Fully crystalline perovskite-perylene hybrid photovoltaic cell capable of 1.2 V output with a minimized voltage loss

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A fully crystalline heterojunction of organo-metal-halide perovskite, CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ (X < 0.24), and perylene constitutes a planar photovoltaic cell that yields a photovoltage exceeding 1.2 V with a single junction cell absorbing up to 800 nm. Here, perylene not only works as a hole conductor but also contributes to photovoltage as a photoconductor. The crystalline plane orientation of perovskite prepared on TiO$_2$ was controlled by thermal annealing such that the lead halide (110) plane that participates in carrier conduction is highly oriented to enhance the photovoltaic performance. The crystal orientation improves the heterojunction structure with perylene. For the best cell with high crystalline orientation, a total voltage loss is significantly minimized to 0.32 V with respect to the absorption band gap of 1.55 eV. The planar crystal cells generate high open-circuit voltages of 1.15–1.22 V, which is close to a theoretical maximal voltage (1.25–1.3 V) described by the Shockley-Queisser efficiency limit. The cell yielded energy conversion efficiency up to 4.96%. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.

After our first report of organo-lead-halide perovskites (CH$_3$NH$_3$PbX$_3$, X = halogen) as photovoltaic absorbers, there has been rapid progress in power conversion efficiency of the perovskite-based solar cells up to 17% or more. Intense band gap absorption over the entire visible wavelength range and quantum conversion efficiency close to unity result in photocurrent density exceeding 20 mA cm$^{-2}$. The perovskite, being an organic and inorganic hybrid semiconductor, exhibits a unique ambipolar carrier conduction property, as revealed by density functional theory (DFT) calculation. It leads to realization of large charge carrier diffusion constants with long lifetime of excited electrons in the order of 100 ns. Supported by such an excellent property of light absorbance and minimal charge recombination, various kinds of electron and hole acceptors sandwiching the perovskite absorber have been found to produce cells with high performance. Moreover, the spectral sensitivity of such perovskites can be easily tuned by changing the cationic and anionic groups in the structure, leading to improvement in photocurrent density and eventually enhances the efficiency.

Although improving the cell efficiency is the ultimate target, understanding the origin of photocurrent and voltage is also important for finding the possibility to enhance the cell performance. The most important nature of the perovskite that enables high efficiency is its high open-circuit photovoltage ($V_{oc}$). In optimized cell structures, the $V_{oc}$ reaches up to the range of 1.0–1.07 V. This voltage output of the single cell structure largely exceeds those of cells absorbing entire visible light (400–800 nm) such as amorphous Si, CdTe, and CIGS and is close to the highest $V_{oc}$ (1.12 V) of GaAs. While a wide band gap bromide perovskite, CH$_3$NH$_3$PbBr$_3$ (2.3 eV, 542 nm), gives $V_{oc}$ reaching 1.3 V, iodide perovskite, which is a narrow band gap absorber (1.55 eV, 800 nm),
is particularly of our interest because of its small voltage loss, 0.45–0.55 V. It is considered that a work function gradient of around 0.2 eV is normally required for rectified carrier transfers across a single heterojunction. Therefore, two heterojunction interfaces that sandwich perovskite layer may involve a thermal loss of energy up to 0.4 eV. In this respect, small voltage loss in the perovskite cell is a rare advantage ever found in inorganic and organic photovoltaic cells. Here, the $V_{oc}$ is strongly affected by hole transport material (HTM) in contact with perovskite. For example, the most widely used organic HTM spiroMeOTAD (2,2′,7,7′-tetrakis (N,N-dimethoxyphenylamine)-9,9′-spirobifluorene) (HOMO, 5.22 eV) shows a voltage loss of around 0.26 eV at the junction with perovskite, CH$_3$NH$_3$PbI$_3$ (valence band, 5.48 eV).

