

F-containing cations improve the performance of perovskite solar cells

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Organic–inorganic halide perovskite solar cells (PSCs) have delivered power conversion efficiency (PCE) on par with that of crystalline silicon solar cells, due to the considerable effort on the optimization of perovskite materials and devices^[1]. The three-dimensional (3D) perovskite-based PSCs with the standard n–i–p architecture gave a certified PCE of 25.5%^[2]. However, the poor device stability under operating conditions remains an obstacle to commercialization. The 3D hybrid perovskite materials are susceptible to oxygen, UV light, humidity, heat, and electric fields^[3]. To improve device stability, two main strategies are applied: (1) improving the intrinsic stability^[4]; (2) providing sufficient protection. In the first case, tremendous efforts have been devoted to optimizing the perovskite absorbers: i) compositional engineering (mixing cations or anions, adding additives); ii) dimensional engineering (Ruddlesden-Popper and Dion-Jacobson type 2D perovskites); iii) passivating 3D perovskites using low-dimensional perovskites. In the second case, three approaches are used: i) developing moisture-resistant charge-transporting materials and electrodes; ii) engineering the interface between perovskite layer, transport layer, and electrodes; iii) encapsulating devices^[5].

Ionic defects cause hysteresis and poor stability^[6]. In conventional 3D PSCs (Fig. 1(a)), the perovskites suffer from two types of defects. One type is the intrinsic point defect in the bulk. These defects can interact with carriers through electrostatic interaction, harming charge transport. The built-in field is not enough to extract the carriers, and some of them can be trapped by these defects. The other type of defect originates from the dangling bonds, which act as the recombination centers. Two methods were used to passivate these defects: (1) adding additives into precursor solution^[7–11] or anti-solvents^[12] to control crystal growth and passivating defects at grain boundaries (GBs); (2) coating functional molecules onto perovskite layer^[13].

The gain in long-term stability was often accompanied by the sacrifice of PCEs^[14]. 2D/3D heterostructures can improve device stability without sacrificing the efficiency. A com-

mon approach to form a 2D/3D structure is to use bulky ammonium salts to do post-treatment. Hu *et al.* first developed a cation infiltration process to prepare layered perovskite (LP) structures on MAPbI₃ film^[15]. The bottom MAPbI₃ layer ensures efficient light absorption and charge generation, while the top layer serves as the charge extraction layer and moisture barrier. Among the bulky cations for LP structure, n-butylammonium (BA⁺)^[16, 17] and 2-phenylethylammonium (PEA⁺) are the most popular^[18, 19].

To further enhance the hydrophobicity of the bulky cations, fluorination is an effective strategy (Fig. 1(b))^[20]. Recently, Bi *et al.* used an aliphatic fluorinated amphiphilic ammonium salt, 1,1,1-trifluoro-ethyl ammonium iodide (FEAI), to improve the stability and performance of PSCs^[21]. In 2017, Karunadasa *et al.* reported that the aromatic amino (e.g., PEA)-based 2D perovskites have lower exciton binding energies than the aliphatic amino (e.g., BA)-based 2D perovskites due to the higher dielectric constant of the polarizable aromatic groups^[22]. They also found that F atoms could improve the moisture resistance.

In 2019, we first introduced 2-(4-fluorophenyl)ethylamine, 4-FC₆H₄C₂H₄NH₂ (pFPEA), to grow a 2D perovskite layer atop 3D perovskite to realize both high efficiency and high stability^[23]. The laser scanning confocal microscope was used to observe the distribution of *in-situ* formed 2D perovskite over 3D perovskite. We used density functional theory (DFT) to calculate the surface energy of the slab model ((100) plane). (pFPEA)₂PbI₄ has the lowest surface energy, consisting with the observed stability trend, i.e., (pFPEA)₂(MA)₂Pb₃I₁₀ > (PEA)₂(MA)₂Pb₃I₁₀ > MAPbI₃^[22] (Fig. 2(a)). The calculation also indicated that the defect formation energy of (pFPEA)₂PbI₄ is much higher than that of (PEA)₂PbI₄, which benefits the stability of 3D perovskite. (pFPEA)₂PbI₄ capping layer can protect 3D perovskite from moisture, reduce charge recombination, and facilitate hole transport. (Fig. 1(a))

