Facile Fabrication of Self-Assembly Functionalized Polythiophene Hole Transporting Layer for High Performance Perovskite Solar Cells

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Crystallinity and crystal orientation have a predominant impact on a materials’ semiconducting properties, thus it is essential to manipulate the microstructure arrangements for desired semiconducting device performance. Here, ultra-uniform hole-transporting material (HTM) by self-assembling COOH-functionalized P3HT (P3HT-COOH) is fabricated, on which near single crystal quality perovskite thin film can be grown. In particular, the self-assembly approach facilitates the P3HT-COOH molecules to form an ordered and homogeneous monolayer on top of the indium tin oxide (ITO) electrode facilitate the perovskite crystalline film growth with high quality and preferred orientations. After detailed spectroscopy and device characterizations, it is found that the carboxylic acid anchoring groups can down-shift the work function and passivate the ITO surface, retarding the interface carrier recombination. As a result, the device made with the self-assembled HTM show high open-circuit voltage over 1.10 V and extend the lifetime over 4,300 h when storing at 30% relative humidity. Moreover, the cell works efficiently under much reduced light power, making it useful as power source under dim-light conditions. The demonstration suggests a new facile way of fabricating monolayer HTM for high efficiency perovskite devices, as well as the interconnecting layer needed for tandem cell.

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Organometal halide perovskite materials have aroused tremendous interest in recent years because of their excellent semiconductor properties such as high absorption coefficient, bandgap tunability, defect tolerance, long carrier lifetime, and diffusion length. These characteristics make perovskites one of the most promising candidates for next-generation thin film photovoltaics materials. The power conversion efficiency (PCE) of perovskite photovoltaics has rapidly surged from 3.8% to 25.2% in the past decade. Among those popular perovskite device architectures, the p–i–n device employing polymer contact layers has gain substantial interests because all the layers can be fabricated at low temperature via solution method, and it allows for flexible device fabrications. In 2013, Snaith et al. adopted poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as the hole transporting material (HTM) to build flexible planar perovskite solar cells (PSCs) on...
polymer substrates with a PCE of around 6%, making perovskite photovoltaic attractive technology for flexible optoelectronics.[9] However, the PEDOT:PSS is strongly acidic and hydrophilic that can corrode the indium tin oxide (ITO) electrode and accelerate the moisture induced degradation, resulting in rapid dropping of the devices’ PCE.[10] It was also reported that the diffusion of indium and tin ions into the perovskite layer without barrier at the interface can significantly degrade the device.[11] More recently, poly[bis(4-phenyl)[2,4,6-trimethylphenyl]-amine] (PTAA) has been widely used as HTM that can extract holes efficiently,[12,13] yet these polymers are still costly compared to PEDOT:PSS. In addition, other HTMs have been prepared by depositing triphenylamine-based molecules on a transparent conductive oxide.[14-17] However, those organic HTMs usually possess lower carrier mobility \((10^{-2} -10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) and required dopants, such as lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) and 4-tert-butylpyridine (TBP), to improve conductivity.[12,18,19] However, the dopants are also hydrophilic compounds that can often expel the perovskite layer degradations when being exposed to a humid environment.[20] To improve stability, several inorganic HTMs such as nickel oxide (NiO)\(^{2-}\) and copper oxide \((\text{CuO})\)\(^{−}\) were developed. However, the inorganic HTMs have several drawbacks such as severe interface recombination and low compatibility with flexible devices. To address the above-mentioned issues and fully realize the advantages of PSCs, an alternative strategy to prepare effective HTM is urgently needed.