The metal oxide underlayer, such as TiO$_2$ and Al$_2$O$_3$, either as compact planar or mesoporous layer plays a significant role as a crystal type scaffold to assist the chemical synthesis and growth of oriented perovskite crystals. Relatively high $V_{oc}$ (1.1 V) has been obtained by formation of Cl-doped CH$_3$NH$_3$PbI$_3$ on an Al$_2$O$_3$ scaffold. This indicates that quality and characteristics of the junction of perovskite with the scaffold and HTM is critical for the overall performance. The choice of HTM may also depend on junction characteristics. For instance, a crystalline/amorphous junction of perovskite and amorphous organic HTMs, such as spiroMeOTAD and conductive polymers, requires doping with charged molecules or ions in order to achieve sufficient hole conductivity. However, replacement of amorphous HTMs with well-oriented crystals of organic or inorganic conductors can lead to formation of an ordered crystalline heterojunction interface. We expect that this fundamental change to minimize the loss in excitation energy results in higher photovoltage.

In the present study, a fully crystalline hybrid heterojunction between a planar film of organolead-halide perovskite and oriented crystalline film of perylene was prepared. We employed Cl-doped perovskite, CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$, as the light absorber, which has been studied for its unique carrier conduction properties. Long diffusion lengths of photo-electron and hole of CH$_3$NH$_3$PbI$_3$, Cl$_x$ are considered to contribute to high voltage performance.

A crystalline film of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ was prepared by spin-coating a 40 wt.% precursor solution of CH$_3$NH$_3$I and PbCl$_2$ (at a 3:1 molar ratio) in N,N-dimethylformamide on the surface of a transparent conducting oxide (TCO) substrate that had been passivated with a thin TiO$_2$ compact layer (TiO$_2$-CL). The TCO used here was composed of an indium and antimony tin oxide (ITO-ATO) composite on a glass substrate, which has relatively a flat surface. The TiO$_2$ compact layer was made by dip coating treatment of the ITO-ATO substrates with 50 mM aqueous TiCl$_4$ solution (for materials and experimental details, see the supplementary material). X-ray fluorescence analysis of the perovskite film showed that Cl occupies only 8% of the total amount of halogens (Cl:I = 6:70), see Table S1 in the supplementary material which are a slightly excess of stoichiometric ratio (3.0) with respect to lead. XRD reveals existence of a negligible amount of CH$_3$NH$_3$PbCl$_3$ contaminant perovskite (see Figure S1 in the supplementary material). The bulk composition of the perovskite layer is given as CH$_3$NH$_3$PbI$_{2.81}$Cl$_{0.24}$. In other way, we can say that fraction of Cl occupying the perovskite crystal cannot be more than 0.24. For hole conduction, a thin crystalline film of perylene was coated on the CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite surface by an atmosphere-controlled vapor deposition method, as reported previously. Au counter electrode (back contact) was deposited on top of the perylene film by thermal vapour deposition method. Figure 1 shows a schematic diagram of the perovskite-perylene photovoltaic cell and a scanning electron microscope (SEM) image of cross-sectional view of the cell. The thicknesses of the perovskite layer and the perylene layer are approximately 400 and 80 nm, respectively.

We controlled the crystallization process of perovskite film by changing annealing conditions after initial deposition of the crystal. To determine crystallinity and orientation of the crystalline places in the film, the two-dimensional X-ray diffraction (2D-XRD) was measured. The method allows fast collection of the X-ray scattering data and direct imaging of the crystal orientation (see XRD measurements in the supplementary material). Figure 2(a) shows 2D X-ray diffraction patterns of perovskite film formed at different annealing conditions. The two main diffraction peaks at 14.1° and 28.4° were assigned to (110) and (220), respectively, which are consistent with Pb-I plane (see Figures S1 and S2 in the supplementary material). In the film that was formed on the TiO$_2$ compact layer by heating up to 100°C from 25°C gradually for 45 min (film A), the (110) and (220) reflections exhibited a noticeable spread along the Debye-Scherrer ring (Figure 2(a), left).
FIG. 1. A schematic diagram of a perovskite-perylene photovoltaic cell with molecular components and the scanning electron microscope (SEM) cross-sectional image of the cell. Configuration: TCO/TiO₂-CL/CH₃NH₃PbI₃₋ₓClₓ/perylene/Au. Scale bar represents 500 nm.