Later, Zhang *et al.* used time-resolved microwave conductivity (TRMC) measurements to compare in-plane and out-of-plane transport in (PEA)₂PbI₄ and (pFPEA)₂PbI₄ films^[24]. The out-of-plane microwave mobility of (pFPEA)₂PbI₄ is ~7 times larger than that of (PEA)₂PbI₄. Fluorine substitution favors intermolecular packing and charge transport. As a result, the quasi-2D perovskite (pFPEA)₂MA₄Pb₅I₁₆ gave a PCE above 13%, which is higher than that of PEA-based perovskite. In ad-

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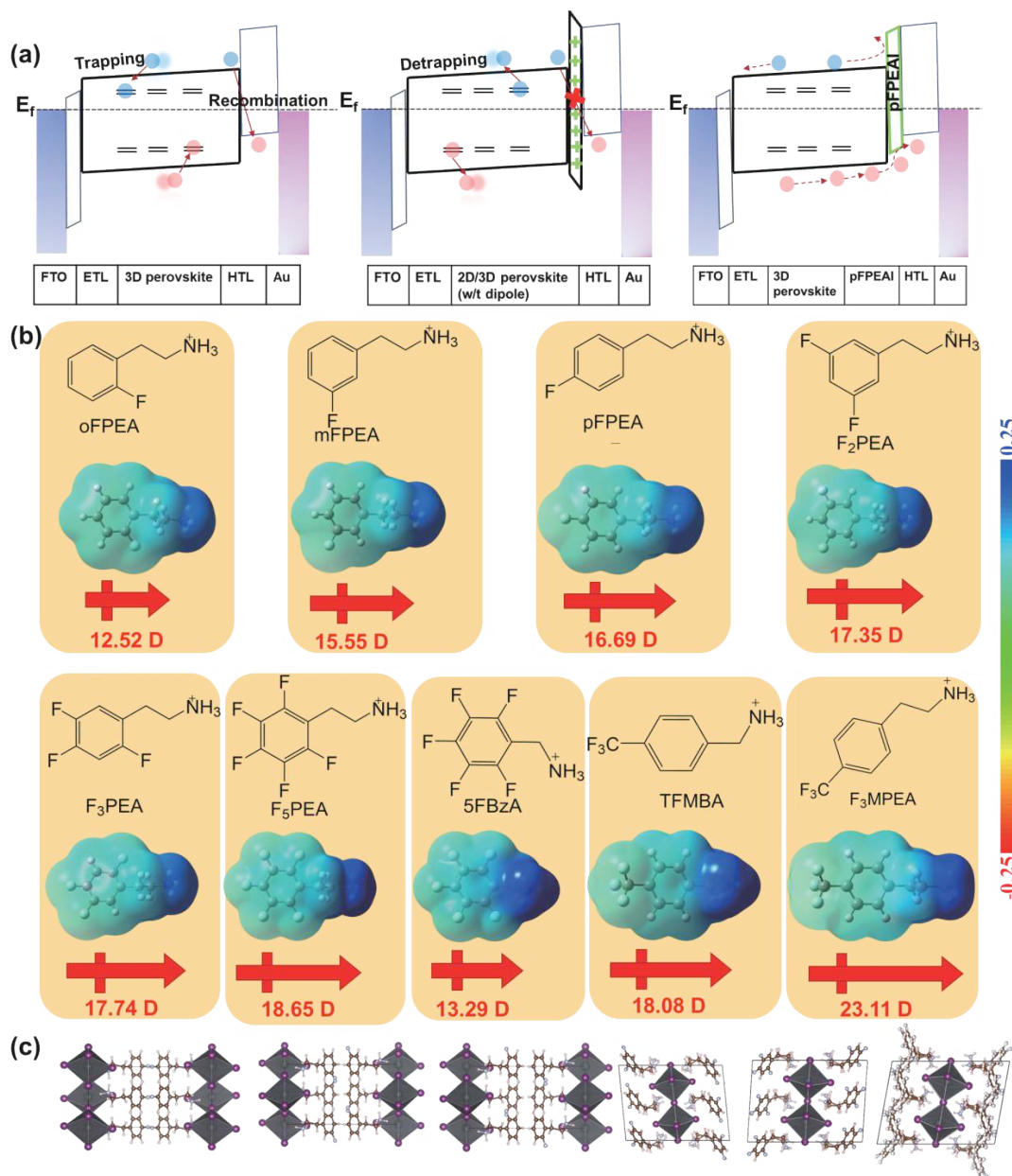