There have been a few encouraging reports on using conjugated polyelectrolyte as HTM recently that improved the charge transport properties in the perovskite devices. For instance, Zhang et al. introduced thiophene-based polyelectrolyte (P3CT-Na) as HTM in perovskite solar cells achieving PCE over 16%, which was 20% improvement compared with PEDOT:PSS devices.[26] Besides, by controlling the aggregation in polyelectrolytes based HTM film where much uniform perovskite layer can grow, Li et al. showed an enhanced performance of PSCs fabricated on both rigid and flexible substrates.[27] Zhang et al. demonstrated that using dopant-free polyelectrolyte (P3CT-BN) as HTM can reduce interfacial recombination to improve the cell stability.[28] More recently, Li et al. showed that using P3CT-Rb as HTM led to a large open circuit voltage \((V_{OC})\) of 1.144 V[29] In addition, the P3HT with carboxylic groups in the ends of the main chain was synthesized by Lohwasser et al. and demonstrated its potential anchor onto mesoporous TiO\(_2\), as a polymer sensitizer in a solid-state dye-sensitized solar cell.[30] Arbati et al. demonstrated a combination of reduced graphene oxide (rGO) nanosheets with carboxyl groups grafted with P3HT to modify the morphology of active layers in the organic photovoltaic devices.[31] These reports demonstrate the potential of polyelectrolyte as promising HTMs for efficient charge collections in high performance photovoltaics with improved device operational stability. However, several fundamental questions remain open, such as the role of crystallinity, molecular structure, and their interface properties when growing MAPb\(_i\)\(_3\) on the polymer thin films, these are all critical issues that impact the performance and stability.

Here, we demonstrate a new self-assembled monolayer, poly[3-(6-carboxyhexyl)]thiophene-2,5-diy] (P3HT-COOH), on the conducting oxide electrode as HTM to interface with the photoactive perovskite layer, which facilitate the perovskite layer growth and suppress the interface recombination. Especially, perovskite film grown on the self-assembled P3HT-COOH layer exhibits greatly enhanced crystallinity with characteristic X-ray diffraction peak splitting similar to that from the single crystal. Utilizing the synchrotron grazing incident wide-angle X-ray scattering (GIWAXS) technique, we find the perovskites layer shows slight preference for being oriented with (002) planes parallel to the substrate. This results in high performance, reproducible, and hysteresis free PSC with high efficiency over 20%. Notably, the \(V_{OC}\) substantially increase from 0.86 ± 0.06 to 1.09 ± 0.01 V. Extensive morphology, optical spectroscopy, and device characterizations reveal a suppressed interfacial recombination in the perovskite device prepared on the P3HT-COOH HTM. Because of the greatly suppressed dark current, we demonstrate a sensitive photo detector under low light conditions. The enhanced crystallinity and preferred out-of-plane orientation play a key role to suppress the device degradation process, thus extend the device lifetime over 4300 h when storing at 30% relative humidity.

First, we fabricate self-assemble (SA) P3HT-COOH monolayer on ITO as HTM. To directly compare the conjugated polyelectrolyte P3HT-COOH with the benchmark material PEDOT:PSS as HTM and their chemical structures, here we also deposited the HTMs on ITO substrates with commonly used spin-coating (SP) approach (Figure 1a). We first measure the contact angles of water on these three HTMs with SP method on ITO substrates to determine the surface hydrophobicity. Figure 1b is the PEDOT:PSS film (top panel) and P3HT-COOH film (bottom panel) fabricated by SP method, the contact angles are 47.95° and 53.20°, respectively, which suggest both HTMs have similar surface energy. This is because both surfaces have partial carboxylic or sulphonate group that are randomly oriented on the surface, leading to more hydrophilic surface.[32,33] On contrary, the contact angle for SA P3HT-COOH film increases to 71.78°. This is because the carboxylic group in P3HT-COOH polymer chains can freely rotate and adjust their carboxylic group to ITO surface in the liquid phase that consequently increases the anchoring density of carboxylic groups on the ITO surface and forming a highly oriented electric dipole layer, leaving less density of hydrophilic groups pointing toward the surface of P3HT-COOH film (Figure 1c). We use photoluminescence (PL) to probe the quality of the interface. As shown in Figure S1 (Supporting Information), the P3HT-COOH (SA) layer yields a much higher PL intensity compared to the spin coated P3HT-COOH layer, indicating the SA P3HT-COOH film possesses a lower defect density.[27,34] Note that, the arrangement of carboxylic groups on ITO has been reported to induce an interfacial dipole and passivate the ITO surface which can facilitate the holes collection and blocking the carrier recombination.[11] It may also arise from weak P3HT aggregation and the well oriented polymer chain arrangement with a coil-like conformation.[27]

