## Supporting Information

## Surface Ligands for Methylammonium Lead Iodide Films: Surface Coverage, Energetics, and Photovoltaic Performance

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## Experimental section

## Materials

Methylammonium iodide (MAI) was purchased from Great Cell Solar and used after recrystallizing twice in ethanol and drying in a vacuum oven overnight at $60^{\circ} \mathrm{C}$. Lead iodide ( $\left.\mathrm{PbI}_{2}, 99.99 \%, \mathrm{TCI}\right)$, poly(triaryl amine) (PTAA, Sigma Aldrich), C60 (Nano-C, 99.5\%), bathocuproine (BCP, TCI, >99\%), and aluminum (Al, 99.99\%, Angstrom Engineering) were used as received. Anhydrous solvents including N,N-dimethylformamide (DMF, Drisolv, anhydrous, 99.8\%), dimethyl sulfoxide (DMSO, Millipore SeccoSolv, 99.9\%), 2-propanol (IPA, Alfa Aesar, $99.5 \%$ ), and toluene (Alfa Aesar, 99.8\%) were used as received. The surface ligands phenyltrichlorosilane (TCI, 98\%), phenylphosphonic acid (Sigma-Aldrich, 98\%), 4bromobenzoic acid (Alfa Aesar, 98\%), p-toluic acid (TCI, 98\%), anilinium chloride (Alfa Aesar, 99\%), phenylethylammonium iodide (Great Cell Solar), hydroiodic acid (Alfa Aesar, 55-58\%), thiophenol (Alfa Aesar, 99\%), 1-octylphosphonic acid (Alfa Aesar, 99\%), octanoic acid (Alfa Aesar, 98\%) were used as received.

Octylammonium iodide (OAI): OAI was synthesized by reacting octylamine ( $12.6 \mathrm{~mL}, 0.076$ mol, Alfa Aesar, $99 \%$ ) and hydroiodic acid ( $10 \mathrm{~mL}, 0.076 \mathrm{~mol}$ ) in 20 mL of ethanol at $0^{\circ} \mathrm{C}$ for 2 h with stirring. The resulting solution was dried at $50^{\circ} \mathrm{C}$ with a rotary evaporator to remove the solvents. The product was dissolved in ethanol and recrystallized from diethyl ether. The product was rinsed three times with diethyl ether and dried in a vacuum oven at $60^{\circ} \mathrm{C}$ overnight before use.

## PV device fabrication

Patterned ITO coated glass substrates ( $15 \Omega / \square$ ) were sequentially sonicated in aqueous detergent (sodium dodecyl sulfate, Sigma-Aldrich), deionized water, acetone, and 2-propanol
(IPA) each for 10 min . After drying with nitrogen the substrates were exposed to UV-ozone treatment for 10 min to remove organic contaminants. $100 \mu \mathrm{~L}$ of PTAA $(2.5 \mathrm{mg} / \mathrm{mL}$ in toluene) was spun-cast at 4000 rpm for 35 s with a 2 s ramp inside the nitrogen-filled glovebox ( $<0.1 \mathrm{ppm}$ of $\mathrm{O}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ ). For the $\mathrm{MAPbI}_{3}$ films, 461 mg of $\mathrm{PbI}_{2}, 159 \mathrm{mg}$ of MAI, and 78 mg of DMSO (1:1:1 molar ratio) were dissolved in 600 mg of DMF and stirred at room temperature for 1 h before use in the nitrogen-filled glovebox. Following PTAA coating, $80 \mu \mathrm{~L}$ of $\mathrm{MAPbI}_{3}$ solution (prepared as detailed above) was deposited and spun-cast at 1000 rpm for 5 s followed by 3000 rpm for $80 \mathrm{~s} .100 \mu \mathrm{~L}$ of toluene was dropped on the spinning substrate after 10 s of reaching 3000 rpm , resulting in the formation of transparent films that were then annealed on a hot plate at $100^{\circ} \mathrm{C}$ for 10 min . For surface modification, $100 \mu \mathrm{~L}$ of surface ligand solution $(1 \mathrm{mg} / \mathrm{mL})$ in IPA was then deposited on the dark $\mathrm{MAPbI}_{3}$ films and left to sit for 10 s before spinning at 4000 rpm for 30 s with a 2 s ramp. To remove excess unbound ligands, the substrates were rinsed with toluene ( $3 \times 200 \mu \mathrm{~L}$ aliquots during spinning). The control device was treated in the same way but without surface ligands in the IPA. Both control and treated films were then transferred to the thermal evaporator without air exposure and $\mathrm{C}_{60}(30 \mathrm{~nm})$ and $\mathrm{BCP}(8 \mathrm{~nm})$ were deposited sequentially with a rate of $1 \AA / \mathrm{s}$ and $0.5 \AA / \mathrm{s}$, respectively, at a pressure of $c a .2 \times 10^{-6} \mathrm{mbar}$. Finally, aluminum ( 100 nm ) electrodes were evaporated through a shadow mask that defined 12 cells of $0.1 \mathrm{~cm}^{2}$ area per substrate. Solar cell performance was measured using a solar simulator (ABET technologies, 11002) at $100 \mathrm{~mW} / \mathrm{cm}^{2}$ illumination (AM 1.5G). The intensity was adjusted to $\left(100 \mathrm{~mW} / \mathrm{cm}^{2}\right)$ based on a photodiode calibrated with a KG5 filter (ABET technologies).

