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Highly Efficient and Stable FA-Based Quasi-2D Ruddlesden-Popper Perovskite Solar Cells by the Incorporation of β -Fluorophenylethanamine Cations

Yunxin Zhang[#], Mingqian Chen[#], Tengfei He, Hongbin Chen, Zhe Zhang, Hebin Wang, Haolin Lu, Qin Ling, Ziyang Hu, Yongsheng Liu^{*}, Yongsheng Chen^{*}, Guankui Long^{*}

Y. Zhang, H. Wang, H. Lu, Dr. T. He, Prof. G. Long

School of Materials Science and Engineering, Smart Sensing Interdisciplinary Science Center, Tianjin Key Lab for Rare Earth Materials and Applications, Renewable Energy Conversion and Storage Center (RECAST), Nankai University, 300350, Tianjin, China.

M. Chen, Prof. Y. Liu, Prof. Y. Chen

The Centre of Nanoscale Science and Technology, Key Laboratory of Functional Polymer Materials, Institute of Polymer Chemistry, Renewable Energy Conversion and Storage Center (RECAST), College of Chemistry, Nankai University, 300071, Tianjin, China.

H. Chen, Z. Zhang, Dr. T. He, Prof. Y. Chen

State Key Laboratory and Institute of Element-Organic Chemistry, The Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials, Renewable Energy Conversion and Storage Center (RECAST), College of Chemistry, Nankai University, 300071, Tianjin, China.

Q. Ling, Prof. Z. Hu

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Department of Microelectronic Science and Engineering, Ningbo University, 315211, Ningbo, China

Corresponding E-mails: longgk09@nankai.edu.cn (G. L.); liuys@nankai.edu.cn (Y. L.); yschen99@nankai.edu.cn (Y. C.)

Abstract

Two-dimensional Ruddlesden-Popper (2D RP) perovskite, with attractive environmental and structural stability, has shown great application in perovskite solar cells (PSCs). However, the relatively inferior photovoltaic efficiencies of 2D PSCs limit their further application. To address this issue, β -fluorophenylethanamine (β -FPEA) as a novel spacer cation is designed and employed to develop stable and efficient quasi-2D RP PSCs. The strong dipole moment of the β -FPEA enhances the interactions between the cations and [PbI₆]⁴⁻ octahedra, improving the charge dissociation of quasi-2D RP perovskite. Additionally, the introduction of the β -FPEA cation optimizes the energy level alignment, improves the crystallinity, stabilizes both the mixed phase and α -FAPbI₃ phase of the quasi-2D RP perovskite film, prolongs the carrier diffusion length, increases the carrier lifetime and decreases the trap density. By incorporating the β -FPEA, the quasi-2D RP PSCs exhibit a power conversion efficiency (PCE) of 16.77% (*vs.* phenylethylammonium (PEA) based quasi-2D RP PSCs of 12.81%) on PEDOT:PSS substrate and achieve a champion PCE of 19.11% on the PTAA substrate. It's worth noting that the β -FPEA-based unencapsulated quasi-2D RP PSCs exhibit significant improvements in both thermal and moisture stability.

These findings provide an effective strategy for developing novel spacer cations for high-performance 2D RP PSCs.

Key Words: Ruddlesden-Popper perovskite, perovskite solar cell, quasi-2D perovskite, organic spacer, trap density

1. Introduction

In the past decade, perovskite materials have been used in photovoltaics,^[1-11] light-emitting diodes (LEDs),^[12] photodetectors,^[13] and spintronic devices,^[14-16] owing to their superior optoelectronic properties, such as large light absorption coefficients, long carrier lifetimes and high carrier mobilities. Recently, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has increased rapidly to over 25%.^[11, 17] However, the inherent instability of 3D perovskites and their mixed analogs under operational environments limits the commercial development of PSCs.^[18] Compared with 3D analogs, the low-dimensional Ruddlesden-Popper (RP) PSCs exhibit excellent long-term stability owing to the increased formation energy.^[19-21] The typical formula of 2D RP perovskites is described as $(RNH_3)_2A_{n-1}M_nX_{3n+1}$ (<n> = 1, 2, 3...), where RNH_3^+ represents a large organic ammonium spacer cation, the shape and size of RNH₃⁺ effectively influence the relative rotation and tilt of the $[PbI_6]^{4-}$ octahedra in the inorganic slab, thereby tuning the optoelectronic properties of 2D PSCs.^[22, 23] A is a small monovalent cation, such as CH₃NH₃⁺ (MA^+) and $HC(NH_2)_2^+$ (FA⁺), M is a metal cation (Pb²⁺, Sn²⁺), X is a halide anion (I⁻, Br⁻), and n indicates the number of $[PbX_6]^{4-}$ slabs.^[22-24] It was found that larger organic cations prevent moisture invasion and guarantee the superior environmental stability of 2D RP PSCs.^[24-26] However, the PCE of 2D RP PSCs still lags behind that of their 3D counterparts, it is highly mandatory to further improve their PCE towards the final goal of commercialization.^[25-29]

