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Phenylalkylamine Passivation of Organolead Halide Perovskites Enabling High-Efficiency and Air-Stable Photovoltaic Cells

Feng Wang, Wei Geng, Yang Zhou, Hong-Hua Fang, Chuan-Jia Tong, Maria Antonietta Loi, Li-Min Liu, and Ni Zhao*

Perovskite materials with the general formula APbX_3 (A = methylammonium (MA), formamidinium (FA) or cesium (Cs); X = Br, I) have attracted remarkable attention in the photovoltaic community. Recently, APbX_3 perovskite-based solar cells have demonstrated high power conversion efficiencies over 20%,^[1] comparable to those of crystalline silicon and thin film solar cells. However, the poor stability of the perovskite materials against moisture may limit their practical applications.^[2] In general, APbX_3 perovskites tend to hydrolyze in the presence of water, resulting in destruction of the lattice structure. One approach to suppress this process is to create a 2D layered structure by introducing in the lattice a small amount of larger sized amines, such as phenethylamine, polyethylenimine, and trifluoroethyl amine.^[3] The enhanced stability of the 2D structure is believed to be associated with the increased van der Waals (vdW) interactions between the organic molecules and the perovskite lattice.^[3b] Crosslinking perovskite crystalline grains with bifunctional amino additives, such as alkylcarboxylic acid ω -ammonium,^[4] is another approach that has been proposed to improve the compactness of the perovskite films and thus enhance the film stability. Most recently, surface treatment of perovskite films with a water-resisting layer of dodecyltrimethoxysilane or tetraethyl ammonium has been shown to endow the films excellent moisture tolerance.^[5]

Despite the stability improvement, the above approaches have yet to produce cells with high power conversion efficiencies (PCEs) that are close to the current record (20–22%) for perovskite solar cells. A possible limitation is that the approaches incorporate insulating moieties in the perovskite

lattice or film surfaces, which may hamper the charge separation and charge transport processes in perovskite films or charge extraction from perovskite to its neighboring layers.^[2a,3a] Efforts have been devoted to achieve a balance between the moisture stability and photovoltaic performance. For instance, Quan et al. showed that increasing the ratio of quasi-2D structures in a 3D perovskite lattice improves the film stability while at the same time reduces the solar cell efficiency.^[3b] As such the method induces a trade-off between efficiency and stability.

In this work we demonstrate that, by utilizing small sized “moisture resistive” passivation molecules with proper steric arrangement, it is possible to fabricate air stable perovskite solar cells with PCEs above 19%. Here we introduced amine functional molecules through a simple post-deposition process, i.e., solution casting the additive solution after formation of perovskite films. We selected a conjugated water resistive group, benzene, and compared the passivation efficacy of three structurally similar benzene-amine molecules, including aniline, benzylamine, and phenethylamine, through experimental and theoretical studies. We found that the water-resistivity of the modified perovskite films is extremely sensitive to the steric arrangement of the molecules, and that only benzylamine provides the optimal configuration. The benzylamine modified formamidinium lead iodide (FAPbI₃) films remain unchanged for >2900 h after air exposure (50 ± 5 RH%), while unmodified FAPbI₃ films degrade completely within 90 h under the same storage condition. The modified FAPbI₃ solar cells exhibit a champion efficiency of 19.2% and an open-circuit voltage (V_{oc}) of 1.12 V, representing the lowest loss-in-potential reported so far for perovskite solar cells.

We select phenylalkylamine (Figure 1a) containing a benzene ring and an amino group as the passivation molecules based on the following rationale: Benzene ring is hydrophobic and its π -conjugation structure favors charge transport;^[6] amino group anchors the molecule to the Pb–I framework through coordination with the Pb ions or hydrogen bonding with the iodide ions.^[4,5b,7] For the perovskite material, we choose FAPbI₃ over MAPbI₃, as the latter has other stability issues such as phase transition and thermal decomposition at 70–80 °C.^[8] Herein-after, the aniline, benzylamine, and phenethylamine modified FAPbI₃ films are denoted as A-FAPbI₃, BA-FAPbI₃, and PA-FAPbI₃, respectively, for short.