## Characterization

X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI 5600 ultrahigh vacuum system (UHV) with a hemispherical electron energy analyzer, an $\mathrm{Al} \mathrm{K} \alpha$ source (1486.6 eV, PHI 04-548 dual anode X-ray source) for excitation, and a pass energy of 23.5 eV for XPS acquisition. Ultraviolet photoelectron spectroscopy (UPS) measurements were taken with an Excitech H Lyman- $\alpha$ photon source $(10.2 \mathrm{eV})$ with an oxygen-filled beam path coupled with the same PHI 5600 UHV and analyzer system. A sample bias of -5 V and a pass energy of 5.85 eV were used for UPS acquisition. IPES measurements were performed in the Bremsstrahlung isochromat mode with electron kinetic energies below 5 eV and an emission current of $2 \mu \mathrm{~A}$ to minimize sample damage. A Kimball Physics ELG-2 electron gun with a BaO cathode was used to generate the electron beam. Emitted photons were collected with a bandpass photon detector consisting of an optical bandpass filter ( 254 nm, Semrock) and a photomultiplier tube (R585, Hamamatsu Photonics). Samples were held at a -20 V bias during all IPES measurements and the UHV chamber was blacked-out to exclude external light.

Samples for scanning electron microscopy (SEM) were prepared on unpatterned ITO-coated glass substrates in an identical manner as the PV cells (through surface ligand treatment) and probed with a Hitachi S-4300 SEM with an accelerating voltage of 10 kV . UV-Vis absorbance and PL measurements were recorded on thin films in a nitrogen-filled glovebox using an Ocean Optics fiber-optic spectrometer with a thermoelectric cooled CCD detector. Films for UV-Vis, PL, and XRD measurements were prepared directly on ITO substrates without PTAA. XRD spectra were collected with a Bruker-AXS D8 advance diffractometer with $\mathrm{Cu} \mathrm{K} \alpha$ radiation ( $\lambda=$ $1.5418 \AA$ ) operating at 40 kV and 40 mA . External quantum efficiency (EQE) measurements were conducted as detailed previously. ${ }^{1}$


Figure S1. Scanning electron microscope images of control and surface ligand treated $\mathrm{MAPbI}_{3}$ films on PTAA hole transport layers. Surface ligand treatment was applied through spin coating solutions of the surface ligands in isopropanol. The scale bar is $1 \mu \mathrm{~m}$ and applies to all images.


Figure S2. UV-Vis absorbance spectra of thin films of untreated and surface ligand treated $\mathrm{MAPbI}_{3}$ films.


Figure S3. Photoluminescence spectra of $\mathrm{MAPbI}_{3}$ films treated with varying surface ligands. Solid and dashed lines correspond with aryl and alkyl containing ligands.


Figure S4. XRD spectra of untreated and surface ligand treated $\mathrm{MAPbI}_{3}$ films.

## Surface Ligand Coverage Calculations and Measurements



Figure S5. (a) $\mathrm{MAPbI}_{3}$ cubic crystal structure with the (001) and (002) planes shown in pink. $\mathrm{MAPb}_{3}$ tetragonal crystal structure showing the (b) (100) and ( $\overline{4} 00$ ) planes and (c) the (001) and $(00 \overline{4})$ planes. Pb atoms are shown in black, I in orange and MA molecules in green. The indicated planes were used in surface coverage calculations.