After understanding the surface properties of these HTMs layers, we then fabricate the perovskite photovoltaic layer on the HTMs and characterize their morphology and crystallinity (Figure 1e–j). From the scanning electron microscope (SEM) images of the perovskite grown on different HTMs in Figure 1e, we find the crystal grain of the perovskite layer can grow larger when the surface energy of the HTMs increases. The average perovskite grain size on these HTMs (PEDOT:PSS (SP), P3HT-COOH (SP),
and P3HT-COOH (SA) are 155, 394, and 409 nm, respectively (Figure S2, Supporting Information). This might due to the non-wetting surface of P3HT-COOH layer not only can assist the crystal formation but also can form high-quality perovskites on top of it. The observation is consistent with the literature report[14] where a nonwetting surface can assist the crystal formation. In general, a large crystal grain is beneficial to the creation of long-lived carriers to enable efficient charge transport (Figure S3, Supporting Information).[36]

We further characterized the crystallinity and crystal orientation of these perovskite films with GIWAXS, as illustrated in Figure 1f and their GIWAXS line-cut in Figure 1g along out-of-plane direction. After indexing the peaks, we found all the samples follow the tetragonal phase signatures as expected in MAPbI₃ samples,[37] without the non-converted precursor or other impurity phase. The full-width-at-half-maximum (FWHM) of the (110) peak at \( q \approx 1.0 \text{ Å}^{-1} \) are 0.041, 0.028, and 0.021 Å\(^{-1}\), corresponding to crystallite sizes of 14, 20, and 27 nm for the perovskite films grown on the PEDOT:PSS (SP), P3HT-COOH (SP), and P3HT-COOH (SA) surface, respectively. Notably, the grain size observed by SEM is much larger than the crystallite sizes extracted by GIWAXS, indicating that the perovskite grains observed from SEM may be formed by small crystallites.[38] Moreover, we performed detailed analysis on GIWAXS patterns and peak indexing for the perovskite thin film grown on these HTMs (Figure 1h–i), the P3HT-COOH (SA) thin film exhibits the splitting in (002)/(110) and (004)/(220) planes which are observed in single crystals of MAPbI₃.[39] In sharp contrast, the perovskite thin films fabricated on PEDOT:PSS (SP) and P3HT-COOH (SP) only exhibit broadened (110) and (220) peaks that covers the peak splitting signatures. To evaluate the crystallite size and strain distribution, we performed a detailed structural analysis using an integral breadths (IB) analysis of all the diffraction planes based on the Halder–Wagner equation (Figure 1j). The coherence length, which describes the average crystallite size, was obtained from the slope of the linear fit of the Halder–Wagner plot. The observed reduction in the slope that resulted from an increase in the average crystallite size. These results suggest that the
perovskites thin film fabricated on P3HT-COOH (SA) exhibits enhanced crystallinity compare with sample grown on PEDOT:PSS (SP) and P3HT-COOH (SP).

To further investigate the crystalline orientation of the perovskite layer grown on different HTMs, we plot azimuthal profiles of the X-ray scattering intensity for the feature at $q \approx 1.0 \text{ Å}^{-1}$ in Figure S4 in the Supporting Information. We find that the highest scattering intensity is close to $\chi = 0^\circ$, and the reflection rings of perovskite film grown on P3HT-COOH (SA) surface have a stronger nonuniform intensity distribution in the azimuthal direction. The resulting scattering patterns reveal two major characteristics for the perovskite films fabricated on different HTMs. The perovskite layer grown on P3HT-COOH (SA) is more crystalline where the (002) plane are oriented most along out-of-plane direction, indicating the crystal domains are parallel to the substrate surface. In contrast, the perovskite grown on PEDOT:PSS films exhibit more isotropic rings, which indicates considerable randomness in the 3D orientation of the crystal domains. Note that previous works have suggested that the perovskite films with large grain are mostly oriented out-of-plane direction in parallel to the substrate surface, and such orientation can strongly impact the device performance. Combining the high degree of crystallinity and preferable orientations in MAPbI$_3$ grown on our SA layers, we expect a high performance from the perovskite solar cell fabricated by our samples.