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Although numerous works have been reported on quasi-2D PSCs, most of them focus on MA-based quasi-2D PSCs,^[22, 25, 30] and a few works are about their FA analogs. Please note it is difficult to obtain high-quality FA-based perovskite films compared with their MA-based analogs, this is because the phase instability of FAPbI₃ films and the stronger interactions between the FA cations and corner-sharing $[PbI_6]^{4-}$ octahedra, and thus the more complicated crystallization of FA-based 2D PSCs.^[31-33] However, compared with MA-based quasi-2D PSCs, FA-based quasi-2D PSCs exhibit decreased bandgaps and higher absorption coefficients and thus larger short-circuit currents density (J_{sc}) .^[34] Therefore, to stabilize the α-FAPbI₃ phase/mixed phase of FA-based quasi-2D perovskite film and improve the PCE of quasi-2D PSCs, an effective and feasible strategy of adjusting the functionality of organic spacer cations has been put forward given the synthetic and structural versatility of organic spacers.^[23, 35-39] In particular, we choose the phenylethylammonium (PEA) which is widely used in MA-based 2D PSCs but rarely in FA-based 2D PSCs. Among the current reported PEA-based FA systems, their performance (PCE = 13.24% for <n>=9) shows great potential.^[40] Additionally, fluorinated organic spacer cations can enhance the efficiency and stability of PSCs by increasing the dipole moment of the chosen organic cation. This could be rationalized to enhance the interactions between the organic molecules and inorganic layers, which improve the crystal quality and charge separation ability and increase the carrier lifetime.^[41-46] According to the theoretical calculation, the fluorine-substituted organic spacer could distort the crystal structure of perovskite.^[42, 43] By using the above-mentioned strategy, we developed a novel fluorine-substituted PEA to improve the crystal quality of the quasi-2D RP perovskite film and boost the device's performance.

Herein, we synthesized a novel β -fluorine-substituted phenylethylamine (β -FPEA) cation to construct the quasi-2D RP perovskite and replace the conventional MA with FA to fabricate the inverted planar 2D RP PSCs. Compared with PEA-based 2D RP PSCs, the β -

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FPEA-based devices drastically increase the PCE from 12.81% to 16.77% on PEDOT:PSS substrate and achieved an encouraging PCE of 19.11% on the PTAA substrate (nominal <n> = 5). The β -FPEA-based 2D RP perovskite film optimizes the energy level alignment, enhances the crystal quality, promotes the dissociation of charges, and increases the carrier lifetime. Furthermore, we systematically investigated how β -FPEA cations improve the device performance by combining multiple structural, morphological and photophysical characterizations. Our findings demonstrate that the introduction of the fluorine atom in the β -site of organic spacer cations can provide a new facile strategy for the fabrication of high-performance and stable inverted 2D RP PSCs.

2. Results and Discussion.

Recently, fluorination has been proved to be an efficient molecular design strategy to improve the performance of organic solar cells through promoting exciton dissociation and charge transport.^[47-49] And fluorine substitution on the benzene ring of PEA cations was shown to induce a strong electric dipole moment for charge separation.^[22, 37] The β -FPEAI was synthesized from mandelic acid (1) through a series of reactions, as shown in **Scheme 1**. The detailed synthetic procedures are shown in the Supporting Information. The thermal gravimetric analysis (TGA) shows the β -FPEAI has good thermal stability with a decomposition temperature around 162 °C (Figure S1).



Scheme 1. Synthetic routes of β -FPEAI (8).

CCCDDLCC

Density functional theory (DFT) is employed to calculate the electric dipole moments of PEA (1.26 Debye) and β -FPEA (1.71 Debye) molecules (Figure S2). The higher polarity of β -FPEA could reduce the exciton binding energy, leading to a reduction in the Coulomb force between electron-hole pairs.^[43] The electrostatic potential (ESP) map of the β -FPEA and PEA cations is shown in **Figure 1a**. The large electronegativity of fluorine atoms could withdraw electrons and induce more positive charge accumulation on NH₃⁺ and thus a stronger Coulomb force between β -FPEA and the [PbI₆]⁴⁻ framework, which could make the perovskite crystal structure more stable.^[50, 51] The intrinsic high polarity and electron density of β -FPEA could change the dielectric environment around the perovskite lattice and promote the charge dissociation in the marginal states of the layered perovskite, thus leading to the enhanced J_{sc} .^[43] Then, FA-based 2D RP perovskite films of $(\beta$ -FPEA)₂(FA)_{n-1}Pb_nI_{3n+1}/(PEA)₂(FA)_{n-1}Pb_nI_{3n+1} (<n> = 5) were fabricated with β -FPEA or PEA as spacer cation by a one-step spin-coating method on the PEDOT:PSS substrate (note

that PSCs based on PEDOT:PSS substrates use simple additives, which could clearly reflect

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the influence of spacer cations on the device performance.^[36, 37, 52] The details of device fabrication are shown in the Supporting Information). A schematic illustration of the crystal structure of $(\beta$ -FPEA)₂FA₄Pb₅I₁₆ is shown in **Figure 1b**. To explore the interactions between the spacer cations and inorganic lattices, X-ray photoelectron spectroscopy (XPS) is performed on the PEA-and β -FPEA-based 2D RP perovskite films. As shown in **Figure 1c-d** and Figure S3, the incorporation of β -FPEA makes the F 1s peak clearer. The slight shift of the peaks for Pb 4f and I 3d towards the lower binding energy range may be related to the change of chemical environment and phase distribution around Pb and I atoms.^[23, 36]