Following up with equation (1) and (2) in the main paper, for the case of OPA the I 3d signal from $\mathrm{MAPbI}_{3}$ is attenuated by the whole molecule of OPA ( $\lambda^{I} O P A$ ), but the O 1 s signal from OPA is only attenuated by the octyl group on top of it ( $\lambda^{O}$ Octyl). Self-assembled monolayers (SAM) typically do not stand straight up and so a title angle, $\beta$, is included. By following the work done by Gao at. el. ${ }^{2}$ we can approximate the ratio of atomic densities by assuming they bind to Pb atoms. We expect that all ligands except for the ammonium containing ligands will indeed bind to Pb . In case of a cubic crystal structure, Figure S 5 a , for each unit cell ( 3 iodide and 1 Pb ) there will be 1 ligand adsorption cite. As shown in figure S 5 b and c , by assuming a tetragonal crystal structure for $\mathrm{MAPbI}_{3}$ ( 100 and 001 face), for each unit cell there can be 2 Pb atoms on the surface that can bind to 2 ligands (i.e., one ligand per Pb atom) at $100 \%$ coverage. In each unit cell there are a total of 12 iodide atoms and for each PA containing ligand there are 3 oxygen atoms (total of 6 oxygens for a unit cell).:

Cubic $^{\text {PbI }_{2}}: \frac{\rho_{a, \text { modifier }}^{o}}{\rho_{a, M A P b I 3}^{I}}=\frac{\frac{3}{\operatorname{Area}^{\prime} d_{P A} \operatorname{Cos}(\beta)}}{\frac{3}{\text { Area }_{\text {a }}^{\text {cubic }}}}=\frac{a_{\text {cubic }}}{d_{P A} \operatorname{Cos}(\beta)}$
Tetragonal ${ }_{100}^{M A_{2} P_{2} I_{2}}: \frac{\rho_{a, \text { modifier }}^{o}}{\rho_{a, \text { MAPbI3 }}^{I}}=\frac{\frac{6}{\operatorname{Area} \times d_{P A} \operatorname{Cos}(\beta)}}{\frac{12}{\operatorname{Area} \times \sqrt{2} a_{c u b i c}}}=\frac{\sqrt{2}}{2} \frac{a_{\text {cubic }}}{d_{P A} \operatorname{Cos}(\beta)}$
Tetragonal $l_{001}^{P b_{2} I_{4}}: \frac{\rho_{a, \text { modifier }}^{O}}{\rho_{a, \text { MAPbI3 }}^{I}}=\frac{\frac{6}{\operatorname{Area} \times d_{P A} \operatorname{Cos}(\beta)}}{\frac{12}{\text { Area } \times 2 a_{\text {cubic }}}}=\frac{a_{\text {cubic }}}{d_{P A} \operatorname{Cos}(\beta)}$
In these equations $d_{P A}$ is the length of phosphonic acid (PA) group, acubic is the lattice unit cell length for a cubic $\mathrm{MAPbI}_{3}$ crystal structure, which equals 0.635 nm , and Area is the cross sectional area of the particular plane for the unit cell. The details of the length of modifiers are shown in Figure S6 on average, we use a ratio of $0.9 \frac{a_{c u b i c}}{d_{P A} \operatorname{Cos}(\beta)}$. Sensitivity factors for I $3 \mathrm{~d}_{5 / 2}$ and O 1 s are 6.206 and 0.711 respectively. ${ }^{3}$

Table S1. Experimentally determined and calculated O:I ratios for the surface ligands at varying electron take-off angles.