Figure 2a illustrates the device architecture with energy level for each component used in this study. It has been recognized that the highest occupied molecular orbit (HOMO) energy level of the polymer HTM is one of the key factors determining the $V_{OC}$ of PSCs and a low-lying HOMO is beneficial for a high-$V_{OC}$ in the solar cell. As shown in Figure 2a and Table S1 in the Supporting Information, the ionization potentials ($I_p$) measured by photoelectron spectrometer (Figure S5, Supporting Information), the carboxyl groups at the alkyl chain-ends in the P3HT based HTMs have negligible influence on the energy levels of the conjugated backbones, where the $I_p$ of a P3HT-COOH bulk ($-5.10 \text{ eV}$) is comparable to that of P3HT bulk ($-5.11 \text{ eV}$). Interestingly, both SP and SA layers of P3HT-COOH exhibit a noticeably deepened $I_p$ of $-5.32$ and $-5.42 \text{ eV}$, respectively. We attribute the deeper HOMO in thin P3HT-COOH films to the reduced polymer aggregations (see UV–vis absorption analysis in Figure S6 in the Supporting Information). We then deposited the photoactive MAPbI$_3$ films on these substrates and assemble the PSCs. Here, the MAPbI$_3$ layers have a comparable thickness (Figure S7, Supporting Information) and exhibit almost overlapped absorption spectra (Figure S8, Supporting Information), so that the light-harvesting capability of the perovskite layer is not the main factor causing the difference in these three PSCs. Note the thickness of P3HT-COOH (SP) layer was kept around 1 nm, comparable to that of the SA monolayer. Figure 2b and Figure S9 (Supporting Information) display the current density–voltage ($J–V$) characteristics and steady-state output of the PSCs using multiple approach for fabrication of HTM, respectively. The photovoltaics device based on self-assembled PEDOT:PSS exhibited an extremely poor performance due to an uneven surface and discontinuous coverage which would not be further discussed (see Supporting Information and Figures S10–S12 in the

Figure 2. a) Energy level diagrams of MAPbI$_3$ and various HTMs. b) $J–V$ curves of PSCs using PEDOT:PSS or P3HT-COOH as HTM prepared by either SP or SA method. c) Statistics of 60 devices fabricated with different HTMs as collected over 5 different batches. We note that all device parameters and the standard deviation, a metric for the reproducibility, improved. d) EQE Spectra of PSCs with different HTMs. e) $V_{OC}$ versus light intensity and f) Nyquist plots of the PSCs fabricated with different HTMs.
The relationship between time is consistent with the reduced charge recombination. From these results, we believe the greatly suppressed recombination and efficient charge collection originate from the high-quality perovskite layers deposited on ordered P3HT-COOH (SA), which builds a clean interface.