The FAPbI₃ films were produced through a one-step spin-coating process with the use of chlorobenzene as an antisolvent.^[9] The method produced dense and uniform perovskite films as shown in Figure S1 and S2 in the Supporting Information. The passivation molecules were introduced onto

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Figure 1. a) The chemical structures of aniline, benzylamine, and phenethylamine. b) Schematic illustration of amine treatment of perovskite films through a spin-coating method, followed by an annealing process.

the perovskite films through a successive spin-coating method (Figure 1b), followed by an annealing process to completely remove the solvent. (Details can be found in the Experimental Section.) The film morphology remained unchanged after the amine modification. The presence of the passivation layer and its chemical bonding to the perovskite were confirmed by the Fourier transform infrared spectroscopy (FTIR) and ^1H nuclear magnetic resonance measurements (Figure S3 and S4, Supporting Information).

We compared the moisture-resistance of the modified FAPbI₃ films by exposing them in air with $50 \pm 5\%$ RH. Note that the black α -FAPbI₃ would be converted into yellow δ -FAPbI₃ in a humid atmosphere.^[10] Accordingly, the degradation process can be traced through the change in the film color and the emergence

of the δ -FAPbI₃ characteristic peaks in the X-ray diffraction (XRD) patterns. As shown in Figure 2a, the unmodified FAPbI₃ film changed to clear yellow within 3 days (72 h) and completely decomposed within 90 h (Figure S5, Supporting Information), while the extent of such conversion was reduced, yet still pronounced, in the A-FAPbI₃ (Figure 2c). In contrast, BA-FAPbI₃ exhibited excellent stability, showing no δ -FAPbI₃ XRD signal (Figure 2d) even after exposure in air ($50 \pm 5\%$ RH) for four months, meanwhile the color of the unmodified FAPbI₃ was nearly white with the formation of PbI(OH) (Figure S6, Supporting Information). Under an even higher humidity of $70 \pm 5\%$ RH, BA-FAPbI₃ still exhibits excellent moisture stability, showing no impurity in the XRD patterns after exposure for two months (Figure S7, Supporting Information). Interestingly, the PA-FAPbI₃ films, which have an extra $-\text{CH}_2-$ in the amine passivation molecule, exhibited a noticeable δ -FAPbI₃ peak after air exposure ($50 \pm 5\%$ RH) for 3 d, suggesting that a slight change in the configuration of the amine functional molecule could largely vary the efficacy of the passivation.

It is intriguing that BA-FAPbI₃ shows much better moisture-resistance as compared to A-FAPbI₃ and PA-FAPbI₃, despite the similarity in their chemical structures. In order to understand this phenomenon, we conducted density functional theory (DFT) calculations to evaluate the interaction between water molecules and the perovskite lattice at their interface. In the modeling atomic structures, the surface FA molecules were replaced with aniline, benzylamine, and phenethylamine and the stabilized molecular configurations are shown in Figure S8 in the Supporting Information. The corresponding formation energy for the amine substitution is -0.19 eV per molecule for A-FAPbI₃, -0.26 eV per molecule for BA-FAPbI₃ and -0.49 eV per molecule for PA-FAPbI₃, verifying the thermodynamic stability of the amine modification.

To check whether the modification can reduce water adsorption, we first evaluated the water adsorption energy (E_{ad}) on the

Figure 2. a) Images of unmodified FAPbI₃, A-FAPbI₃, BA-FAPbI₃, and PA-FAPbI₃ films under different durations (fresh, 3 d, 4 months) of exposure under $50 \pm 5\%$ RH% air. b–e) XRD patterns of unmodified FAPbI₃, A-FAPbI₃, BA-FAPbI₃, and PA-FAPbI₃ films after exposure in moisture air ($50 \pm 5\%$ RH% air). Except for the BA-FAPbI₃ film, which was exposed for four months, all other films were exposed for 3 d. * and # highlight the XRD peaks corresponding to the (110) plane of α -FAPbI₃ and δ -FAPbI₃, respectively.