Then the energy levels of PEA- and β -FPEA-based 2D RP perovskite films are measured by ultraviolet photoelectron spectroscopy (UPS), and the corresponding energy levels are depicted in Figure 1e and Figure 1f. The valence band maximum (VBM) and the conduction band minimum (CBM) of the perovskite films were determined to be -5.42 and -5.95 eV, -3.89 and -4.42 eV for β -FPEA- and PEA-based 2D RP perovskite films, respectively. Therefore, the β -FPEA-based 2D RP perovskite film shows better compatible energy level alignments with both the hole and electron transport layers, which could result in more efficient charge transport and collection.^[53-55] Compared with that of the PEA-based 2D RP perovskite film, the work function of β -FPEA-based 2D RP perovskite film shifts from -4.55 eV to -3.98 eV, and the energy level difference between the Fermi level ($E_{\rm F}$) and the CBM is only 0.09 eV, which is much lower than that of the PEA-based 2D RP perovskite film (0.13 eV). This indicates a more n-type characteristic of β -FPEA-based 2D RP perovskite film leading to reduce trap-assisted recombination and enhance open circuit voltage.^[44, 56, 57] The difference in energy level structure and work function between β -FPEAand PEA-based perovskite films may be caused by the different molecular dipoles of organic space ligands and phase distribution in perovskite films.^[44, 56]



Figure 1. (a) Top and cross views of the ESP maps of β -FPEA⁺ and PEA⁺. (b) Schematic illustration of the crystal structure of (β -FPEA)₂FA₄Pb₅I₁₆. XPS spectra of the (c) Pb 4f and (d) I 3d orbitals of PEA- and β -FPEA-based 2D RP perovskite films. (e) Energy diagrams of PEA- and β -FPEA-based 2D RP PSCs. (f) Schematic energy level diagrams of PEA- and β -FPEA-based 2D RP perovskite films.

The morphology of the PEA- and β -FPEA-based 2D RP perovskite films are characterized by scanning electron microscope (SEM). As shown in Figure S4, the PEA-based 2D RP perovskite film shows small needle-shaped crystals parallel to the substrate with a large grain boundary and rough morphology. The β -FPEA-based 2D RP perovskite film displays larger plate-shaped crystals perpendicular to the substrate, which is beneficial for charge transport due to the fewer grain boundaries and reduced traps.^[53] The change from needle-shaped morphology to plate shape indicates that β -FPEA ligand could improve the crystallinity of FA-based quasi-2D RP perovskite films.

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X-ray diffraction (XRD) is further employed to investigate the crystallinity of quasi-2D RP perovskite films. As shown in Figure 2a, both the PEA- and β -FPEA-based 2D RP perovskite films exhibit two dominant diffraction peaks, corresponding to the (111) and (202) crystal planes of the 2D RP perovskite. The β -FPEA-based 2D RP perovskite film shows a much stronger diffraction intensity than that of the PEA-based 2D RP perovskite film, indicating a higher film crystallinity of the β -FPEA-based 2D RP perovskite film. Typically, the (111) and (202) oriented peaks of 2D RP perovskites represent the crystal planes of the inorganic [PbI₆]⁴⁻ octahedral layer perpendicular and inclined to the substrate, respectively.^{[3,} ^{57]} The (202)/(111) diffraction intensity ratio increases from 0.32 to 0.47 for the PEA- and β -FPEA-based 2D RP perovskite films, respectively, demonstrating that more layered 2D perovskite prefers to grow perpendicular to the substrate for the β -FPEA-based 2D RP perovskite film. This could promote efficient charge transport between the active layer and transport layer.^[58] While the PEA-based 2D RP perovskite film exhibits obvious diffraction peaks of (0k0), indicating that low-*n*-value perovskite slabs grow along the direction parallel to the substrate, which is detrimental to the charge transport and collection in PSCs.^[3] Moreover, the amplified diffraction pattern in Figure 2a shows that the main peaks of the β -FPEA-based 2D RP perovskite film shift slightly to a lower diffraction angle, implying a small lattice expansion of the perovskite crystal after the introduction of the fluorine atom.^[59] To better evaluate the growth orientation of the PEA- and β -FPEA-based 2D RP perovskite films, Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) measurements are performed. As shown in Figure 2b, the PEA-based 2D RP perovskite film shows obvious (0k0) diffraction peaks, which is consistent with the film XRD as discussed above. The β -FPEA-based 2D RP perovskite film exhibits strong (111) diffraction spots, which correspond to a higher preferential vertical orientation to the substrate (Figure 2c). This

could promote effective charge transport and collection between anode and cathode, thereby enhancing the photovoltaic performance.^[58]

Conductive atomic force microscopy (c-AFM) is employed to investigate the surface local photocurrent distributions over the 2D RP perovskite films. **Figure 2d** and **Figure 2e** show the topography and corresponding photocurrent mapping of the PEA- and β -FPEA-based 2D RP perovskite films. The larger photocurrent density of the β -FPEA-based 2D RP perovskite film demonstrates that the accumulated electrons could induce the shifting of Fermi level to the conduction band, which is consistent with UPS results. The more unified surface photocurrent distribution of the β -FPEA-based 2D RP perovskite film (**Figure 2f**) confirms the better charge transport channel and therefore the enhanced performance of PSCs as discussed below.^[60]