The rise of Internet of Things (IoT) demands an efficient off-grid energy provider for potentially billions of discrete sensing nodes. Among all energy types including thermal, vibration, and photon energy, photon energy exhibits much higher energy density in the general environment and hence, photovoltaics devices which are suitable for environmental dim-light energy harvesting become one of the most promising power providers for numerous IoT sensing nodes. However, the grand challenge of low-light application is the high dark current noise, which would affect the photocurrent of PSCs under low-light illumination, resulting in poor performance. While measuring the dark current, we realized that the P3HT-COOH based PSCs maintains the photo-response at much lower light intensity than the PEDOT:PSS device. The SA P3HT-COOH HTM device shows ultralow dark current of 7.3 × 10^{-8} mA cm^2, which is three orders of magnitude lower than the PEDOT:PSS device (4.9 × 10^{-7} mA cm^2) at the reverse bias, because of the efficient dark current blocking and suppressed interface recombination (Figure S14, Supporting Information). It is thus an excellent candidate for ultra-sensitive low light detection, as well as novel power sources for applications like indoor PSCs and image sensor. Therefore, we collected the J–V curves of PSCs at various low light intensities. Figure 3 shows the J–V characteristic curve under light intensities from 0.9 nW cm^{-2} to 196 µW cm^{-2}. The data reveal that the increase of illuminated light intensity from 0.9, 800 to 1490 nW cm^{-2} significantly shifted the V_{OC} from 59, 487 to 653 mV for the SA-cell, and from 9, 165 to 448 mV for the SP-cell but hardly moved the V_{OC} of the PEDOT:PSS cell from 0 mV. Owing to the reciprocity relationship between V_{OC} and reverse bias saturated dark current described by following Equation: V_{OC} = n k T q \ln(I_{OC}/I_n) where n is the ideality Factor, k is the Boltzmann constant, T is the temperature in Kelvin, q is the elementary charge, I_{OC} is the photocurrent and, I_{n} is the reverse bias saturated dark current) and the suppressed dark current does contribute to the increase in V_{OC}. This observation further evidences that the interfacial charge recombination which is significantly suppressed in the P3HT-COOH based cells and, therefore, the photoinduced charge carriers can build up the photovoltage rapidly. We further plot V_{OC} and J_{SC} against logarithm of light intensity in Figure 3d,e to investigate the carrier recombination losses near open circuit. The P3HT-COOH (SA) device maintain the slope of K = 1.08 k_{B} T/q in the linear V_{OC}–Ln(power) curve whereas the plot slope decreased to K = 2.01 k_{B} T/q for P3HT-COOH (SP). In contrast, the V_{OC} for the PEDOT:PSS (SP) device follows two linear regimes, one at high power with a slope of about K = 2.10 k_{B} T/q and the other shows a much lower threshold for the change in slope of V_{OC} then deviate from linear relationship, which probably due to the high dark current. This observation further validates that the interfacial charge recombination is significantly suppressed in the P3HT-COOH based cells. To compare with PEDOT:PSS (SP) and P3HT-COOH (SP) cells, the photovoltage of the P3HT-COOH (SA) devices are extremely sensitive to low light intensity (nW–µW range), indicating its potential application as a highly responsive low-light detection.
It is known that perovskite materials decomposition with moisture is one of the key factors that limits the device operational lifetime. Moreover, it has been reported that the diffusion of metal ions in ITO, such as indium and tin, into the perovskite layer can significantly degrade the PCE. To further examine device operation stability, we performed a series of un-encapsulated solar cells stability test under relative humidity (RH), constant thermal and 1-sun light intensity conditions. The specific parameter employed to evaluate the stability is the time when the device performance drops to 80% of the initial value (T\textsubscript{80} lifetime). Figure 4a,b is the device operation under different humidity conditions (RH 30% and 55%). In the RH of 30%, the P3HT-COOH (SA) and P3HT-COOH (SP) devices exhibit impressive T\textsubscript{80} lifetime with T\textsubscript{80} = 4300 and 2000 h, respectively. In sharp contrast, the PEDOT:PSS (SP) device only have T\textsubscript{80} lifetime of less than 240 h. Moreover, we increase the environmental humidity to RH = 55%, the T\textsubscript{80} lifetime for these three devices are all decreased dramatically. The P3HT-COOH (SA) and P3HT-COOH (SP) cells remain T\textsubscript{80} lifetime of 700 and 288 h whereas the PEDOT:PSS (SP) device undergoes rapid degradation with T\textsubscript{80} of 90 h for and losses its function within 600 h. This is attribute to the highly hydrophilic nature and strongly acidic -SO\textsubscript{3}H groups in PEDOT:PSS can induce a fast water uptake and further cause the material decompositions which results in rapid dropping of PCE. We also carry out a series of stability tests under fixed temperature of 65 °C and continuous 1-sun illumination in a nitrogen atmosphere (Figure 4c,d). We first fit the post “burn-in” section of the PCE to a straight line and extrapolate the curve back to zero time to obtain the t = 0 efficiency. Under constant thermal stability test, the P3HT-COOH (SA) and P3HT-COOH (SP) devices showed decent thermal stability with T\textsubscript{80} of 470 and 250 h. In contrast with PEDOT:PSS (SP) device, it quickly reached T\textsubscript{80} lifetime with less than 83 h and completely nonfunction at 170 h. Under light-soaking aging tests, we determined the lifetime to 80% degradation (T\textsubscript{80}) from this t = 0 post burn-in efficiency for the P3HT-COOH (SA) devices to be 220 h, which is nearly 11 times longer than the T\textsubscript{80} lifetime of the PEDOT:PSS (SP) devices (20 h). However, all of these three devices have short T\textsubscript{80} lifetime under constant light stress which suggest the degradation mechanism is different than humidity and heat stress which detail discussion can be found in the Supporting Information. Here, the P3HT-COOH (SA) device demonstrated a much robust and stable performance among P3HT-COOH (SP) and PEDOT:PSS (SP) devices in moisture, thermal and photo stability testing, which is clearly due to the better crystallinity and high quality perovskites layer formation and suppression of the degradation process. Further study and improvement are needed for extending the operation lifetime under light. However, the both P3HT-COOH cells exhibited higher threshold for degradation than spin coated PEDOT:PSS device.