Fig. 1. (Color online) (a) Energy level diagrams for the devices with pristine 3D perovskite, 2D/3D bilayer perovskite, and pFPEAL passivated perovskite. (b) Calculated electrostatic potential surface (EPS) and electric dipole moment (EDM) for the ammonium salts. (c) Crystal structures of 2D perovskites. From left to right, $(\text{pFPEA})_2\text{PbI}_4$, $(\text{mFPEA})_2\text{PbI}_4$, $(\text{oFPEA})_2\text{PbI}_4$, $(\text{F}_2\text{PEA})_2\text{PbI}_4$, $(\text{F}_3\text{PEA})_2\text{PbI}_4$, $(\text{F}_5\text{PEA})_2\text{PbI}_4$.

dition, the thermal stability of pFPEA perovskites is significantly enhanced. Hu *et al.* demonstrated that mono-fluorination of PEA at different positions could influence the structure of 2D perovskites (empirical $(\text{xFPEA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$) and device performance^[25]. They concluded that phase distribution, surface morphology, and crystal orientation determined the properties of 2D perovskite films and device performance. By performing photoluminescence (PL) and transient absorption (TA) measurements, more random phase distribution was found in oFPEA 2D perovskite film than mFPEA and pFPEA 2D perovskite films. This trend is consistent with DFT-calculated formation energies ($\text{oFPEA}_2\text{PbI}_4 \gg \text{PEA}_2\text{PbI}_4 > \text{mFPEA}_2\text{PbI}_4 \approx \text{pFPEA}_2\text{PbI}_4$) (Fig. 2(b)).

The influence of F position on the surface dipole (Fig. 1(b)), photophysical properties, electrochemical properties, and photovoltaic performances of corresponding 2D/3D perovskites was elucidated by Zhou *et al.*^[26]. The combined

theoretical and experimental studies revealed that oFPEA provides the best passivation, possibly due to the highest formation energy. By using $(\text{oFPEA})_2\text{PbI}_4$ as the passivation layer on 3D perovskite, the planar PSCs demonstrated a PCE of 23.80% with a V_{oc} deficit of 0.39 V, which is the highest PCE for the 2D/3D architectures^[27].

As for interface passivation, the bulky cations only anchor on perovskite surface. Jiang *et al.* proposed an effective passivation by using pFPEAL^[13]. They confirmed that mono-fluorinated cations could passivate the defects at interfaces and GBs, increase moisture resistance, and improve device performance.

Polyfluorinated cations were also used, which produced an ultra-hydrophobic layer, protecting perovskite from ambient moisture while mitigating ion diffusion in the device. Liu *et al.* treated 3D perovskite with pentafluoro-phenylethylammonium iodide (F_5PEAI) to form an ultra-hydrophobic 2D per-