FIG. 2. X-ray diffraction patterns of the perovskite films. (a) 2D X-ray diffraction patterns of CH₃NH₃PbI₃₋ₓClₓ with different annealing conditions. (b) The χ rocking curves produced by the (110) diffraction pattern of the film A (blue line) and B (red line). (c) In-plane XRD patterns of the film A (blue line) and B (red line), together with assignments of the Bragg reflections.

χ rocking curve produced by the (110) diffraction profile along arc-like feature (Figure 2(b)) was found to be broad with the full width at half-maximum (FWHM) of 34.0°, indicating no specific ordered orientation occurring in the film A. On the other hand, the film (film B) that was annealed at 60°C for 10 min followed by 100°C for 20 min exhibited improved crystal plane orientation (film B, Figure 2(a), right). In this case, the diffraction ring of (110) plane displayed rather sharp χ rocking curve with FWHM of 15.4°. It confirms that the film B is highly orientated along the out-of-plane direction (i.e., the normal direction to the substrate surface). The XRD patterns of the samples along the in-plane direction, shown in Figure 2(c), also support the fact that crystal planes
FIG. 3. 2D X-ray diffraction patterns of the perylene films. (a) Perylene on the perovskite film A and (b) perylene on the perovskite film B.

in film B are preferably oriented along out-of-plane direction. In case of film A, as involving some degree of misalignment, the (110) and (220) reflections were strongly observed, respectively, at 14.1° and 28.4°, indicating no preferred orientation. In contrast, the (110) and (220) planes in the film B almost disappeared while a new (200) reflection was detected. The (200) plane involves CH₃NH₃⁺ and Pb in the plane of CH₃NH₃-Pb-X (see Figure S2 in the supplementary material). These results supported that the (200) crystal planes are vertically aligned in the film B with tilted alignment of the (110) plane. So, highly orientated crystalline perovskite film can be obtained by controlling the annealing process.

An 80 nm thick perylene was deposited on both of films A and B by vapour deposition method. Here, the substrate temperature and deposition rate were changed in the ranges from 50 °C to 100 °C and 0.1 Å/s to 0.5 Å/s, respectively, in an atmosphere of 2.0 × 10⁻⁵ Pa. 2D XRD patterns of perylene formed on the perovskite films A and B are shown in Figures 3(a) and 3(b), respectively. As reported previously, the XRD pattern of perylene crystal typically shows a monoclinic structure with lattice parameters of a = 11.267(4), b = 10.835(3), c = 10.19(3) and α = 90.00, β = 100.81(7), γ = 90.00. On the highly oriented perovskite film (film B), the diffraction patterns of perylene film were more enhanced than that on the weakly oriented film (film A). This indicates that highly crystalline perylene was formed on the highly orientated perovskite film, as exhibited in XRD patterns of Figure 3. Additionally, the 2D XRD diffraction pattern of the perylene film corresponded to the single crystal β-phase, in which 2D intermolecular π-π interactions are formed along the (001) direction that corresponds to the carrier conductive direction. Here, the orientated (110) plane of perovskite film seems to be assisting nucleation and crystal growth of perylene, leading to improved hole conductivity.