We have demonstrated a new type of polyelectrolyte P3HT-COOH as a promising HTM for planar PSCs. This conjugated polyelectrolyte has a relatively low-lying HOMO level with less surface defects and hydrophobicity which facility the perovskite MAPb\textsubscript{1} layer growth with high degree of crystallinity. The perovskite solar cells fabricated by P3HT-COOH as the HTM show substantially improved V\textsubscript{OC} as well as the J\textsubscript{SC} and F.F.. The self-assembly approach is a simple, materials-saving, and cost-effective method to fabricate a uniform and highly reproducible HTM. Such a method enables a homogeneous packing of polymer chains on the ITO surface as a coil-like structure conformation and forces more carboxylic acid moietyes to face toward ITO surface, forming a more organized interface dipole layer. The
ordered and defect free P3HT-COOH layer down-shifts the HOMO for enhanced $V_{OC}$ in device performance and reduces carrier recombination at the interfaces. As a result, both spin coated and self-assembled P3HT-COOH cells outperform the conventional PEDOT:PSS cell significantly on the devices’ $V_{OC}$ and $J_{SC}$, leading to an average $PCE$ of P3HT-COOH for 19.21 ± 0.66% (self-assembled) and 17.01 ± 0.47% (spin coated). In addition, due to a large charge recombination resistance, the photovoltage and photocurrent of the P3HT-COOH (SA) devices remain extremely sensitive to low light intensity (nW–µW range), indicating its potential application as a highly responsive low-light detection. Finally, we show a greatly extended cell lifetime using the new P3HT-COOH layer.

**Experimental Section**

**Materials:** The P3HT-COOH with a weight-average molecular weight, a polydispersity index, and a regioregularity of $59,000$ g mol$^{-1}$, $2.4$ and $9.1$%, respectively, was purchased from Rieke Metals and used as received. Regioregular P3HT-COOH was dissolved in N,N-dimethylformamide (DMF) solution with different concentrations of 0.005–1.0 mg mL$^{-1}$. The ITO substrate was treated with O$_2$ plasma for 10 min and then dipped into the dilute P3HT-COOH solution for 16 h. Thereafter, the substrate was immersed into DMF bath and sonicated to remove the residues to get a thin coating layer (Figure S16, Supporting Information). The detailed studies on the effect of P3HT-COOH solution concentration on the performance of P3HT-COOH (SP) and P3HT-COOH (SA) are summarized in Tables S3–S4 in the Supporting Information, respectively. Methylammonium iodide (MAI) was synthesized by reacting hydroiodic acid (40 mL, 40% in methanol, Junsei Chemical Co. Ltd) in a 250 mL round bottom flask at 0 °C for 4 h (h) with stirring. The precipitate was recovered by evaporating solvents at 50 °C for 1 h with a rotary evaporator. To purify MAI, the products were firstly washed with diethyl ether, then dissolved in methanol, recrystallized from diethyl ether, and finally dried at room temperature in a vacuum oven for 24 h.