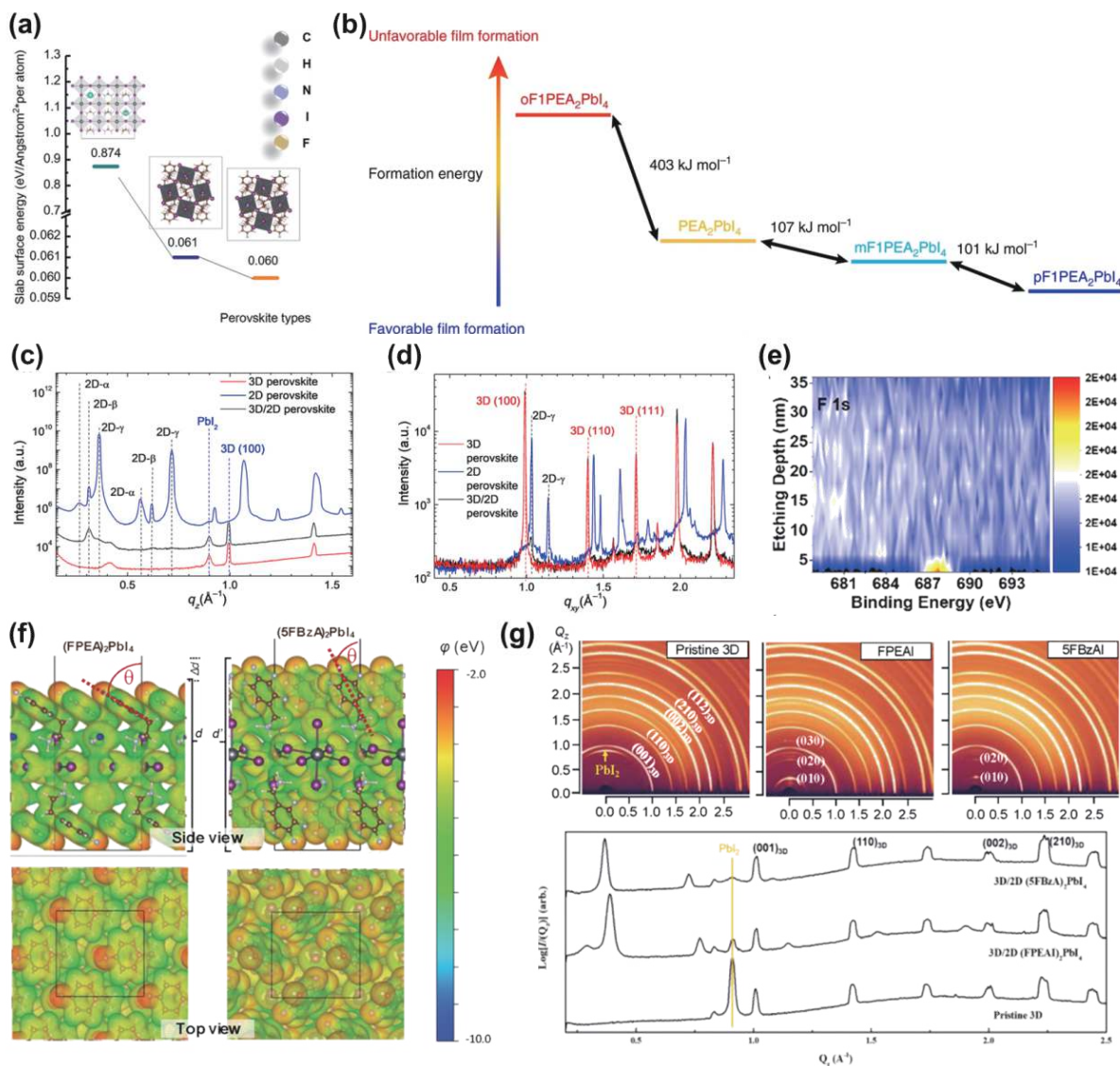


Fig. 2. (Color online) (a) DFT calculation for slab surface energy. From left to right, 3D perovskites, 2D (PEA)₂PbI₄ perovskites, 2D (pFPEA)₂PbI₄ perovskites. Reproduced with permission^[23], Copyright 2019, Wiley-VCH. (b) The formation energy for PEA₂PbI₄, oFPEA₂PbI₄, mFPEA₂PbI₄, and pFPEA₂PbI₄. Reproduced with permission^[25], Copyright 2019, Nature Publishing Group. (c) XRR profiles for 2D, 3D, and 2D/3D perovskite films. (d) GIXD data for 2D, 3D, and 2D/3D perovskite films. Reproduced with permission^[28], Copyright 2019, American Association for the Advancement of Science. (e) F 1s XPS depth profiles of the perovskite film with TFMBAl. Reproduced with permission^[32], Copyright 2021, ACS Publications. (f) Electrostatic potential at the surface of 2D perovskites containing FPEAI and 5FBzAI cations. (g) 2D-GIWAXS plots and azimuthally integrated intensity of pristine 3D and 2D/3D films. Reproduced with permission^[29], Copyright 2020, Wiley-VCH.