In addition, for PSCs, the charge carrier diffusion length is also another key factor reflecting the crystal quality, charge transport and collection efficiency of the respected perovskite films.^[61] Thus, the diffusion lengths of the electron/hole in the PEA- and β -FPEA-based 2D RP perovskite films are quantified by time-resolved photoluminescence (TRPL). The quenching layers were PC₆₁BM (electron extraction layer) and PEDOT:PSS (hole extraction layer), respectively, and the electron and hole diffusion length is estimated by the simplified 1D diffusion model (Equation 1):^[62]

$$\frac{L_{\rm D}}{L} = \frac{2}{\pi} \sqrt{\frac{\tau}{\tau_{\rm D}} - 1} \tag{1}$$

where L_D stands for the charge diffusion length, L represents the thickness of the tested perovskite film, and τ_D and τ are the PL lifetimes of the perovskite film with and without the quenching layer, respectively. The fitting results are shown in Figure S5. Both the electron and hole diffusion lengths (L_D^E and L_D^H) were less than 1000 nm for the PEA-based 2D RP

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perovskite film. In contrast, the β -FPEA-based 2D RP perovskite film exhibits more prolonged diffusion lengths of 2761 nm and 2379 nm for the electrons and holes, respectively, which reconfirms the enhanced charge transport and collection efficiency after introducing β -FPEA as the organic spacer.

The high-resolution transmission electron microscopy (HRTEM) and fast Fourier transform (FFT) analyses of the PEA- and β -FPEA-based 2D RP perovskite films are further performed and shown in **Figure 2g**. The (0k0) lattice spaces are used to estimate the distance of the adjacent inorganic layers.^[57] The (0k0) lattice planes and corresponding calculated lattice distances for different *n*-values are summarized in Figure S6, Table S1 and Table S2. As shown in **Figure 2g**, for the 2D RP perovskite (PEA)₂(FA)_{n-1}Pb_nI_{3n+1} (<n> = 5), the interplanar spacings of 7.34 and 3.92 Å in regions A and B are well matched with the (0010) and (060) diffractions of the <n> = 1 and 2 phases, respectively. The phases of <n> = 4 and <n> = 6 in regions C and D could also be observed in the 2D RP perovskite (β -PEA)₂(FA)_{n-1}Pb_nI_{3n+1} (<n> = 5). The interplanar spacing calculated by FFT (Tables S1 and S2) matches well with the corresponding XRD results. The HRTEM results indicate that mixed 2D (different *n*-values) and 3D-like phases coexist in the PEA-/ β -FPEA-based 2D RP perovskite film, which could be attributed to the different thermodynamically stabilized 2D phases with different *n*-values.^[44]



Figure 2. (a) XRD patterns of 2D RP perovskite films (<n> = 5). GIWAXS of (b) PEA- and (c) β -FPEA-based 2D RP perovskite films. Conductive AFM images of (d) PEA- (e) β -FPEA-based 2D RP perovskite films and (f) the corresponding surface current curves. (g) TEM images of the PEA/ β -FPEA-based 2D RP perovskite films.

The phase stability of PEA-/ β -FPEA-based 2D RP perovskite films are further evaluated. It is worth noting that the color of the PEA-based 2D RP perovskite film spin-coated on glass changes from black to red when exposed to air at RH 40 ± 5%, which indicates the instability of the mixed phase. In contrast, the color of the β -FPEA-based 2D RP perovskite films barely changed (as shown in Figure S7). To elucidate these changes, we

performed time-resolved PL and XRD to analyze the structure evolution of the respected 2D RP perovskite film. Figure 3a and Figure 3b show the PL intensity mapping versus wavelength and time for the PEA- and β -FPEA-based 2D RP perovskite films. The PEA-based 2D RP perovskite film exhibits a noticeable change, and the PL peak of the 3D-like phase showed an obvious blueshift during the first 5 min. Then, at 10 min, distinct excitonic emission peaks dominated by $\langle n \rangle = 2$ appeared at 575 nm, and some slight excitonic emission peaks occurred at 621 and 665 nm, which were assigned to the $\langle n \rangle = 3$ and 4 phases according to the UV-vis absorption spectra (Figure 3c). Subsequently, the PL intensity of the low-dimensional phase gradually increased with time, indicating the composition of PEA-based 2D RP perovskite film changed under a certain humidity condition.^[63, 64] In contrast, the β -FPEA-based 2D RP perovskite film does not exhibit a clear change in the PL mapping. To further confirm the phase stability, we studied the in-situ phase change using a time-resolved XRD technique. As shown in Figure 3d, the main diffraction peaks (111) and (202) lattice planes were observed at 14.44° and 28.65° during the first 5 min for the PEA-based 2D RP perovskite film. Then, a series of diffraction peaks appeared at 4.31° , 8.33° , 16.25° and 20.20° , which were attributed to the $\langle n \rangle = 2$ phase (according to Figure S6). Moreover, a weak diffraction peak occurred at $2\theta = 12.23^\circ$, which was assigned to δ -FAPbI₃, and the relative peak intensity ratio between δ -FAPbI₃ and α -FAPbI₃ was calculated. The intensity of the δ -FAPbI₃ diffraction peaks gradually increased over time (Figure 3f). The β -FPEA-based 2D RP perovskite film showed strong diffraction peaks at 14.11° and 28.25° over time, and we did not observe the appearance of δ -FAPbI₃ (Figure 3e). Note that the weak diffraction feature at $2\theta = 12.8^{\circ}$ was assigned to exceed PbI₂, which facilitates the trap passivation at grain boundaries.^[65, 66] Therefore, we inferred the process of film phase transformations based on the in-situ test data (Figure 3g). First, the mixed phase in the PEA-based 2D RP perovskite film exhibits an instability state, especially under humid

