Perovskite Solar Cells



Improved Performance of Printable Perovskite Solar Cells with Bifunctional Conjugated Organic Molecule

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A bifunctional conjugated organic molecule 4-(aminomethyl) benzoic acid hydroiodide (AB) is designed and employed as an organic cation in organicinorganic halide perovskite materials. Compared with the monofunctional cation benzylamine hydroiodide (BA) and the nonconjugated bifunctional organic molecule 5-ammonium valeric acid, devices based on AB-MAPbI₃ show a good stability and a superior power conversion efficiency of 15.6% with a short-circuit current of 23.4 mA cm⁻², an open-circuit voltage of 0.94 V, and a fill factor of 0.71. The bifunctional conjugated cation not only benefits the growth of perovskite crystals in the mesoporous network, but also facilitates the charge transport. This investigation helps explore new approaches to rational design of novel organic cations for perovskite materials.

The past few years have witnessed a rapid evolution of hybrid organic–inorganic perovskite solar cells (PSCs) with both low cost and boosted high power conversion efficiency (PCE) over 22%.^[1] The rapid growth of PCE attributed to many research efforts on the evolution of device architectures as well as processing techniques and material compositions.^[2] In particular, methylammonium lead iodide (MAPbI₃) possess an appropriate bandgap, high absorption coefficient,^[3] long-range balanced ambipolar photocarrier diffusion lengths,^[4] and high defect tolerance.^[5]

Despite the achievements, MAPbI₃ suffers from inherent instability over ambient operation conditions due to the low formation energy of the material itself and the high hydrophilicity of the organic cations.^[6] Efforts such as developing novel device architectures as well as exploring novel materials have

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.201705786.

DOI: 10.1002/adma.201705786

been tried to improve the device stabilities. Among them, the 2D perovskites that are crafted using bulkier alkylammonium cations in place of methylammonium exhibit appealing environmental stability. However, the insulating alkylammonium spacer cations hinder charge transport and limit the efficiencies of the devices based on such perovskites. As a consequence, Ruddlesden-Popper 2D perovskites have been explored as fashionable alternatives to pure 2D or 3D perovskite with the aim to balance the PCE of these PSCs and their long-term stability.^[7] The general formula of such 2D/3D perovskites is $A_2(MA)_{n-1}Pb_nI_{3n+1}$, where A is a primary aliphatic or aromatic alkylammo-

nium cation and n represents the number of octahedra layers within each quantum well. It consists a network of inorganic layers of corner sharing [PbI6]4- octahedra confined between interdigitating bilayers of intercalated bulky spacer cations. In this respect, Cao et al. synthesized (n-BAM)₂(MA)₂Pb₃I₁₀ (BAM = *n*-butylammonium), yielding a PCE of 4.02%.^[8] Smith et al. reported the application of (PEA)₂(MA)₂Pb₃I₁₀ (PEA = 2-phenylethylammonium) with a PCE of 4.73%.^[9] Enhanced moisture stability was reported for both studies. Later on, an advance in deposition technique using "hot-casting" (HC) method induced preferential out-of-plane alignment of (n-BAM)₂ (MA)₃Pb₄I₁₃ and increased the PCE to 12.52%.^[10] Tuning the dimensionality to give (PEA)₂ (MA)₅₉Pb₆₀I₁₈₁^[7] or replacing *n*-BAM with a shorter branched-chain butylamine (iso-BAM) to give (iso-BAM)₂ (MA)₂Pb₃I₁₀^[11] improved the efficiency to 15.30% and 8.82%, respectively. The enhanced PCE mainly comes from an enhanced charge transport between the inorganic layers. On the other hand, recent work suggested that the degradation of perovskite films starts from grain boundaries.^[12] By adding BAM into the FA_{0.83}Cs_{0.17}Pb(I_vBr_{1-v})₃ perovskites, Snaith and co-workers illustrated a model of 2D perovskite platelets interspersing between 3D perovskite grains that improved the stability of perovskite without sacrificing the efficiency.^[13] Other molecules, such as phenyl-C61-butyric acid methyl ester,^[14] thiophene, pyridine,^[15] urea,^[16] or quaternary ammonium halide^[17] have also been proven to effectively protected the perovskites boundaries and prolonged the lifetime.