Figure 3. a–c) DFT simulation of one water molecule adsorption on the A-FAPbI₃, BA-FAPbI₃, and PA-FAPbI₃ surface. d–f) The infiltration of one water molecule into the A-FAPbI₃, BA-FAPbI₃, and PA-FAPbI₃ subsurface, i.e., between the passivation molecule and the Pb–I lattice surface. g–i) electronic total charge density slices of the A-FAPbI₃, BA-FAPbI₃, and PA-FAPbI₃ after infiltration of one water molecule. The water molecules are marked in green circles. *d* indicates the distance between a water molecule to perovskite lattice.

surface of the films. The calculated E_{ad} for unmodified FAPbI₃, A-FAPbI₃, BA-FAPbI₃, and PA-FAPbI₃ are -0.58 , -0.54 , -0.40 , and -0.40 eV, respectively. The significantly reduced E_{ad} in BA-FAPbI₃ and PA-FAPbI₃ suggests that the phenylalkylamine passivation molecules have better water repelling ability; however, E_{ad} alone cannot explain the different moisture resistance of BA-FAPbI₃ and PA-FAPbI₃. We therefore further examined the steric arrangement of the amine molecules on the perovskite surface. As shown in **Figure 3**, the benzylamine molecules are packed almost perpendicular to the perovskite surface, while the aniline and phenethylamine molecules orient in a relatively irregular fashion. As a result, the distance d_1 between water molecules and the surface of the Pb–I lattice is larger in BA-FAPbI₃ ($d_1 = 6.90$ Å) as compared to A-FAPbI₃ ($d_1 = 6.48$ Å) and PA-FAPbI₃ ($d_1 = 6.56$ Å) (Table S1, Supporting Information), even though the size of benzylamine is smaller than phenethylamine.

Since water adsorption on the perovskite surface cannot be completely avoided, we further investigated the tendency of water penetration into the subsurface of the perovskite lattice, which is the key to initiate the hydrolysis process in bulk perovskite.^[11] In the initial setting of the simulation, we put a water molecule between the amine passivation layer and the first Pb–I lattice layer. Interestingly, the water molecule is automatically repelled from the site of the Pb–I layer to the benzylamine layer in the

case of BA-FAPbI₃, resulting in a water to perovskite distance (d_2) of 4.88 Å; in contrast, the water molecule stays much closer to the Pb–I lattice layer for the A-FAPbI₃ ($d_2 = 2.64$ Å) and PA-FAPbI₃ ($d_2 = 3.99$ Å) structures. This phenomenon can also be observed from the electronic total charge density slices (Figure 3g–i), which again suggests that the benzylamine molecules effectively keep water molecule away from the perovskite lattice.

In the following we compare the photovoltaic performance of the unmodified and modified perovskite films. Solar cells with a structure of F-doped SnO₂ (FTO)/compact-TiO₂/perovskite/2,2',7,7'-tetrakis-(*N,N*-di-4-methoxyphenylamino)-9,9'-spirobifluorene(spiro-MeOTAD)/Au were fabricated (**Figure 4a**). The current-density–voltage (*J*–*V*) characteristics of the devices are shown in Figure 4b and the photovoltaic parameters are presented in Table S2 in the Supporting Information. It can be clearly seen that the three amine molecules also show different modification effects on the electronic properties of the perovskite cells. For instance, aniline or phenethylamine modification reduced the average PCE of the perovskite solar cells from 14.2% (for unmodified FAPbI₃) to $\approx 13.8\%$ and 13.3%, respectively; on the other hand, benzylamine modification resulted in a significantly improved average PCE of 17.3% (averaged over 90 devices from 10 different batches) and the champion PCE of 19.2%. Particularly, the highest V_{oc} of the BA-FAPbI₃ devices reaches 1.12 V. Considering that the energy