ovskite (F₅PEA)₂PbI₄^[28]. They estimated the thickness of the 2D perovskite layer to be ~8 nm by X-ray reflectivity (XRR, out-of-plane direction) and grazing incidence X-ray diffraction (GIXRD, in-plane direction) measurements (Figs. 2(c) and 2(d)). A PCE of 22.2% was achieved. The unsealed 2D/3D PSCs retained 90% of their initial efficiency after 1000 h operation in humid air under simulated sunlight. Paek *et al.* used a highly hydrophobic cation, perfluorobenzylammonium (5FBzA⁺), to form 2D perovskite with reinforced intermolecular interactions^[29]. Owing to the strong halogen-halogen interaction, (5FBzA)₂PbI₄ layer aligned in the in-plane orientation (Figs. 2(f) and 2(g)) and induced an increase in V_{oc} (60 mV), which is much higher than its monofluorinated analog pFPEAI. A high PCE of 21.65% and enhanced operational stability were obtained.

Moreover, Qiu *et al.* studied dipole moments of fluorin-

ated cations pFPEA⁺ and 4-(trifluoromethyl)phenethylammonium (F₃MPEA⁺) to understand the effect of fluorine numbers on the properties of 2D/3D perovskite and device performance^[30]. They found that the enlarged dipole moment can upshift Fermi level and increase the built-in field across 2D/3D perovskite heterojunction, thus facilitating charge transport. The 2D/3D PSCs delivered a PCE of 22.4%. Recently, 2D/3D perovskites with a series of *in-situ* grown (F_xPEA)₂PbI₄ (x = 1, 2, 3, 5) were tested^[31]. They systematically studied the performance and stability of the PSCs with different numbers of F. Among them, F₃PEA-based 2D/3D perovskite gave the best PCE (23.04%). F₅PEA-based device retained 95.0% of its initial PCE under ambient atmosphere (RH 60%) without encapsulation for 300 h.

F-containing bulky cations were also used for interface modification. Zhu *et al.* employed 4-(trifluoromethyl)benzy-

lammonium iodide (TFMBAI) as an amphiphilic modifier for interfacial defect mitigation. 4-(trifluoromethyl)pyridine (TFP) dopant was used to further enhance HTL's hydrophobicity^[32]. By using X-ray photoelectron spectroscopy (XPS) depth profiling, the thickness of TFMBAI layer is estimated to be ~5 nm (Fig. 2(e)). The nonradiative recombination is suppressed, and the PCE was enhanced from 20.9% to 23.9% with suppressed hysteresis. Besides the post-treatment, Wang *et al.* incorporated 0.3 mol% F₃PEAI into MAPbI₃ solution and obtained a maximum PCE of 21.1% for the inverted cell^[33].

Fluorinated aryl ammonium salts have recently been used in other fields. Shi *et al.* used fluorinated cations to make 2D perovskite ferroelectrics^[34]. They found that the position of fluorine is particularly essential. (oFBA)₂PbCl₄ (oFBA: 2-fluorobenzylammonium) is the first ferroelectric 2D perovskite, possessing a high phase transition temperature of 448 K. However, (3-fluorobenzylammonium)₂PbCl₄ and (4-fluorobenzylammonium)₂PbCl₄ showed no ferroelectric properties. Jiang *et al.* used polar pFPEA molecule to make quasi-2D perovskites for light-emitting diodes (LEDs)^[35]. The LEDs presented a peak external quantum efficiency (EQE) of 20.36%.

In short, fluorinated cations can improve the performance and stability of perovskite solar cells. To develop new F-containing cations is an interesting project in PSC field.

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