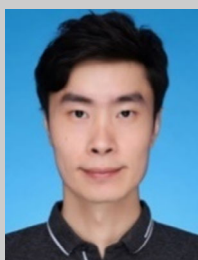
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