Figure 4. a) Schematic configuration of the solar cell structure. b) Representative forward and reverse J - V curves of unmodified FAPbI₃, A-FAPbI₃, BA-FAPbI₃, and PA-FAPbI₃ devices at a scan rate of 0.15 V s⁻¹ under simulated AM 1.5 illumination. c) The J - V curve of the champion BA-FAPbI₃ solar cell. The photovoltaic parameters are summarized in Table S1 in the Supporting Information. *The unit of J_{sc} is mA cm⁻². d) Stabilized photocurrent and power output as a function of time for the champion BA-FAPbI₃ device under a bias of 0.91 V. e) Moisture stability of unmodified FAPbI₃ (black line) and BA-FAPbI₃ (red and blue lines) devices under air exposure (50 ± 5 RH%). "Half cells" means that only the BA-FAPbI₃ films on the TiO₂/FTO substrates were exposed to air and that the spiro-MeOTAD and Au layers were deposited onto the films before the J - V measurement.

bandgap of FAPbI₃ is 1.48 eV,^[12] the loss-in-potential of the BA-FAPbI₃ cells is as low as 0.36 eV, which is the smallest value reported so far for all perovskite solar cells.

Figure 4c demonstrates the J - V curve of the champion BA-FAPbI₃ device. This cell was held at the voltage of 0.91 V to monitor the stabilized power output as a function of time (Figure 4d). The photocurrent density reached 20.9 mA cm⁻², resulting in a stabilized PCE of 19.0% over 6000 s. The external quantum efficiency (EQE) spectra of the modified and unmodified cells are provided in Figure S9 in the Supporting Information.

Besides affecting cell efficiency, the amine modification also influences the J - V hysteresis between the forward and reverse scans. As shown in Figure 4b, the hysteresis loop of the FAPbI₃ devices is enlarged after aniline modification, but decreased after benzylamine and phenethylamine modification. Previous studies suggest that the hysteresis behavior of perovskite solar cells is caused by a combination effect of charge trapping and ion transport.^[13] Reduced ionic defects (e.g., iodide and formamidinium vacancies) in bulk perovskite films and their interfaces with the neighboring charge transport layers could both reduce hysteresis.^[14] Through DFT calculations, we also estimated the formation energy of iodine defects (Figure S10 and Table S3, Supporting Information). We found that benzylamine and phenethylamine passivation increases the formation

energy of the defects, especially for the surface vacancy, implying the increased energy barrier for the formation of the interface I vacancy. This result may explain the reduced hysteresis behavior after amine modification.

Since the BA-FAPbI₃ films exhibit the best moisture-resistance and photovoltaic performance, we now focus on examining the moisture and thermal stability of the BA-FAPbI₃-based solar cells. The unmodified FAPbI₃ and BA-FAPbI₃ devices were stored at an ambient condition with 50 ± 5 RH%, and their J - V characteristics were monitored for up to four months. As shown in Figure 4e, the PCE of the unmodified FAPbI₃ devices was reduced to nearly zero after 3 d, while the BA-FAPbI₃ devices maintained 50% of their initial efficiency after more than four months' exposure to moisture air. In a control experiment, we stored "half cells", i.e., BA-FAPbI₃/TiO₂/FTO samples, in the same ambient condition and deposited the spiro-MeOTAD layer and top electrode right before the J - V test. In this case we found almost no decrease in the PCE after an exposure period of more than four months (Figure 4e). These results suggest that the decreased PCE of the full cells may mainly originate from the degradation of the spiro-MeOTAD layer or its associated interfaces. This is not surprising as the additive *bis*(trifluoromethane)sulfonimide lithium salt (LiTFSI) in the spiro-MeOTAD layer can adsorb H₂O easily.^[2b] We also found that the "half cells" exhibited

excellent thermal stability at 80 °C, while “full cells” degraded gradually at the same temperature (Figure S11, Supporting Information). Clearly, spiro-MeOTAD also affects the thermal stability of the devices.^[15] By replacing this layer with other materials, e.g., metal oxides or carbon electrodes,^[16] the stability of the full cells could be further improved.