**Device Fabrication:** ITO substrates were cleaned with detergent, deionized water, and sonicated with acetone and isopropanol alcohol for 30 min. MAPbI$_3$ solution (40 wt%) was prepared by mixing the MAI powders and PbI$_2$ (1:1 molar ratio, Alfa-Aeser) in and adding 2 moles dimethyl sulfoxide (DMSO) as an additive at room temperature for 12 h. For the inverted MAPbI$_3$ PSCs with different HTMs, PEDOT:PSS/isopropanol/deionized water solution with a volume ratio of 10:1:1 was spin-coated on cleaned ITO with 3500 rpm for 40 s and annealed at 140 °C for 10 min. The P3HT-COOH solution was spin-coated on ITO substrate at 4500 rpm for 40 s, and dried at 140 °C for 10 min. A 40% MAPbI$_3$ solution containing DMSO as additive was spin coated on top of hole transport layer at 4000 rpm for 25 s, and then washed with ether at 6 s, and then dried at 65/100 °C for 4 min and 1 h. Later, the PCBM (25 mg mL$^{-1}$) in chlorobenzene was coated on top of perovskite at 2000 rpm for 30 s to form a 50 nm layer film as electron transporting layer. PEI with 0.1 mg mL$^{-1}$ in methanol was coated at 4000 rpm for 30 s as an interlayer. Finally, a 100-nm-thick silver layer was deposited by thermal evaporation to complete the device fabrications.

**Characterization:** The $J$–$V$ characteristics were performed with forward and reverse scan between −0.1 and 1.1 V with a voltage step of 0.01 V and delay time of 10 ms by a Keithley 2400 source meter (Keithley Instrument, Inc.). The photovoltaic performance measurements were conducted under one-sun intensity (100 mW cm$^{-2}$) using a Xenon-lamp based solar simulator calibrated with AM1.5G spectrum (Enli Tech.). The intensity of the solar spectrum was calibrated by a SRC2020 monocrystalline silicon solar cell (Enli Tech.). The SEM measurement were performed using a S-4800 SEM instrument (Hitachi, Japan) at 5 kV. The XRD data of the...
perovskite were obtained using a Bruker D8 focus powder XRD instrument with Cu-Kα radiation (λ = 0.154 nm). The UV–vis absorption spectrum was investigated on a Jasco V-670 spectrometer (Jasco Company, Hachioji, Tokyo, Japan). For the environmental storage test, the devices were placed in an environmental chamber TEN-H40 (temperature: 0–100°C ± 1 °C, Humidity: 25–95% ± 3%) (Tender Scientific Co., Ltd.) at the preset relative humidity and temperature. The active area was defined by a photomask with an aperture of 0.09 cm². The work function was measured by an AC-2 photoelectron spectrometer (Riken Keiki Instrument, Inc.). The static PL spectra were measured by an Edinburg PLS 920. Time-resolved PL decay curves were obtained by a time-correlated single photon counting (TCSPC) setup. The device was illuminated with a 485 nm laser head LDH-P-485 (PicoQuant GmbH) controlled by picosecond pulsed diode laser driver PDL 800-B (PicoQuant GmbH) at frequency 2.5 MHz, counting (TCSPC) setup. The device was illuminated with a 485 nm laser head LDH-P-485 (PicoQuant GmbH) controlled by picosecond pulsed diode laser driver PDL 800-B (PicoQuant GmbH) at frequency 2.5 MHz, with a pulse duration of 400 ns and fluence of ≈25.4 µW cm⁻². The PL signal was collected using an ultralow noise single photon avalanche detector ID-100-50 (Becker & Hickl GmbH). The EIS measurements were performed using a Metrohm Autolab PGSTAT 302N. A Xenon lamp at 100 mW cm⁻² providing an air mass AM1.5G spectrum and was used as the light source. A small AC perturbation voltage of 15 mV was applied to the devices, and the different output current was measured throughout a frequency range of 1 MHz–1 Hz.

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

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Conflict of Interest
The authors declare no conflict of interest.

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hole extraction layer, out-of-plane orientation, self-assembled

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