The perovskite material instability was controlled to a certain extent by using these quasi-3D or boundary protected perovskites. However, the solar cell degradation is not only due to the decomposition of perovskite layer, but can also be





accelerated by the lattice mismatch between perovskite and TiO₂ and the defects at the interfaces. Our group first introduced a bifunctional 5-ammonium valeric acid hydroiodide (AVAI) as a primary aliphatic alkylammonium cation into the perovskites.^[18] The perovskites were employed in the printable HTM-free carbon-based PSC. By infiltrating the perovskite precursor solution into a mesoscopic TiO₂/ZrO₂/carbon scaffold using a simple one-step dropping strategy followed by a slow drying process, the components in the film reorganized and self assembled the desired perovskites.^[19] The small-area cell based on this material gave a PCE of 12.8% and larger module gave a PCE of 10.4%.^[20] In addition, the cells exhibited high stability under AM 1.5G illumination over 10 000 h^[21] and under a range of harsh tests outdoor in Jeddah, Saudi Arabia.^[22] The high stability is a synergy consequence of both the protection of boundaries and the protection of perovskite/TiO₂ interface, showing the advantages of bifunctional molecular. However,

the problem of such perovskites is that the insulating aliphatic alkylammonium cation organic spacer cations hinder charge transport thus limits the fill factor (FF) of PSCs. In this scenario, an exploration of alternative yet effective organic spacer cations that increase the charge transfer is imperative to enhance the efficiency.

Herein, we designed such an alternative bifunctional conjugated organic cation 4-(aminomethyl) benzoic acid hydroiodide (AB) and synthesized a novel perovskite AB-MAPbI₃. By applying this perovskite in HTMfree printable PSCs, we obtained a best PCE of 15.6% with a short-circuit current (J_{SC}) of 23.4 mA cm⁻², an open-circuit voltage (V_{OC}) of 0.94 V, and an FF of 0.71. In addition, the devices based on AB-MAPbI₃ showed improved stability compared with MAPbI₃.

The bifunctional molecule 4-(aminomethyl) benzoic acid hydroiodide (structure in Figure 1a) was synthesized and characterized by ¹H NMR (Figure S1, Supporting Information). The nonconjugated cation, 5-aminovaleric acid hydroiodide (AVA; structure in Figure 1a) and the monofunctional cation, benzylamine hydroiodide (BA) were also synthesized from the according starting materials for comparison. Density functional theory (DFT) calculations were carried out to investigate the influence of conjugated bridge to the molecular structure and electron distributions. The calculations were performed by Gaussian 09 program^[23] at B3LYP/6-31G* level in vacuum. Through DFT calculation, we found that AB and AVA have similar chain length (10.206 Å for 5-AVA and 10.163 Å for AB) while BA is shorter (7.063 Å). The highest occupied molecular orbitals (HOMOs) of the molecule are shown in red and green while the lowest unoccupied molecular orbitals (LUMOs) are shown in blue and yellow. It can be observed that the

HOMO of AB and BA locates mainly on the iodide atom and the LUMO lies over the whole molecule. On the contrary, the LUMO of AVA only locates on the acid group while extends toward the nearest CH₂. The long distance between the HOMO and LUMO of AVA certainly hinders charge transport through the molecule. In addition, AB showed a conjugation-induced rigidity in the molecule. The benzene part and the acid part of AB are on the same platform as evidenced from the ~0.2° dihedral angle.

Then the perovskites were prepared by mixing BA, AB, AVA, methylammonium iodide (MAI), and PbI₂ at judiciously chosen stoichiometry to give $(BA)_2$ $(MA)_{49}Pb_{50}I_{151}$, $(AB)_2$ $(MA)_{49}Pb_{50}I_{151}$, $(AVA)_2$ $(MA)_{49}Pb_{50}I_{151}$, and MAPbI₃. For convenience, we denote $(BA)_2$ $(MA)_{49}Pb_{50}I_{151}$ as BA-MAPbI₃, $(AB)_2$ $(MA)_{49}Pb_{50}I_{151}$ as BA-MAPbI₃, $(AB)_2$ $(MA)_{49}Pb_{50}I_{151}$ as AB-MAPbI₃, and $(AVA)_2$ $(MA)_{49}Pb_{50}I_{151}$ as AVA-MAPbI₃. The perovskite films were prepared by one-step drop-casting method on 500 nm/2 μ m mesoporous TiO₂/ZrO₂ substrates. As shown by X-ray diffraction (XRD) in Figure 1b,



Figure 1. a) The structures of AB, AVA, and BA together with their calculated properties, such as the molecular length and the dihedral angles. The HOMOs of the molecule are shown in red and green while the LUMOs are shown in blue and yellow. b) The XRD spectra of MAPbI₃, BA-MAPbI₃, AVA-MAPbI₃, and AB-MAPbI₃ on 500 nm/2 μ m mesoporous TiO₂/ZrO₂ substrates.