To understand the high V_{oc} and thus the low loss-in-potential of the BA-FAPbI₃ devices, we carried out optical and electrical characterizations on the perovskite films and devices. First, we found that the photoluminescence (PL) intensity of the FAPbI₃ films was increased by about 1.5 times after benzylamine modification (Figure 5a). Meanwhile, the time-resolved PL (TRPL) measurement (Figure 5b) revealed an increased carrier lifetime from 12.5 ns for the unmodified FAPbI₃ films to 23.1 ns for the BA-FAPbI₃ films. Both results suggest that recombination centers are effectively reduced after benzylamine modification.^[7]

We further performed transient photovoltage (TPV) measurement on the unmodified FAPbI₃- and BA-FAPbI₃-based

solar cells to probe the recombination process of free charge carriers in the devices.^[17] Figure 5c compares the light intensity dependence of V_{oc} of the two cells. It can be seen that the BA-FAPbI₃ device exhibits a higher V_{oc} value than the unmodified device under each light intensity. For the unmodified FAPbI₃ device, the V_{oc} value drops rapidly with light intensity in the low intensity region (<5 mW cm⁻²), indicating a predominant trap-assisted recombination process caused by deep-level trap states. In contrast, the BA-FAPbI₃ device exhibits a constant light intensity— V_{oc} slope across all light intensity tested, suggesting that the passivation treatment has effectively reduced trap-assisted recombination.^[17b] This hypothesis is further supported by the measurement of the recombination rate constant K_r , which shows smaller K_r for the BA-FAPbI₃ device under all light intensity levels (Figure 5d).

The TPV measurement was complemented with the electrochemical impedance spectroscopy (EIS).^[18] In the EIS measurement, a 0.8 V bias was applied under constant illumination to

Figure 5. a) PL spectra of unmodified FAPbI₃ and BA-FAPbI₃ films on glass substrates. b) Time-resolved PL decay of unmodified FAPbI₃ and BA-FAPbI₃ films on glass substrate. c) The light intensity dependence of V_{oc} in transient TPV measurements for unmodified FAPbI₃ (black line) and BA-FAPbI₃ (blue line) devices. The solid lines are fits to guide the eye. d) The light intensity dependence of the recombination rate constant K_r extracted from the TPV spectra. e) Nyquist plots of unmodified FAPbI₃ and BA-FAPbI₃ devices measured at a bias of 0.8 V under simulated AM1.5 illumination.

monitor the device impedance as a function of frequency. Two distinct regimes can be observed in the Nyquist plot shown in Figure 5e: a high frequency regime (>500 Hz) correlated with the charge recombination process, and low frequency regime (<500 Hz) correlated with slow dielectric and ionic relaxation in perovskite films.^[19] The fitting results reveal that the BA-FAPbI₃ device exhibits a much larger recombination resistance (741 Ω) than that of the unmodified FAPbI₃ devices (114 Ω). We also found the series resistance (R_s) of devices was dropped from $10.4 \pm 1.3 \Omega \text{ cm}^2$ to $4.8 \pm 1.0 \Omega \text{ cm}^2$ after benzylamine modification (calculated from J - V curves in Figure 4b), indicating improved hole extraction from BA-FAPbI₃ to spiro-MeOTAD.

Taking together, the optical and electrical characterization results all suggest that benzylamine modification effectively reduces the recombination centers and improves charge extraction. It has been demonstrated previously that defect passivation by hydrogen atoms or by coordination bonding with functional molecules, such as iodopentafluorobenzene, thiophene, pyridine or guanidinium, can improve the efficiency of perovskite solar cells and in particular, their V_{oc} .^[7,20] The benzylamine passivation may follow a similar principle through the interaction between the amino anchoring group and the Pb-I lattice.