| Surface ligand | Exp. $\frac{I_{I V}^{x}}{I_{\text {Sub }}^{v}} \text { at } 0^{\circ}$ | $\begin{aligned} & \text { Calc. }{ }^{\text {a) }} \\ & \frac{I_{O V}^{x}}{I_{\text {Sub }}^{y}} \text { at } 0^{\circ} \end{aligned}$ | $\begin{gathered} \text { Exp. } \\ \frac{I_{O V}^{x}}{I_{S u b}^{y}} \text { at } 45^{\circ} \end{gathered}$ | $\begin{gathered} \text { Calc. }{ }^{\text {a) }} \\ \frac{I_{O V}^{X}}{I_{\text {Sub }}^{y}} \text { at } 45^{\circ} \end{gathered}$ | Exp. $\frac{I_{O V}^{x}}{I_{\text {sub }}^{y}} \text { at } 75^{\circ}$ | $\begin{gathered} \text { Calc. }{ }^{\text {a) }} \\ \frac{I_{O V}^{x}}{I_{\text {Sub }}^{V}} \text { at } 75^{\circ} \end{gathered}$ | Surface Coverage (\%) | Penetrates into $\mathrm{MAPbl}_{3}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| PPA | 0.52 | 0.04 | 0.63 | 0.06 | 0.78 | 0.22 | N/A | Yes |
| OPA | $<0.09{ }^{\text {b }}$ | 0.09 | $<0.07{ }^{\text {b }}$ | 0.13 | 0.6 | 0.65 | 96 | No |
| BrBA | $<0.15^{\text {b }}$ | 0.05 | <0.19 ${ }^{\text {b }}$ | 0.08 | 0.15 | 0.35 | 69 | No |
| OCA | <0.08 ${ }^{\text {b }}$ | 0.05 | $<0.08{ }^{\text {b }}$ | 0.08 | 0.15 | 0.33 | 71 | No |
| AnCl ${ }^{\text {c }}$ | 1.5 | N/A | 2 | N/A | 3 | N/A | N/A | Yes |
| PEAI ${ }^{\text {c }}$ | 2.7 | N/A | 3.5 | N/A | 4.4 | N/A | N/A | Yes |
| OAI ${ }^{\text {c }}$ | 2.5 | N/A | 3.5 | N/A | 4.7 | N/A | N/A | Yes |

${ }^{\text {a) }}$ All calculated values are for a molecular tilt angle of $30^{\circ}$ and complete $(\Phi=1)$ surface coverage; ${ }^{\text {b }}$ The intensity from the overlayer is less than the listed limit of detection. Details on the limit of detection calculation are provided in the Supporting Information; ${ }^{\text {c }}$ The ammonium containing ligands use the non-MA C to MA C ratio as the $\frac{I_{O V}^{x}}{I_{S u b}^{y}}$ ratio.
a)

b)

c)



Figure S6. Schematics of geometry and lengths of 4 ligands (a) OPA, (b) OCA, (c) PPA, and (d) BrBA. Pubchem (http://pubchem.ncbi.nlm.nih.gov/) was used to estimate all the geometric values. For each modifier it is assumed that the bond lengths and angles do not change upon binding to Pb . The blue and green arrows are from the references, and red arrows are calculated values based on the covalent radii of each atom. ${ }^{4}$

The attenuation lengths can be approximated by equation (S4). ${ }^{5,6}$
$\lambda=0.316 \times 10^{8}\left(\frac{A}{\rho_{\mathbf{m}} N}\right)^{1 / 2}\left[\frac{E}{Z^{0.45}\left(3+\ln \frac{E}{27}\right)}+4\right]$
Where $A$ is the atomic molar mass in $\mathrm{g} \mathrm{mol}^{-1}, \rho_{m}$ is mass density in $\mathrm{g} \mathrm{cm}^{-3}, N$ is Avogadro's number, Z is the total atomic number of the layer and $E$ is kinetic energy of the element of interest. Calculated attenuation lengths for various molecules and their parameters are shown in Table S2.

Table S2. Attenuation length and parameters required to calculate it for various layers.

| Film | Molar Mass <br> $\left(\mathrm{g} \cdot \mathrm{mol}^{-1}\right)$ | Density $\left(\rho_{m}\right)$ <br> $\left(\mathrm{g} \cdot \mathrm{cm}^{-3}\right)$ | Atomic <br> Number | Element | Kinetic <br> Energy $(\mathrm{eV})$ | Attenuation <br> Length $(\mathrm{nm})$ | Symbol |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| MAPbl $_{3}$ | 619.97 | 3.947 | 260 | I | 886.76 | 2.41643 | $\lambda_{\text {MAPbl3 }}^{\prime}$ |
| PA | 81.996 | 1.651 | 45 | O | 954 | 2.741 | $\lambda^{0}$ PA |
| OPA | 194.208 | 1.1 | 109 | I | 886.76 | 3.46074 | $\lambda^{\prime}$ OPA |
| Octane | 114.232 | 0.703 | 66 | O | 954 | 4.27699 | $\lambda^{\circ} 0_{\text {Octyl }}$ |
| PPA | 158.092 | 1.4 | 85 | I | 866.76 | 3.03066 | $\lambda^{\prime}$ PPA |
| Phenyl <br> (benzene) | 78.114 | 0.8765 | 42 | O | 954 | 3.77222 | $\lambda^{\circ_{\text {Phenyl }}}$ |