Photocurrent density-voltage (J-V) characteristics for the TCO/TiO₂-CL/CH₃NH₃PbI₃₋ₓCℓₓ/perylene/Au photovoltaic cells were measured under AM 1.5 simulated sunlight. The active area of the cell receiving incident light was 2 mm × 2 mm by setting a black square mask. Voltage was scanned at a rate of 100 mV/s in terms of retention time of stepwise scanning (for detailed conditions, see photovoltaic measurements in the supplementary material). The effect of light intensity was studied by varying incident intensity between high (1.5 sun), standard (1 sun = 100 mW/cm²), and low (0.25 sun) conditions. In order to examine the effect of light absorption by perylene on photovoltage, irradiation was done with a cut-off filter that removed the short wavelength light (<450 nm) where perylene absorbs. The results of J-V curves for perovskite films with high and low orientation were compared with that of a standard cell made with a mesoporous structure of TiO₂ (Figure 4(a)). Here, mesoporous TiO₂ film was annealed at 500 °C before coating the perovskite precursor solution and a perovskite film was formed by heating up to 100 °C from 25 °C gradually for 45 min. This heating process gave the best cell performance for the mesoporous TiO₂ sample. The J-V characteristics of these cells are summarized in Table I along with the additional data obtained for different incident light intensities. The data indicate average values and standard deviations taken for eight cells made in same conditions. The results show that all the cells made with perovskite films A and B are capable of generating open-circuit voltage (Vₜ) exceeding 1.1 V.
FIG. 4. J-V and IPCE spectra. (a) Photocurrent density-voltage characteristics for the TiO2-CL/CH3NH3PbI3−xClx/perylene photovoltaic cell with lower (blue line) and higher (red line) film orientation, under AM 1.5 sunlight (100 mW/cm²). A dotted black line shows the photovoltaic cell with mesoporous structure of TiO2. (b) The corresponding incident photon-to-electron conversion spectra.

TABLE I. J-V characteristics of perovskite-perylene photovoltaic cells with different film crystallinity, together with a meso-structured cell as a reference.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>Light intensity (mW/cm²)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2-CL/CH3NH3PbI3−xClx (film A)/perylene</td>
<td>100</td>
<td>1.12 ± 0.01</td>
<td>4.51 ± 0.32</td>
<td>0.510 ± 0.056</td>
<td>2.59 ± 0.12</td>
</tr>
<tr>
<td>TiO2-CL/CH3NH3PbI3−xClx (film B)/perylene</td>
<td>100</td>
<td>1.15 ± 0.01</td>
<td>6.16 ± 0.29</td>
<td>0.527 ± 0.053</td>
<td>3.73 ± 0.10</td>
</tr>
<tr>
<td>TiO2-CL/CH3NH3PbI3−xClx (film B)/perylene (without UV)</td>
<td>100</td>
<td>0.85 ± 0.03</td>
<td>2.24 ± 0.25</td>
<td>0.365 ± 0.073</td>
<td>0.70 ± 0.10</td>
</tr>
<tr>
<td>TiO2-CL/CH3NH3PbI3−xClx (film B)/perylene</td>
<td>150</td>
<td>1.22 ± 0.01</td>
<td>9.22 ± 0.34</td>
<td>0.553 ± 0.093</td>
<td>4.15 ± 0.15</td>
</tr>
<tr>
<td>TiO2-CL/CH3NH3PbI3−xClx (film B)/perylene</td>
<td>25</td>
<td>1.10 ± 0.02</td>
<td>1.73 ± 0.21</td>
<td>0.520 ± 0.087</td>
<td>3.98 ± 0.11</td>
</tr>
<tr>
<td>TiO2-CL/meso-TiO2/CH3NH3PbI3−xClx/perylene</td>
<td>100</td>
<td>1.01 ± 0.05</td>
<td>6.40 ± 0.49</td>
<td>0.494 ± 0.133</td>
<td>3.18 ± 0.21</td>
</tr>
</tbody>
</table>