In summary, we have demonstrated a molecular passivation treatment of perovskite films, which significantly improves the moisture-resistance of the perovskites, while at the same time enhances their electronic properties, enabling $>19\%$ efficiency perovskite solar cells. The simultaneous enhancement of stability and efficiency is achieved through: i) the use of a small-sized hydrophobic aromatic group, i.e., a benzene ring, in the passivation molecule, and ii) the formation of edge-on packing of the benzene rings on the perovskite surface. Through DFT calculations we found that the steric arrangement of the benzene rings is extremely sensitive to their anchoring groups with the perovskite lattice. Out of aniline, benzylamine, and phenethylamine, only benzylamine can raise the solar cell efficiency and stabilize the perovskite films for more than four months in moisture air. These experimental and theoretical findings elucidate the molecular passivation principles to achieve simultaneous efficiency and stability improvement, which is critical for advancing the material optimization processes toward practical applications of perovskite solar cells.

Experimental Section

Amine Modification and Solar-Cell Fabrication: Nippon Sheet Glass was cleaned by sonication in 2% Hellmanex water solution for 30 min. After rinsing with deionized water and ethanol, the substrates were further cleaned with isopropyl alcohol, acetone, and isopropyl alcohol for 30 min, respectively. Then, the TiO₂ precursor solution was prepared by dissolving 0.3 M titanium isopropoxide (Sigma-Aldrich, 99.999% purity) and 0.01 M HCl in ethanol. An ≈ 40 nm-thick compact TiO₂ film was coated on the FTO substrate by spinning the precursor solution at 5000 rpm, followed by annealing at 500 °C for 30 min. Formamidinium iodide (FAI) (Dyesol) and lead iodide (PbI₂) (Sigma-Aldrich, $\geq 98.0\%$ purity) were mixed with anhydrous Dimethylformamide (DMF) at a molar ratio of 1:1, stirred for 1.0 h, and then filtered with a 0.45 μm polytetrafluoroethylene filter. The concentration of the precursor solution was 1 M. The precursor solution was spin-coated onto the TiO₂/FTO substrates in a two-step procedure at 500 and 7000 rpm for 2 and 40 s respectively. During the second step, 40 μL of chlorobenzene was casted onto the substrate 3 s after

the beginning of the second spinning step. The films were placed on a hotplate at 100 °C for 10 min and at 160 °C for about 40 min.

For the amine modification, 50 μL of 3 vol% amine (aniline, benzylamine or phenethylamine, all from Sigma-Aldrich, $\geq 99.0\%$ purity) solution in chlorobenzene was dropped onto the perovskite substrate, immediately followed by spinning coating at 3000 rpm for 60 s and then annealing at 160 °C for 5 min to completely remove the solvent.

The hole-transport layer was prepared by: i) dissolving 72.3 mg spiro-MeOTAD (TRC, Canada), 30 μL 4-*tert*-butylpyridine (Sigma-Aldrich, 96%) and 20 μL *bis*(trifluoromethane)sulfonimide lithium salt (Sigma-Aldrich) solution (520 mg Li-TFSI in 1 mL acetonitrile) in 1 mL chlorobenzene, and ii) spin-casting the solution on the perovskite layer at 5000 rpm for 30 s. Finally, an 80 nm Au electrode layer was deposited under a vacuum of $<1 \times 10^{-4}$ Pa. All fabrication steps were performed in an N₂-purged glovebox.

The relative humidity was controlled by an electronic moisture proof box (Noble Cabi), which was also monitored using a calibrated hygrometer.