conditions. This should be attributed to the weak interactions between the PEA cations and $[PbI_6]^{4-}$ octahedra, which results in inferior crystal quality and more defects at the grain boundaries.^[67] When the film is exposed to humid conditions, the defects at the grain boundaries are susceptible to H₂O-ingress which leads to the unfavorable $\alpha \rightarrow \delta$ phase transformation. Moreover, the mixed phase spontaneously forms a more stable low-dimensional phase, which inhibits H₂O from eroding the deeper structure of the perovskite. In comparison, the β -FPEA-based 2D RP perovskite film exhibits superior crystal quality and hydrophobicity (contact angle: 75.33° for β -FPEA and 56.47° for the PEA-based 2D RP perovskite film, as shown in Figure S8), which makes the mixed phase stable under humid conditions.

The optical properties of quasi-2D RP perovskite films are investigated by UV-vis spectroscopy, as shown in **Figure 3c** and Figure S9. The absorption intensity of the β -FPEA-based 2D RP perovskite film is significantly improved, presumably due to the increased light absorption capacity resulting from the increased crystal quality of the perovskite film. The PEA-based 2D RP perovskite film shows multiple exciton peaks at 570, 622 and 662 nm due to strong quantum confinement, which is detrimental to carrier transport. The optical bandgap slightly decreases from 1.54 eV (PEA) to 1.53 eV (β -FPEA), which are determined by the Tauc plots (Figure S10).

To elucidate the charge carrier dynamics in the 2D RP perovskite films, steady-state photoluminescence (PL) is performed. As shown in **Figure 3c**, the PL intensity of the β -FPEA-based 2D RP perovskite film is much stronger than that of the PEA-based 2D RP perovskite film, which should be attributed to the suppressed nonradiative recombination loss in the β -FPEA-based 2D RP perovskite film. Compared with the 3D FAPbI₃ film, both the PEA- and β -FPEA-based 2D RP perovskite films show clear blueshifts (Figure S11), which is

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due to the quantum confinement in the layered 2D perovskite.^[57] Compared with the PL peaks, the β -FPEA-based 2D RP perovskite film exhibits a significant redshift, which suggests a narrowed bandgap of (β -FPEA)₂(FA)₄Pb₅I₁₆ due to a larger Pb-I-Pb bond angle and a decrease in the inorganic octahedral structure spacing caused by the β -FPEA cation.^[26, 27] The PEA-based 2D RP perovskite film shows a low-*n*-value PL peak at approximately 570 nm, indicating an inhomogeneous phase distribution, which is harmful to exciton diffusion. However, the β -FPEA-based 2D RP perovskite film shows only one PL peak around 800 nm, and the lack of low-*n*-value emission peaks in the PL spectrum should be ascribed to the fast energy transfer from the doping of a low-to-high *n* area.^[57, 67]



Figure 3. Time-resolved PL mapping of (a) PEA- and (b) β -FPEA-based 2D RP perovskite films. (c) UV-vis and PL spectra of the corresponding 2D RP perovskite films. Time-resolved XRD mapping of (d) PEA- and (e) β -FPEA-based 2D RP perovskite films (δ : δ -FAPbI₃, *: PEA₂FAPb₂I₇) and (f) the ratio of δ -FAPbI₃ and α -FAPbI₃ XRD peaks intensity. (g) Schematic diagram of the film degradation process.

To investigate the photovoltaic properties of β -FPEA-based 2D RP PSCs, the inverted planar devices of $(\beta$ -FPEA)₂(FA)₄Pb₅I₁₆ (<n> = 5) with the architecture of ITO/PEDOT:PSS/2D RP perovskite/PC₆₁BM/BCP/Ag (Figure 4a) are fabricated. The detailed photovoltaic parameters under different scan directions based on PEDOT:PSS are summarized in Table 1. The current-voltage (J-V) curves of the PEA- and β -FPEA-based devices measured under standard AM 1.5 G (100 mW cm⁻²) light illumination are plotted in Figure 4b. The PEA-based device shows a lower PCE of 12.81% with J_{sc} of 19.03 mA cm⁻², $V_{\rm oc}$ of 1.04 V and FF of 64.79%. In contrast, the β -FPEA-based PSCs achieved a higher PCE of 16.77% with overall enhancements in the J_{sc} of 21.40 mA cm⁻², the V_{oc} of 1.05 V and the FF of 74.89%. The integrated current densities calculated from the external quantum efficiency (EQE) spectra (Figure 4c) were 18.82 and 21.39 mA cm⁻² for the devices based on the PEA and β -FPEA films, respectively, and matched well with the J_{sc} values obtained from the J-V curves. The steady-state photocurrent and power output of the β -FPEA-based 2D RP perovskite devices are measured to determine the actual power output by monitoring the photocurrent at the maximum power point (MPP) of the device under AM 1.5 G illumination. It exhibited a stabilized efficiency of 16.5%, which matched the PCE value of 16.77% shown in Figure 4d.