Figure 2. The top view scanning electron microscopy (SEM) images for a) MAPbI₃, c) BA- MAPbI₃, e) AVA-MAPbI₃, and g) AB-MAPbI₃ on 500 nm TiO₂/ $2 \mu m ZrO_2$ and their cross-sectional SEM images of the cells filled with b) MAPbI₃, d) BA- MAPbI₃, f) AVA-MAPbI₃, and h) AB-MAPbI₃.

BA-MAPbI₃, AB-MAPbI₃, and AVA-MAPbI₃ showed similar crystal structure of MAPbI₃. No peak at 12.6° was detected in all samples, indicating a quantitative transformation of PbI₂ into the perovskite material.^[24] In addition, we found that the (202) plane is highly preferred in the pristine MAPbI₃ perovskite while (110) became the main preferred direction for BA-MAPbI₃, AB-MAPbI₃, and AVA-MAPbI₃.

The top view scanning electron microscopy (SEM) images gave a more intuitive view of the perovskite morphologies (Figure 2a,c,e,g). The simple drop-casting method usually resulted in a poor morphology. The huge discontinued crystals gave a poor coverage of the surface and resulted in many boundaries. On the contrary, perovskites with larger cations showed much denser morphology with less voids. The same behavior is also observed by other researchers that use one-step spin-coating method to prepare perovskite films.^[8] The perovskites containing bifunctional cation showed better morphology than the one using monofunctional cation, due to strong adherence of the acid group.^[25] We then infiltrated these solutions in the printable carbon-based HTM-free PSCs. As shown in the cross-sectional SEM images in Figure 2b,d,f,h, the solar cell architecture used is a stack of glass/fluorine-doped tin oxide (FTO)/compact TiO₂/mesoporous TiO₂/mesoporous ZrO₂/mesoporous C and perovskite solution is filled in the triple mesoporous scaffold followed by annealing.^[18] The mesoporous materials are prepared by screen-printing technique followed by sintering. Then the perovskite precursors are infiltrated into the scaffold by a simple one-step dropping strategy. However, the morphology control of the perovskite film in such triple-layer structures remains a critical challenge because dropping the perovskite precursor directly into the scaffold usually causes an incomplete perovskite crystal growth and a deficient interface contact. As shown in Figure 2b, MAPbI₃ does not go into the TiO₂ mesopores. Clear particles of TiO₂ and ZrO₂ can be observed from SEM. BA-MAPbI₃ did not infiltrate in TiO₂ mesopores either. On the contrary, both

AB-MAPbI₃ and AVA-MAPbI₃ showed a superior pore-filling ability. The –COOH groups anchor a monolayer of AB or AVA to the surface of the mesoporous TiO_2 and ZrO_2 by coordinative binding to the exposed Ti(IV) or Zr(IV) ions, attaching the perovskites close to the metal oxides and serve as nucleation sites from perovskite growth.

The excellent loading and desired morphology of the perovskite is also evident from the UV-vis spectra as shown in Figure 3a. The identical absorption onsets of all perovskites on TiO₂ indicate the same bandgap. The perovskites containing larger cations exhibited enhanced light absorption through the whole absorption profile due to the improved surface coverage while the ones with bifunctional cations showed even higher absorbance. The time-resolved photoluminescence (TRPL) decay measurements can be used to investigate the carrier lifetimes of the perovskite films and the charge-carrier extraction at the interface between charge collection layer and the perovskite layer.^[26] Figure 3b shows the TRPL spectra and the fitting curves of the perovskites on TiO₂ and Figure 3c shows the TRPL spectra and the fitting curves of those on TiO₂. The TRPL decay was fitted to a biexponential equation: $y = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)^{[27]}$ in which the shorter PL lifetime can be attributed to the defect-induced nonradiative recombination and the longer PL lifetime can be attributed to the radiative recombination.^[4b,28] The fitted parameters are summarized in Table S1 in the Supporting Information. On ZrO₂, the MAPbI₃, BA-MAPbI₃, AVA-MAPbI₃, and AB-MAPbI₃ perovskite gave carrier lifetimes of 10.83, 18.38, 24.03, and 29.48 ns, respectively. The longer charge-carrier lifetime observed with the perovskites containing bifunctional cations may be attributed to a lower defect concentration and an increase in crystallinity.^[1a] With the TiO₂, the MAPbI₃, BA-MAPbI₃, AVA-MAPbI₃, and AB-MAPbI₃ perovskite gave carrier lifetimes of 3.30, 2.48, 2.07, and 1.70 ns, respectively, indicating the charge carrier extraction speed at the perovskite/TiO₂ interface orders by