First-Principles Calculations: The calculations were performed based on DFT using Quickstep module in the CP2K Package.^[21] The hybrid Gaussian and plane wave basis sets were employed to describe electronic charge density and Goedecker–Teter–Hutter pseudo-potentials to represent the ion–electron interactions.^[22] The valence electrons were treated using a double- ζ with one set of polarization basis set.^[23] The energy cutoff for the real space grid was 500 Ry, and total energies were relaxed to per atom less than 0.001 eV.^[24] This study applied the Perdew–Burke–Ernzerhof functional as exchange correlation. The vdW correction was considered with the Grimme approach (DFT-D3).^[25] In order to avoid the interaction between the adjacent images, a vacuum spacing of 20 Å was employed for all the systems. The formation energies of the modified ions were calculated by $E_{\text{form}} = (E_{\text{ms}} - E_{\text{os}} + 8 \times E_{\text{FA}} - 8 \times E_{\text{am}})/8$. Here, the E_{ms} , E_{os} , E_{FA} , and E_{am} are energies of modified surface, original surface, isolated FA ions and isolated amine ions, respectively. The tetragonal FAI layer terminated FAPbI₃(001) surface was modeled by eleven layer of FAPbI₃. To model the modified surfaces, the surface FA ions were replaced with aniline, benzylamine, and phenethylamine ions, respectively. Starting from different orientation of the amine ions with the benzene ring parallel or perpendicular to the surface, the surface-modified FAPbI₃(001) structures were optimized.

Measurement and Characterization: The XRD patterns of the samples were recorded using a Rigaku RU-300 diffractometer equipped with Cu K α_1 irradiation ($\lambda = 1.5406$ Å). The film morphology was characterized using scanning electron microscopy (Quanta 400) and tapping-mode atomic force microscopy (Nanoscope IIIa). Sample thicknesses were measured using an Alpha-step 500 surface profiler. The current density–voltage (J - V) curves were measured under simulated AM 1.5 sunlight (94011A-ES, ABB) at a scan rate of about 0.15 V s⁻¹. The effective area of a cell was about 0.05 cm². For the photoluminescence spectroscopy measurement, the optical emission was spectrally dispersed in a single spectrometer and recorded by an Imaging EM CCD camera from Hamamatsu (Hamamatsu, Japan). The second harmonic Ti:sapphire laser (400 nm, Coherent, Mira 900) was used to excite the samples. Time-resolved PL spectra were detected using a Hamamatsu streak camera operating in single sweep mode. The excitation density was reduced to be 0.7 and 1.4 $\mu\text{J cm}^{-2}$ by a neutral density filter for steady state PL and TRPL measurements, respectively. The attenuated total reflection FTIR spectra were recorded using a JASCO FT/IR 4000 spectrophotometer with samples on the FTO/TiO₂ substrate. EQEs were measured with a Keithley 2400 Source Meter under monochromatic illumination generated by passing the light beam from a 250 W quartz tungsten halogen lamp into a Newport 74215 Oriel Cornerstone 260 1/4 m monochromator. A calibrated silicon diode with a known spectral response was used as the reference.

For the transient photovoltage measurements, the background illumination was provided by a white light source (OSL 1-EC Fiber Illuminator, Thorlabs) with 100 mW cm⁻² light intensity at its maximum. The light intensity could be attenuated with a neutral density filter. The solar cell devices were connected to the 1 M Ω input of the oscilloscope (TDS-3014C, Tektronix). The small-perturbation pulsed excitation

was provided by a 635 nm laser (LQD635-08C, Newport), with the repetition rate of 1 kHz and the pulse duration of 40 ns. The intensity of the pulsed laser was modulated by a continuous filter to keep the induced transient photovoltage ΔV within 2% of the V_{oc} induced by the background illumination. All transients were recorded with the average of 512 scans. The impedance measurement was carried out by Bio-logic SP200 Potentiostat with a DC bias of 0.8 V and 20 mV AC perturbation under simulated AM 1.5 illumination at an intensity of 100 mW cm⁻².

Supporting Information

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

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