A thin layer of highly crystalline perylene has a relatively deep HOMO level (−5.40 eV, see Figure S3 in the supplementary material), compared to non-crystalline conductors such as spiroMeOTAD (−5.22 eV). This HOMO level is situated near the valence band of the perovskite (−5.48 eV, Figure S3 in the supplementary material). An energy gap of around 1.47 eV between the perylene HOMO level and conduction band (CB) of CH3NH3PbI3−xClx (−3.93 eV) becomes a theoretical limit for photovoltage generation at the perovskite/perylene heterojunction, although it is also considered that the absolute levels in vacuum of HOMO and CB are not precisely applicable for the interfaces of actual cell. In our experiments, the photovoltaic cell with oriented crystalline junction of perovskite and perylene could generate a Voc of 1.15 V in the 1 sun incident condition. Further, with irradiance of 1.5 sun, the cell showed Voc as high as 1.22 V. Here, the resultant voltage loss of 0.25–0.32 V from the perovskite/perylene gap of 1.47 eV is assumed to include a potential gap, 0.17 eV, which belongs to the interface between perovskite (CB, −3.93 eV) and TiO2 (CB, −4.10 eV). In conclusion, the practical voltage loss due to the resistance of carrier conduction (IR loss) at the heterojunction interfaces as well as inside of the perovskite layer can be slightly more or less than 0.1 eV, which is remarkably a very small value for Gibbs energy loss. Due to thermodynamic constraints, the maximum Voc that a heterojunction-type solar cell can generate is 250–300 mV lower than the band.
The band gap of the absorber material, as described by the Shockley-Queisser treatment, is determined by the absorption coefficient of the material. For the perovskite material used here, the band gap is around 1.55 eV, which indicates that the theoretical maximum voltage for this material is between 1.25 and 1.3 V. The voltage, V_{oc}, obtained from this material is 1.22 V, which is the highest voltage ever realized for a photovoltaic device using perovskite as the absorber material. Moreover, such a high voltage is possible due to the low internal resistance of the cell, as is indicated by the high FF values. The FF values for the perovskite/perylene cells are greater than 0.543, which is comparable to the FF values obtained for hybrid cells using metallocene complex dye absorbers, which also absorb in the wavelength range of 400–750 nm. This high FF value is due to the minimal voltage loss realized by the perovskite/perylene cells, which could be attributed to the oriented crystalline structure through the heterojunction of absorber and HTM.

Moreover, such orientation of crystal structures not only improved photovoltage but also increased the photocurrent. The cell with the oriented junction of perovskite and perylene crystal showed much higher photocurrent density than those of less oriented samples, as shown in Figure 4(a). The photocurrent enhancement is assumed to be due to reduction in internal resistance, as is reflected by an increase in fill factor (FF), which is possibly caused by highly oriented junction structure. A reference non-planar cell with a mesoporous TiO₂ underlayer yields a photocurrent density comparable with the highly oriented planar cell but apparently produces lower V_{oc}, indicating that the non-planar structure causes a large loss in voltage. The corresponding incident photon-to-current conversion efficiency (IPCE) data are given in Figure 4(b). The action spectra cover a wavelength range extended to 800 nm and more, following the optical absorption of the CH₃NH₃PbI₃Cl (see Figure S4 in the supplementary material). There is an additional peak at 400 nm, which can be assigned to the response intrinsic to the perylene crystal. It is therefore assumed that the perylene also contributes, in the short-wavelength region, to photovoltage generation as a p-type photoconductor. This was confirmed by the J-V measurement taken under illumination with wavelengths cut off below 450 nm, where perylene absorbs. In absence of perylene photo-excitation, V_{oc} decreased from 1.15 V to 0.85 V, accompanied by a significant drop in FF and photocurrent (see Table I and Figure S5 in the supplementary material). With this evidence, we know that the high V_{oc} and minimal energy loss realized by crystalline junction of perovskite and perylene is assisted by photoconductivity of perylene which participates in photovoltage generation. It is assumed that the mechanism and photovoltaic energetics in these perovskite-perylene full-crystalline cells can essentially differ from those of the most common cells with perovskite and amorphous organic HTMs.