Figure 3. a) The UV–vis absorption spectra on TiO_2 , b) the time-resolved photoluminescence spectra on ZrO_2 , and c) the time-resolved photoluminescence spectra on TiO_2 of MAPbI₃, BA-MAPbI₃, AB-MAPbI₃, and AVA-MAPbI₃ perovskite. d) The *J*–V curves for the champion devices using MAPbI₃, BA-MAPbI₃, AB-MAPbI₃, AB-MAPbI₃, and AVA-MAPbI₃, Perovskite. d) The *J*–V curves for the champion devices using MAPbI₃, BA-MAPbI₃, and AVA-MAPbI₃, BA-MAPbI₃, AB-MAPbI₃, and AVA-MAPbI₃, BA-MAPbI₃, and AVA-MAPbI₃, and AVA-MAPbI₃, BA-MAPbI₃, and AVA-MAPbI₃, BA-MAPbI₃, and AVA-MAPbI₃, BA-MAPbI₃, BA-MAPbI₃, BA-MAPbI₃, AB-MAPbI₃, AB-MAPbI₃, AB-MAPbI₃, BA-MAPbI₃, BA-MAPbI₃, BA-MAPbI₃, BA-MAPbI₃, AB-MAPbI₃, BA-MAPbI₃, BA-MAPbI₃, AB-MAPbI₃, BA-MAPbI₃, BA-MA

 $MAPbI_3 < BA-MAPbI_3 < AVA-MAPbI_3 < AB-MAPbI_3$. The anchoring group attaches the perovskite more intimately with the TiO₂ while at the same time the conjugated cation facilitates charge transfer.

Figure 3d shows *I*–V curves for the champion cell using AB-MAPbI₃, AVA-MAPbI₃, BA-MAPbI₃, and MAPbI₃. The device photovoltaic statistics (V_{OC}, J_{SC}, FF, and PCE) measured under a simulated air mass (AM) 1.5 irradiance of 100 mW cm⁻² are summarized in Table 1. The control device fabricated with pristine MAPbI₃ exhibits a poor performance of 6.47 %, with a V_{OC} of 0.88 V, a J_{SC} of 13.1 mA cm⁻², and a FF of 0.56, which is comparable with the state-of-art device prepared with the same perovskite composition and device architecture.^[29] This poor performance is a result of the incomplete perovskite crystal growth and deficient interface contact in tens of micrometers thick mesoporous layers. The electrons from the perovskite have to travel the entire thickness of ZrO2, which can sometimes exceed hundreds of nanometers or even micrometers. Most electrons recombine with the holes before they reach and inject into TiO₂, thus resulting in an extremely low photocurrent

Table 1. The characterization of ${\rm TiO}_2$ films modified with different functional molecular and their devices performances.

Additive	E _f [eV]	$J_{\rm SC}$ [mA cm ⁻²]	V _{oc} [V]	PCE [%]	FF
None	4.04	13.1	0.88	6.47	0.56
BA	4.04	20.3	0.90	12.0	0.65
5-AVAI	4.14	22.8	0.92	14.1	0.67
AB	4.16	23.4	0.94	15.6	0.71

of such devices. Thanks to a better morphology of the perovskites, the BA-MAPbI₃ cell gives a PCE of 12.0 %, with a $V_{\rm OC}$ of 0.9 V, a J_{SC} of 20.3 mA cm⁻², and an FF of 0.65. When the monofunctional cation is replaced by a bifunctional cation, the PCE increased further. The AVA-MAPbI3 cell gives a PCE of 14.1%, with a $V_{\rm OC}$ of 0.92 V, a $I_{\rm SC}$ of 22.8 mA cm⁻², and an FF of 0.67 while the AB-MAPbI3 cell gives a PCE of 15.6 %, with a $V_{\rm OC}$ of 0.94 V, a $J_{\rm SC}$ of 23.4 mA cm⁻², and an FF of 0.71. Device hysteresis is checked and shown in Figure S3 in the Supporting Information. The largely enhanced ISC, not only comes from the better crystallinity of the perovskite, but also from a more intimate contact of perovskite with TiO2 and a down-shifted TiO₂ work function (as evidenced by ultraviolet photoelectron spectroscopy measurement. As shown in Figure S4 in the Supporting Information, the work function of bare TiO₂ is \approx 4.04 eV. With AVA and AB, the work function of the TiO₂ shifted to \approx 4.16 and \approx 4.14 eV, respectively). The –COOH group from the bifunctional cations can attach with TiO₂ layer by chemical bonding as we learnt from dye-sensitized solar cells.^[30] This adds a surface dipole moment on TiO₂ and thus

varied the energy level. The positively shifted TiO₂ allows a larger driving force with an increased density of acceptor states available in the TiO₂ film for interfacial electron injection from the Fermi level of perovskite, thus facilitates the charge transport. Both cells based on perovskites with bifunctional cations show extremely high photocurrent around 23 mA cm⁻², and the enhanced J_{SC} of AB-MAPbI₃ than AVA-MAPbI₃ is revealed by