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To investigate the origin of the improved device performance, the trap densities and the carrier mobilities are determined by fabricating the electron-only (ITO/SnO₂/2D RP

perovskite/PC₆₁BM/Ag) and hole-only (ITO/PEDOT:PSS/2D RP perovskite/Spiro-OMeTAD/Ag) devices based on the space charge limited current (SCLC) method. The trap state density is calculated with the following Equation 2:

$$N_{\rm t} = \frac{2\varepsilon_0 \varepsilon_{\rm r} V_{\rm TFL}}{qL^2} \tag{2}$$

where V_{TFL} is the onset voltage of the trap-filled limit region, ε_0 stands for the vacuum permittivity, ε_r is the relative dielectric constant, q stands for the elemental charge, and L is the thickness of the perovskite film.^[53] As shown in Figure 4e and Figure S12a, both electron $(8.14 \times 10^{15} \text{ vs. } 5.59 \times 10^{15} \text{ cm}^{-3})$ and hole $(2.28 \times 10^{16} \text{ vs. } 1.06 \times 10^{16} \text{ cm}^{-3})$ trap densities of PEA-based 2D RP perovskite film are much higher than that of the β -FPEA-based 2D RP perovskite film. The decreased electron and hole trap densities in the β -FPEA-based 2D RP perovskite film is consistent with the enhanced and more balanced carrier mobility, which could reduce the trap-assisted recombination and facilitate the efficient charge transport.^[46] To further investigate the charge carrier recombination loss in PSCs, the corresponding light intensity-dependent J-V characteristics are performed. The J_{sc} versus light intensity shows a linear correlation on the double logarithmic scale for both devices (Figure S12b). The β -FPEA-based device displays an α value of 0.99, which is near 1 and higher than that of the PEA-based device (0.97), indicating less nongeminate recombination due to the reduced grain boundary and trap states, leading to improved FF and J_{sc} for the β -FPEA-based device. The V_{oc} versus the seminatural logarithm of light intensity (Figure 4f) shows a linear relationship with a slope of 1.62 $k_{\rm B}T/q$, where q refers to the elementary charge, $k_{\rm B}$ stands for the Boltzmann constant, and T denotes the temperature. This value is much lower than that of the PEA-based device (2.24 $k_{\rm B}T/q$), suggesting the suppressed trap-assisted recombination due to the improved film quality and decreased trap states of the β -FPEA-based device.

The TRPL was also used to study the charge carrier dynamics of the 2D RP perovskite films. A biexponential function is used to fit the TRPL curves (Equation 3):

$$Y = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + Y_0 \tag{3}$$

where τ_1 is the shorter lifetime attributed to the trap-assisted recombination at grain boundaries and τ_2 is the longer lifetime related to bulk film recombination. As shown in **Figure 4g**, the β -FPEA-based 2D RP perovskite film exhibited an obviously extended carrier lifetime compared to the PEA-based 2D RP perovskite film, which, combined with the enhanced steady-state PL intensity, suggests significantly reduced trap states and suppressed trap-induced nonradiative recombination losses in the β -FPEA-based 2D RP perovskite layer, resulting in an enhanced V_{oc} .

Transient photovoltage decay (TPV) and transient photocurrent decay (TPC) are performed to evaluate the charge recombination process under operating conditions. The β -FPEA-based device shows a much longer photovoltage decay life (35.5 µs *vs.* 23.4 µs) and shorter photocurrent decay time (526 ns *vs.* 601 ns) than that of the PEA-based device (**Figure 4h** and Figure S12c), indicating the enhanced charge carrier lifetime, improved charge extraction and collection efficiency, suppressed nonradiative recombination of β -FPEA-based 2D RP PSCs. To further understand the device physics with the β -FPEA as spacer cation, the electrochemical impedance spectroscopy (EIS) measurements are carried out at 1 V bias under dark conditions (**Figure 4i**). In the Nyquist plots, the β -FPEA-based device exhibits a much lower charge-transport resistance (R_{CT}) of ~20.7 Ω (~32.9 Ω for the PEA-based device), suggesting faster charge transport in the β -FPEA-based device due to the enhanced crystallinity and reduced trap density. Spacers with large polarities are known to reduce the dielectric limitation of layered RP perovskites, which is expected to reduce the

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exciton binding energy (E_b) and thus allow the further exploration of the exciton dissociation in the layered perovskites through temperature-dependent PL measurement (Figure S13a and 13b). Judging from the PL spectra, which could be found that different low-*n*-value phases exist in the PEA-based 2D RP perovskite film. In contrast, the β -FPEA-based 2D RP perovskite film exhibits a stronger PL intensity and narrower full-width at half-maximum (FWHM). For the 3D-like phases of the two films, a significant redshift is observed when the temperature is reduced from 340 K to 100 K, which may be attributed to the synergistic effect of lattice thermal expansion and electron-phonon coupling.^[59, 68] Furthermore, we chose the emission of the 3D-like phase to determine the E_b , which better reflects the overall properties of the film. The value of E_b was evaluated by fitting the temperature dependence of the PL intensities as a function of temperature (T) based on the Equation 4:

$$I_{\rm T} = \frac{I_0}{1 + A e^{E_b / k_{\rm B} T}} \qquad (4)$$

where $I_{\rm T}$ is the integral PL intensity at different temperatures, I_0 stands for the intensity at 0 K and $k_{\rm B}$ is the Boltzmann constant. As shown in Figure S13, the calculated $E_{\rm b}$ of the PEA- and β -FPEA-based 2D RP perovskite films (<n> = 5) are 156 meV and 140 meV, respectively. The reduced exciton binding energy of β -FPEA-based 2D RP perovskite film should be attributed to the introduction of a polar atom (fluorine) together with the energetically more favorable phase distribution in the film. On the contrary, the co-exist low-dimensional phases in PEA-based 2D RP perovskite film exhibits a larger exciton binding energy, which may hinder the efficient exciton dissociation and charge transport, resulting in poor device performance.^[57]