Additionally, photoconductivity of perylene was observed to be affected by the underlying structures of perovskite. The V_{oc} decreased to 1.0 V when a TiO₂ mesoporous film was used in the structure (Figure 4(a)). In Figure 4(b), the IPCE peak around 400 nm due to perylene is enhanced for the planar heterojunction cell than the non-planar cell with TiO₂ mesoporous layer. The enhanced perylene photoconductance is thought to contribute to maximization of the photovoltage. This effect was reproducibly proved by the planar structure cells. In contrast, use of mesoporous structures caused difficulty in constructing a flat surface of perovskite, which is required to control the orientation of perylene. And hence, mesoporous structure generated lesser V_{oc} (1.0 V).

The planar and fully crystalline heterojunction cell (film B) yields 3.96% and 3.73% power conversion efficiency at incident power of 25 mW/cm² and 100 mW/cm², respectively. The V_{oc} ranged from 1.10 to 1.15 V (see Table I and Figure S6 in the supplementary material). The same cell achieved higher V_{oc} of 1.22 V and 4.15% efficiency under incident power of 150 mW/cm². Short-circuit photocurrent density (J_sc) was linearly dependent on incident light intensity for the range of 0.25–1.5 sun. The V_{oc} improves with increase in light intensity. The latter may reflect a relatively high internal resistance of the cell, as is indicated by low J_{sc} and FFs of the J-V curves. In our cells, the perylene layer affects the internal resistance and may be too thick (80 nm or more) to generate high photocurrent density. At 100 mW/cm², the best cell fabricated with optimized thickness and uniformity of perylene yielded 4.96% efficiency with J_{sc} 8.23 mA/cm², V_{oc} 1.11 V, and FF 0.543 (see Figure S7 in the supplementary material for J-V curve). To minimize the thickness and resistance
of crystalline perylene films, it is necessary to ensure the surface flatness of the perovskite layer to the level of 5–10 nm precision, which has been difficult by the present spin coating method.

In conclusions, we have demonstrated a fully crystalline hybrid photovoltaic cell based on organometal halide perovskites as light absorbers and crystalline perylene as hole conductors that is capable of yielding high open circuit voltage. Orientation of the perovskite crystal planes was controlled by varying post annealing treatments so as to orient the carrier conducting (110) plane along the film thickness. Oriented perovskite film improves the carrier transport properties of the heterojunction interface between perovskite and perylene and enhances hole conductivity in perylene, resulting in high voltage and photocurrent. The best cell with highly orientated junctions was found to be capable of generating $V_{oc}$ up to 1.22 V with conversion efficiency of 4.15%. A higher efficiency was obtained at 4.96% with $V_{oc}$ of 1.11 V. Here, total voltage loss that we could minimize with respect to the band gap (1.55 eV) is 0.33 V. Based on the Shockley-Queisser limit of $V_{oc}$ with respect to band gap, the perovskite cell designed here works with $V_{oc}$ close to the theoretical maximum (1.25–1.30 V) and a minimal loss of Gibbs energy. The minimized voltage loss indicates that the internal IR drop (thermodynamic loss) at the TiO₂/perovskite/perylene junctions was significantly suppressed. For potential performance of the cell, improvement of FF to 0.75 and photocurrent density to more than 20 mA/cm² can lead to conversion efficiency as high as 20% for a single cell capable of $V_{oc}$ 1.2 V and visible light harvesting up to 800 nm.

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A.I. designed the experiments, fabricated and characterized the devices. T.M. planned the study and supervised the work. A.K.J participated in the discussion of the comparison of I-V performance in Table I. All authors discussed the results and contributed to the final version of the paper.