Figure 4. Morphology AFM images of a) AVA-MAPbI₃, c) AB-MAPbI₃, and e) BA-MAPbI₃ film and their corresponding current mappings b) AVA-MAPbI₃, d) AB-MAPbI₃, and f) BA-MAPbI₃ measured by cAFM with 1.0 V bias. g) The *I*–V plots of different films measured by c-AFM.

incident photon-to-current efficiency (IPCE) spectra. (Figure 3e) The IPCE of AVA-MAPbI₃ cell started to drop from 500 nm, as we observed before in such cells.^[18] AB-MAPbI₃ cell showed an ideal square shape IPCE, where the IPCE value is fairly constant across the whole 400-800 nm. IPCE measures the percentage of photons that are converted to electric current as a function of wavelength when the cell is operated under short circuit conditions.^[31] The value corresponds to the photocurrent density produced in the external circuit under monochromatic illumination of the cell divided by the photon flux that strikes the solar cell. It can be affected by the light-harvesting efficiency for photons at a certain wavelength λ , the quantum yield for electron injection, and the electron collection efficiency.^[32] At longer wavelength, the photons have lower energy and thus have more possibilities to be trapped and recombined.^[33] The higher IPCE of AB-MAPbI₃ at the long wavelength region can either be attributed to a lower trap states or a better electron injection and electron collection efficiency of AB-MAPbI₃. We also noticed that the AVA-MAPbI3 cell showed a slower response than the AB-MAPbI3 cell from the stabilized power output under maximum power point tracking (Figure S5, Supporting Information). In addition, we have noticed that the integrated I_{SC} from IPCE measurement is always tiny smaller than the one measured from J-V curve. For the AVA-MAPbI₃ cell we certified before, the integrated current is 18 mA cm⁻² but the certified current density is 22.8 mA cm⁻².^[18] We found that the integrated current agrees closely with the J_{SC} of 18.4 mA cm⁻² which was measured at the beginning of device testing. The value then rose to 21.1 mA cm⁻² after 3 min of light soaking. Some initial stability tests have been performed on the devices using AB-MAPbI3 as shown in Figure S7 in the Supporting Information. Under 1 sun illumination, the cells were held at their maximum power point. The device based on AB-MAPbI₃ shows a much better stability trend with respect to $MAPbI_3$ cell. Using AB-MAPbI₃, the efficiency remained around 90% of the initial value after 100 h continuous illumination, much more stable than $MAPbI_3$ perovskite. Importantly, the stability test was performed without encapsulation. Upon encapsulation and optimization, the stability and efficiency can be further improved. In addition, the cells showed improved shelf-life stability in the dark within 1 month.

To directly investigate the charge-transport behavior of the different perovskites, topography and photocurrent mappings were performed using conductive-AFM (c-AFM) in contact mode. To gain a surface flat enough for c-AFM measurement, the films were prepared by toluene dripping on stoichiometric precursors. As shown in Figure 4a,c,e, the root-mean-square roughness of the perovskite film surfaces did not vary much when we used different perovskites containing conjugated or nonconjugated cations. However, an obvious difference in the conductivity was observed. The current mappings of different films were measured with a bias of 1.0 V. The results show that the conductivities of the perovskite films using BA-MAPbI₃ (Figure 4f) and AB-MAPbI₃ (Figure 4d) are larger (by four times over the conductive parts) than that of AVA-MAPbI₃ (Figure 4b). Photocurrent-voltage (I-V) curves were also measured, as shown in Figure 4g. Higher current response was found for the perovskites with conjugated cations. This indicates that using conjugated cations is an efficient and rational method to increase the conductivity of perovskites.

In summary, we report the first time the incorporation of a bifunctional conjugated cation in perovskites and its implementation on solar cells. The use of bifunctional conjugated cations enhances significantly the performance of the cells, reaching a highest PCE of 15.6% with improved stability. By comparing this cation with a monofunctional cation and a bifunctional nonconjugated cation with similar structure, we found that the



bifunctional conjugated cation not only benefits the growth of perovskite crystals in the mesoporous network, but also facilitates the charge transport. Our approach helps explore new rational designs of cations in perovskites.

Experimental Section

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4-(Chloromethyl) benzoic acid. Materials: NaN₃, tetra-nbutylammonium azide, benzylamine (BA, 99%), ethyl acetate (EtOAc), hydroiodic acid (HI, 57 wt% in H₂O), acetonitrile (MeCN), and N,Ndimethylformamide (DMF, anhydrous) were purchased from Sigma-Aldrich. All materials were used as received without further purification.