To further analyze the possible reason for device performance improvement, the Fourier transform photocurrent spectroscopy-external quantum efficiency (FTPS-EQE) is performed

to quantify the Urbach energy (E_u) .^[69] As shown in Figure S14, the exponential fitting of sub-band-gap FTPS-EQE spectra of β -FPEA-based 2D RP device exhibits much reduced energy disorder with E_u of 20.39 meV (*vs.* 163.85 meV of PEA-based 2D RP device), indicating that β -FPEA-based 2D RP perovskite film has better crystallinity and lower voltage loss.^[34, 70] This is also consistent with the morphological studies and device performances as discussed above.

 Table 1. Optimized device parameters for 2D RP perovskite devices under different scan

 directions based on PEDOT:PSS substrate.

Device	Scan	$V_{\rm oc}$	PCE	FF	$J_{ m sc}$	Integrated $J_{\rm sc}$
		(V)	(%)	(%)	$(mA cm^{-2})$	$(mA cm^{-2})$
PEA	RS	1.04	12.81	64.79	19.03	18.82
	FS	1.01	10.87	57.00	18.96	
β -FPEA	RS	1.05	16.77	74.89	21.40	21.39
	FS	1.05	16.38	73.32	21.35	



Figure 4. (a) Schematic device structure of 2D RP PSCs. (b) J-V curves of PEA- and β -FPEA-based devices. (c) EQE spectra and (d) stabilized power output of the 2D RP PSCs. Dark J-V characteristics of (e) the electron-only devices based on 2D RP PSCs. (f) Voc versus light intensity on a seminatural logarithmic scale. (g) TRPL spectra. (h) TPV decay curves under light conditions. (i) EIS spectra of 2D RP PSCs (measured at 1 V bias voltage under dark conditions).

To obtain high-performance PSCs based on the β -FPEA as spacer cation, the PEDOT:PSS hole transport layer was replaced by a PTAA layer, and the compound additives were used to fabricate the p-i-n planar PSCs with device structure of ITO/PTAA/2D RP

perovskite/PC₆₁BM/BCP/Ag. The detailed device fabrication is shown in the Supporting Information. The device parameters are summarized in Table 2. The β -FPEA-based PSCs achieved a champion PCE of 19.11% with a $J_{\rm sc}$ of 22.13 mA cm⁻², $V_{\rm oc}$ of 1.13 V and FF of 76.71%, the integrated J_{sc} from EQE spectrum is 21.94 mA cm⁻², which matched well with that obtained from the J-V curves (Figure S15a and Figure 15b). The standard box plots of the parameters of 15 devices are shown in Figure S15c-f. The hysteresis of PSCs based on PTAA substrate might be attributed to the additives used to fabricate the inverted PSCs, which lead to an accumulation of net ionic charge at the interface. This could introduce the dipole layers, thus enhancing the electric field near the contacts, and leading to the transient limitation of carrier transport diffusion.^[71, 72] The PL spectra (Figure S16), light intensity-dependent J-V curves (Figure S17) and XRD spectra (Figure S18) indicated that β -FPEA-based 2D RP perovskite film on the PTAA substrate can enhance the hole extraction efficiency and reduce the trap states and trap-induced nonradiative recombination losses due to the improved film crystallinity on the PTAA substrate, consequently enhances the device performance of the 2D RP PSCs. The HRTEM and FFT analyses of the β -FPEA-based 2D RP perovskite film on PTAA substrate exhibit the different low-*n*-value phases (Figure S19), which indicate that mixed 2D (different *n*-values) and 3D or 3D-like phases coexist in the β -FPEA-based 2D RP perovskite film on the PTAA substrate.

Table 2. Optimized device parameters for 2D RP perovskite devices under different scan

 directions based on PTAA substrate.

Device	Scan	$V_{\rm oc}$	PCE	FF	$J_{ m sc}$	Integrated $J_{\rm sc}$

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		(V)	(%)	(%)	$(mA cm^{-2})$	$(mA cm^{-2})$
β -FPEA	RS	1.13	19.11	76.71	22.13	21.94
	FS	1.12	17.67	71.13	22.10	