32 See supplementary material at http://dx.doi.org/10.1063/1.4895039 for experimental details, X-ray fluorescence analysis, photoelectron yield and absorption spectra, XRD data, and J-V curves of the devices.
Supplemental Material

Fully crystalline perovskite-perylene hybrid photovoltaic cell capable of 1.2V output with a minimized voltage loss

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Prosvkite synthesis and device fabrication:

The organic-inorganic hybrid photovoltaic cells were prepared using the following procedure. Transparent conducting oxide (TCO, an ITO-ATO composite) glass (10 Ω/sq, Geomatec Co., Ltd.) was cleaned ultrasonically in acetone, isopropanol, and ultra-pure water sequentially for 10 min each. The TCO glass was pre-treated with a 50 mM aqueous TiCl4 at 70 °C for 60 min. Synthesis of CH3NH3PbI3-xClx was carried out by dropping onto the substrate a 40 wt % precursor solution of CH3NH3I and PbCl2 in N,N-dimethylformamide at a 3:1 molar ratio, which were rotated at 2000 rpm for 45 s and dried. After being heated at 60~100 °C, perylene (Tokyo Chemical Industry Co., Ltd.) was sequentially stacked by the vapor deposition method under a pressure of about 2.0×10^{-5} Pa as hole-transporting layers (80 nm). Finally, Au top electrodes (100 nm) were thermally evaporated on the perylene films. For fabrication of mesoporous TiO2 layer, before prosvkite was coated, a commercial TiO2 paste (Ti-Nanoxide T/SP, Solaronix) diluted in a mixture of ethanol and terpineol was spin-coated at with 2000 rpm for 30 s. After drying at 120 °C, the TiO2 films were annealed at 500 °C.
**XRD measurements:**

The scanning electron microscope (SEM) cross-sectional image was obtained by Ultra-high Resolution Scanning Electron Microscope (SU8000, Hitachi High-Technologies Corporation). X-ray fluorescence analysis was carried out by X-Ray Fluorescence Spectrometry (S8 Tiger, Bruker). Thin film structures of the perylene film were characterized by X-ray diffraction using CuKα radiation (D8 Discover/Hybrid, Bruker).

**Photovoltaic measurements:**

Photocurrent density–voltage (J–V) curves were measured by a computer-controlled digital source meter (Keithley 2400) under irradiation by a PEC-L01 solar simulator (AM 1.5 G, 100 mW/cm², Peccell Technologies, Inc.). The active area of the perovskite/perylene cell receiving incident light was set by attaching a black square mask of 2 x 2 mm. Voltage scanning rate was 100 mV/s in terms of retention time of stepwise scanning. Incident photon-to-current conversion efficiency (IPCE) was recorded with PEC-S20 action spectrum measurement setup (Peccell Technologies, Inc.). Electronic absorption spectra were measured with a UV-1800 spectrophotometer (Shimadzu Corporation). The ionization potential in the air was estimated by the photoelectron yield spectrometer (AC-3, Riken Keiki Co., Ltd.).
Table S1. The molar ratio obtained from X-ray fluorescence analysis of the mixed halide perovskite CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$.

<table>
<thead>
<tr>
<th>CH$_3$NH$_3$ or Pb</th>
<th>I</th>
<th>Cl</th>
<th>I+Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.81</td>
<td>0.24</td>
<td>3.05</td>
</tr>
</tbody>
</table>
Figure S1. Out-of-plane XRD patterns of the film A (week orientation, in blue line) and film B (high orientation, in red line), together with assignments of the Bragg reflections.
Figure S2. Projection views (a) along with 110 plane and (b) on ab plane of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. 
Figure S3. Photoelectron yield spectra of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ (red) and perylene (blue) films in the air.

Figure S4. Absorption spectra of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ (red) and CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ /perylene (blue) films in the air.
**Figure S5.** Photocurrent density-voltage characteristics for the TiO$_2$-CL/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ /perylene photovoltaic cell with higher film orientation under the irradiation light more than 450 nm (100 mW/cm$^2$).

**Figure S6.** $J$-$V$ characteristics of TiO$_2$-CL/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/perylene photovoltaic cells at different light intensities.
Figure S7. $J-V$ characteristics of a TiO$_2$-CL/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/perylene photovoltaic cell yielding an efficiency of 4.96% at 100 mW/cm$^2$ irradiation.