Synthesis of 4-(Aminomethyl) benzoic acid hydroiodide (AB): 4-(Chloromethyl) benzoic acid (2 g, 0.012 mol), NaN₃ (1.5 g, 0.023 mol), and tetra-n-butylammonium azide were dissolved in CH₃CN/DMF (80 mL) and heated at 130 °C for 8 h. The mixture was cooled down to room temperature. Distilled water (100 mL) and EtOAc (200 mL) were added in. The organic layer was washed with water, brine and dried over Na₂SO₄. Then Na₂SO₄ was filtered off and the solvent was removed by evaporation to give 2.3 g yellow solid product. The product was used without further purification. Tetrahydrofuran (THF) (40 mL) and DMF (15 mL) were added to dissolve the yellow solid and triphenylphosphine (3.8 g, 0.015 mol) was added. The mixture was stirred for 10 min before 0.5 mL H₂O was added and the resultant mixture was stirred for another 5 h at ambient temperature. 2 M HI (5 mL) was added and the solution was refluxed for 1 h. Concentrated hydroiodic acid (3.5 mL, 0.014 mol) was added and the mixture was refluxed for 2 h. The solvent was then rotavaporated off and the crude product was washed with diethyl ether to give a white powder (2.5 g, 67.6% yield). ^1H NMR (500 MHz, CDCl_3) δ_{H} : 13.12 (s, 1H), 8.21 (s, 3H), 8.00 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2Hz, 2H), 4.15 (s, 1H).

Synthesis of Other Amino Iodides: 5-Ammonium valeric acid (AVA) and methylamine (MA) were mixed with hydroiodic acid (HI, 57 wt% in water) with a molar ratio of 1:1.1. The mixture was stirred for 4 h before the solvent was removed. The crude product was then washed with diethyl ether to give white powder and dried in a vacuum drying oven.

Precursor Preparation and Device Fabrication: The perovskite precursor solution was obtained by mixing amines and PbI₂ in a mixture of y-butyrolactone/ethanol (4:1). The pristine MAPbI3 solution contains 1 M MAI and 1 M PbI₂. FTO glasses were laser-etched to give the desired patterns. They were cleaned by ultrasonicating the glasses in soap water, distilled water, and ethanol. A compact TiO₂ layer was then deposited on the FTO glass by spray pyrolysis at 450 $^\circ$ C with 20 \times 10⁻³ $_{\rm M}$ titanium diisopropoxide bis(acetylacetonate) in ethanol (Aldrich). A 500 nm nanoporous TiO₂ (NR18) layer was screen-printed onto the compact layer followed by a 2 μ m ZrO₂ space layer. Both layers were sintered at 500 °C in air for 30 min. After that, a 15 µm graphite/carbon black back electrode was screen printed and sintered at 400 °C for 30 min. After cooling down, the perovskite solution was drop casted on the carbon layer to fill the triple layer structure and dried at 50 °C for 4 h.

Characterizations: The XRD spectra were measured with an X'pert PRO X-ray Diffractometer using Cu K α radiation under operation conditions of 40 kV and 40 mA from 5° to 70°, with a scanning speed of 5° per min. Scanning electron micrographs (SEM) were obtained by a Nova NanoSEM 450 field emission SEM. The UV-vis spectra of perovskite-sensitized TiO₂ film were measure by a PerkinElmer Lambda950 spectrophometer. Fourier Transform infrared spectroscopy (FTIR) spectra were recorded by a VERTEX 70 Infrared Fourier transform microscopy. Ultraviolet photoelectron spectroscopy (UPS) was performed on a Kratos Axis Ultra DLD system with He I (hv = 21.22 eV) excitation. Device performance were characterized by a Keithley 2400 source/meter and a Newport solar simulator (model 91192) which offered the simulated AM 1.5G illumination of 100 mW cm⁻², calibration was done using a NIST-certified monocrystalline Si solar cell (Newport 532 ISO1599). The J-V curves were measured both reverse (1.2 to -0.2 V) and forward (-0.2 to 1.2 V) with

a scan rate of 20 mV s⁻¹. The active area of the device is about 0.8 cm^2 and a black mask with a circular aperture (0.126 cm²) was applied for I-V measurements. Incident photo-to-current conversion efficiency was performed using a 150 W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 74004) as a monochromatic light source.