Finally, the stabilities of the unencapsulated devices based on the β -FPEA and PEA spacer cations are examined. The unencapsulated β -FPEA- and PEA-based 2D RP perovskite films (3D FAPbI₃ film is used as the control) are directly exposed to ambient conditions (RT, RH $35 \pm 5\%$, natural light) and measured by monitoring their XRD patterns. As shown in **Figure 5a**, after 24 h, the diffraction peak at $\sim 12.1^{\circ}$ which corresponds to the unfavorable δ -phase appears in the FAPbI₃ film and after 168 h, the α -phase FAPbI₃ completely degraded to the δ -phase FAPbI₃. The PEA-based 2D RP perovskite film after 168 h began to display low-*n*-value peaks that could be observed more obviously after 336 h (Figure 5b). Impressively, no obvious changes were observed in the β -FPEA-based 2D RP perovskite film (Figure 5c), indicating improved environmental stability. The thermal stabilities of the unencapsulated 3D FAPbI₃, PEA- and β -FPEA-based 2D RP perovskite films are tested at 80 °C in ambient air with RH $35 \pm 5\%$. As shown in Figure 5d, after 168 h of storage under the test conditions, the diffraction peak of the δ -phase of the 3D FAPbI₃ perovskite film could be clearly observed, suggesting the degradation of the 3D FAPbI₃ perovskite film. The PEA-based 2D RP perovskite film after 168 h began to display low-n-value peaks that could be observed more obviously after 336 h (Figure 5e). Similarly, no significant changes were observed for the β -FPEA-based 2D RP perovskite film (Figure 5f). These results indicate that the β -FPEA-based 2D RP perovskite film exhibited enhanced mixed/ α -phase, moisture and thermal stabilities compared to the PEA-based 2D RP and 3D FAPbI₃ perovskite films.

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The long-term stabilities of the devices based on (β -FPEA)₂(FA)₄Pb₅I₁₆ and (PEA)₂(FA)₄Pb₅I₁₆ (<n> = 5) are further investigated. The thermal stability is measured in N₂ glove box by annealing the unencapsulated devices on a hotplate at 70 °C (**Figure 5g**). The PEA-based device could maintain ~70% of its initial efficiency after 720 h. Surprisingly, the β -FPEA-based devices could retain ~90% of their initial efficiency after 720 h. However, the degradation of FAPbI₃-based PSCs was rapid, with a loss of over 55% of the initial values, which is consistent with the thermal stability test of the films as discussed above. The humidity stability is measured by storing the unencapsulated devices in dark ambient conditions (RH, 35 ± 5%) (**Figure 5h**). After 500 h, the PCEs of FAPbI₃- and PEA-based devices retained an average of 86% of their initial efficiency after 780 h. The stability of the β -FPEA-based devices was significantly improved, benefiting from stabilizing the perovskite crystal lattice and enhancing the quality of the perovskite film with decreased trap densities.



Figure 5. XRD spectra of (a) FAPbI₃, (b) PEA- and (c) β -FPEA-based 2D RP perovskite films exposed in ambient air with an RH of 35 ± 5% under natural lighting at RT. XRD patterns of (d) FAPbI₃, (e) PEA- and (f) β -FPEA-based 2D RP perovskite films exposed in ambient air with an RH of 35 ± 5% under 80 °C heating in the dark. (g) Normalized PCEs versus time for unencapsulated PSCs heated at 70 °C in N₂ and (h) stored in ambient conditions with an RH of 35 ± 5% at RT in the dark (All the tested perovskite films were deposited on the PEDOT:PSS substrates).

3. Conclusion

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In summary, β -fluorinated PEA, a novel spacer cation, was successfully synthesized and used to enhance the efficiency and stability of FA-based 2D RP PSCs. The employment

of multifunctional β -FPEA as spacer cation enhances the interaction of the [PbI₆]⁴⁻ octahedra and improves the crystallinity and hydrophobicity of the 2D RP perovskite film. Compared with the PEA-based 2D RP perovskite film, the β -FPEA-based 2D RP perovskite film displayed improved crystallinity, phase distribution and preferred crystal vertical orientation, resulting in increased carrier diffusion length and carrier lifetime, decreased trap density, and suppressed nonradiative recombination loss. The β -FPEA-based 2D RP PSCs obtained a champion PCE of 19.11% on PTAA substrate. Additionally, the β -FPEA-based devices could retain ~90% of their original efficiency after 720 h by heating on a hotplate at 70 °C and ~86% of their initial efficiency after 780 h of storage in ambient conditions (RH, 35 ± 5%) without encapsulation, exhibiting improved stability. This work provides a feasible method for fabricating highly efficient and stable 2D RP PSCs by designing novel β -fluorinated PEA derivatives as spacer cations.

Supporting Information

Supporting information is available from the Wiley Online Library or from the author.

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calculations were performed on National Supercomputer Center in Guangzhou. We acknowledge the beam time provided by the 1W1A station (Beijing Synchrotron Radiation Facility) for GIWAXS characterization.

Conflict of Interest

The authors declare no conflict of interest.

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Table of Contents

Accepted Article

Highly Efficient and Stable FA-Based Quasi-2D Ruddlesden-Popper Perovskite Solar Cells by the Incorporation of β -Fluorophenylethanamine Cations

Yunxin Zhang[#], Mingqian Chen[#], Tengfei He, Hongbin Chen, Zhe Zhang, Hebin Wang, Haolin, Lu, Yongsheng Liu^{*}, Yongsheng Chen^{*}, Guankui Long^{*}



ToC figure

A new spacer cation of β -fluorinated PEA (β -FPEA) has been synthesized to enhance the efficiency and stability of FA-based two-dimensional (2D) Ruddlesden-Popper (RP) perovskite solar cells (PSCs). The optimized 2D RP PSCs ($\langle n \rangle = 5$) achieved a champion efficiency of 19.11% with largely improved stability by enhancing the quality and phase stability of the 2D RP perovskite film.