Supporting Information

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

Acknowledgements

Y.H., Z.H.Z. and A.Y.M. contributed equally to this work. The authors acknowledge financial support from the National Natural Science Foundation of China (Grant Nos. 91733301, 91433203, 21702069, 61474049, and 51502141), the Ministry of Science and Technology of China (Grant No. 2015AA034601), the Science and Technology Department of Hubei Province (No. 2017AAA190), the 111 Project (Grant No. B07038), and the China Postdoctoral Science Foundation (Grant No. 2016M600588). The authors thank the Analytical and Testing Center of Huazhong University of Science and Technology (HUST) for performing various characterization and measurements.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

bifunctional, conjugated molecules, perovskites, printable, solar cells

Received: October 4, 2017 Revised: November 24, 2017 Published online:

- [1] a) W. S. Yang, B.-W. Park, E. H. Jung, N. J. Jeon, Y. C. Kim, D. U. Lee, S. S. Shin, J. Seo, E. K. Kim, J. H. Noh, Science 2017, 356, 1376; b) M. A. Green, Y. Hishikawa, W. Warta, E. D. Dunlop, D. H. Levi, J. Hohl-Ebinger, A. W. Ho-Baillie, Prog. Photovoltaics 2017, 25, 668; c) C. Zuo, H. J. Bolink, H. Han, J. Huang, D. Cahen, L. Ding, Adv. Sci. 2016, 3, 7.
- [2] a) M. Saliba, T. Matsui, K. Domanski, J.-Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J.-P. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt, Science 2016, 354, 206; b) X. Li, D. Bi, C. Yi, J.-D. Décoppet, J. Luo, S. M. Zakeeruddin, A. Hagfeldt, M. Grätzel, Science 2016, 353, 58; c) S. S. Shin, E. J. Yeom, W. S. Yang, S. Hur, M. G. Kim, J. Im, J. Seo, J. H. Noh, S. I. Seok, Science 2017, 356, 167; d) H. Tan, A. Jain, O. Voznyy, X. Lan, F. P. G. de Arquer, J. Z. Fan, R. Quintero-Bermudez, M. Yuan, B. Zhang, Y. Zhao, Science 2017, 355, 722; e) C. Zuo, L. Ding, Small 2015, 11, 5528; f) C. Zuo, L. Ding, Adv. Energy Mater. 2017, 7; g) D. Luo, L. Zhao, J. Wu, Q. Hu, Y. Zhang, Z. Xu, Y. Liu, T. Liu, K. Chen, W. Yang, Adv. Mater. 2017, 29, 1604758; h) Q. Hu, L. Zhao, J. Wu, K. Gao, D. Luo, Y. Jiang, Z. Zhang, C. Zhu, E. Schaible, A. Hexemer, Nat. Commun. 2017, 8, 15688.
- [3] E. Guillén, F. J. Ramos, J. A. Anta, S. Ahmad, J. Phys. Chem. C 2014, 118, 22913.
- [4] a) G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar, T. C. Sum, Science 2013, 342, 344; b) S. D. Stranks,

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- G. E. Eperon, G. Grancini, C. Menelaou, M. J. Alcocer, T. Leijtens,
- L. M. Herz, A. Petrozza, H. J. Snaith, Science 2013, 342, 341.
- [5] W.-J. Yin, T. Shi, Y. Yan, Appl. Phys. Lett. 2014, 104, 063903.
- [6] T. A. Berhe, W.-N. Su, C.-H. Chen, C.-J. Pan, J.-H. Cheng, H.-M. Chen, M.-C. Tsai, L.-Y. Chen, A. A. Dubale, B.-J. Hwang, *Energy Environ. Sci.* **2016**, *9*, 323.
- [7] L. N. Quan, M. Yuan, R. Comin, O. Voznyy, E. M. Beauregard, S. Hoogland, A. Buin, A. R. Kirmani, K. Zhao, A. Amassian, J. Am. Chem. Soc. 2016, 138, 2649.
- [8] D. H. Cao, C. C. Stoumpos, O. K. Farha, J. T. Hupp, M. G. Kanatzidis, J. Am. Chem. Soc. 2015, 137, 7843.
- [9] I. C. Smith, E. T. Hoke, D. Solis-Ibarra, M. D. McGehee, H. I. Karunadasa, Angew. Chem. 2014, 126, 11414.
- [10] H. Tsai, W. Nie, J.-C. Blancon, C. C. Stoumpos, R. Asadpour, B. Harutyunyan, A. J. Neukirch, R. Verduzco, J. J. Crochet, S. Tretiak, *Nature* **2016**, *536*, 312.
- [11] Y. Chen, Y. Sun, J. Peng, W. Zhang, X. Su, K. Zheng, T. Pullerits, Z. Liang, Adv. Energy Mater. 2017, 7, 18.
- [12] Q. Wang, B. Chen, Y. Liu, Y. Deng, Y. Bai, Q. Dong, J. Huang, Energy Environ. Sci. 2017, 10, 516.
- [13] Z. Wang, Q. Lin, F. P. Chmiel, N. Sakai, L. M. Herz, H. J. Snaith, *Nat. Energy* 2017, 2, 17135.
- [14] J. Xu, A. Buin, A. H. Ip, W. Li, O. Voznyy, R. Comin, M. Yuan, S. Jeon, Z. Ning, J. J. McDowell, Nat. Commun. 2015, 6, 7081.
- [15] N. K. Noel, A. Abate, S. D. Stranks, E. S. Parrott, V. M. Burlakov, A. Goriely, H. J. Snaith, ACS Nano 2014, 8, 9815.
- [16] J.-W. Lee, S.-H. Bae, Y.-T. Hsieh, N. De Marco, M. Wang, P. Sun, Y. Yang, Chem 2017, 3, 290.
- [17] X. Zheng, B. Chen, J. Dai, Y. Fang, Y. Bai, Y. Lin, H. Wei, X. C. Zeng, J. Huang, *Nat. Energy* **2017**, *2*, 17102.
- [18] A. Mei, X. Li, L. Liu, Z. Ku, T. Liu, Y. Rong, M. Xu, M. Hu, J. Chen, Y. Yang, *Science* **2014**, *345*, 295.
- [19] Y. Rong, X. Hou, Y. Hu, A. Mei, L. Liu, P. Wang, H. Han, Nat. Commun. 2017, 8, 14555.
- [20] Y. Hu, S. Si, A. Mei, Y. Rong, H. Liu, X. Li, H. Han, Sol. RRL 2017, 1, 1600019.
- [21] a) G. Grancini, C. Roldáncarmona, I. Zimmermann, E. Mosconi, X. Lee, D. Martineau, S. Narbey, F. Oswald, F. D. Angelis, M. Graetzel, *Nat. Commun.* 2017, *8*, 15684; b) Y. Rong, L. Liu, A. Mei, X. Li, H. Han, *Adv. Energy Mater.* 2015, *5*, 1501066; c) Y. Rong, Y. Hu, S. Ravishankar, H. Liu, X. Hou, Y. Sheng, A. Mei, Q. Wang, D. Li, M. Xu, *Energy Environ. Sci.* 2017, *10*, 2383.

- [22] X. Li, M. Tschumi, H. Han, S. S. Babkair, R. A. Alzubaydi, A. A. Ansari, S. S. Habib, M. K. Nazeeruddin, S. M. Zakeeruddin, M. Grätzel, *Energy Technol.* **2015**, *3*, 551.
- [23] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford, CT 2016.
- [24] D. Bi, A. M. Elzohry, A. Hagfeldt, G. Boschloo, ACS Photonics 2015, 2, 589.
- [25] X. Li, M. I. Dar, C. Yi, J. Luo, M. Tschumi, S. M. Zakeeruddin, M. K. Nazeeruddin, H. Han, M. Grätzel, *Nat. Chem.* **2015**, *7*, 703.
- [26] J. Chen, Y. Rong, A. Mei, Y. Xiong, T. Liu, Y. Sheng, P. Jiang, L. Hong, Y. Guan, X. Zhu, Adv. Energy Mater. 2015, 6, 1502009.
- [27] Q. Han, S. H. Bae, P. Sun, Y. T. Hsieh, Y. Yang, Y. S. Rim, H. Zhao, Q. Chen, W. Shi, G. Li, Adv. Mater. 2016, 28, 2253.
- [28] L. M. Herz, Annu. Rev. Phys. Chem. 2016, 67, 65.
- [29] Z. Ku, Y. Rong, M. Xu, T. Liu, H. Han, Sci. Rep. 2013, 3, 3132.
- [30] J. Mao, X. Zhang, S.-H. Liu, Z. Shen, X. Li, W. Wu, P.-T. Chou, J. Hua, *Electrochim. Acta* **2015**, *179*, 179.
- [31] M. Grätzel, Acc. Chem. Res. 2009, 42, 1788.
- [32] Z. Chen, T. G. Deutsch, H. N. Dinh, K. Domen, K. Emery, A. J. Forman, N. Gaillard, R. Garland, C. Heske, T. F. Jaramillo, A. Kleiman-Shwarsctein, E. Miller, K. Takanabe, J. Turner, in *Photoelectrochemical Water Splitting: Standards, Experimental Methods, and Protocols* (Eds: Z. Chen, H. Dinh, E. Miller), Springer, New York 2013.
- [33] Y. Jiang, J. Li, S. Xiong, F. Jiang, T. Liu, F. Qin, L. Hu, Y. Zhou, J. Mater. Chem. A 2017, 5, 17632.