Let's take the case where OPA is bonding to the surface. We are probing the integrated intensity of the I $3 \mathrm{~d}_{5 / 2}$ photoelectrons from $\mathrm{MAPbI}_{3}$ and the oxygen signal from the OPA ligand. The equation for calculating surface coverage is shown below:
$\frac{I_{P A}^{O}}{I_{M A P b I_{3}}^{I}}=\frac{S F^{O}}{S F^{I}} \frac{\rho_{a, P A}^{O}}{\rho_{a, M A P b I_{3}}^{I}} \frac{\lambda_{P A}^{O}}{\lambda_{M A P I_{3}}^{I}} \frac{\phi\left(1-\exp \left[-\frac{d_{\text {Heptyl }} \operatorname{Cos}(\beta)}{\lambda_{\text {Heptyl }}^{O} \operatorname{Cos}(\theta)}\right]\right.}{1-\phi+\phi \exp \left[-\frac{d_{O P A} \operatorname{Cos}(\beta)}{\lambda_{O P A}^{I} \operatorname{Cos}(\theta)}\right]}$
The photoelectrons generated from O in the PA group are attenuated by $\lambda^{\mathrm{O}}{ }_{P A}$, and photoelectrons from I generated in $\mathrm{MAPbI}_{3}$ are attenuated by $\lambda^{\mathrm{I}}$ MAPbI3. Oxygen's signal is further attenuated by passing through the octyl group with doctyl $\operatorname{Cos}(\beta)$ thickness and attenuation length of $\lambda^{\mathrm{O}}$ Octyl, and the iodide signal is attenuated by passing though OPA with dopa $\operatorname{Cos}(\beta)$ thickness (the length of the ligand is the average value presented in Figure S6) and attenuation length of $\lambda^{\mathrm{I}}{ }_{\mathrm{OPA}}$. We note that this modeling is based on a flat surface and local variations in surface roughness can result in deviations in the modeled vs. actual surface coverage.

Equation (S6) and (S7) are used to calculate the O to I peak ratio as a function of surface coverage for OCA and BrBA:
$\frac{I_{C A}^{O}}{I_{M A P b I_{3}}^{I}}=\frac{S F^{O}}{S F^{I}} \frac{\rho_{a, C A}^{O}}{\rho_{a, M A P b I_{3}}^{I}} \frac{\lambda_{C A}^{O}}{\lambda_{M A P I_{3}}^{I}} \frac{\phi\left(1-\exp \left[-\frac{d_{\text {Octyl }} \operatorname{Cos}(\beta)}{\lambda_{\text {Octyl }} \operatorname{Cos}(\theta)}\right]\right.}{1-\phi+\phi \exp \left[-\frac{d_{O C A} \operatorname{Cos}(\beta)}{\lambda_{O C A}^{I} \operatorname{Cos}(\theta)}\right]}$
$\frac{I_{C A}^{O}}{I_{M A P I_{3}}^{I}}=\frac{S F^{O}}{S F^{I}} \frac{\rho_{a, C A}^{O}}{\rho_{a, M A P b I_{3}}^{I}} \frac{\lambda_{C A}^{O}}{\lambda_{M A P b I_{3}}^{I}} \frac{\phi\left(1-\exp \left[-\frac{d_{4-\text { Bromopheny1 }} \operatorname{Cos}(\beta)}{\lambda_{4-\operatorname{Bromopheny1}}^{O} \operatorname{Cos}(\theta)}\right]\right.}{1-\phi+\phi \exp \left[-\frac{d_{B r B A C} \operatorname{Cos}(\beta)}{\lambda_{B r B A}^{I} \operatorname{Cos}(\theta)}\right]}$
Where $\frac{\rho_{a, C A}^{o}}{\rho_{a, M A P b I_{3}}^{I}}=0.6 \frac{a_{c u b i c}}{d_{C A} \operatorname{Cos}(\beta)}$ as we have one less oxygen in CA group compared to PA group. The values to calculate attenuation length can be found in Table S3. The calculated Io/II ratios as a function of surface coverage of the OCA ligand are displayed in Figure S7a and the experimentally measured XPS data is shown in Figure S7b and c. The experimental results show an O:I signal ratio of 0.15 at a $75^{\circ}$ takeoff angle, which according to our calculations indicates 71 $\pm 10 \%$ surface coverage. This value is not sensitive to the molecular tilt angle within the experimental limits. As we decrease $\theta$ to 45 and $0^{\circ}$, the ratio between the O and I signal drops to below 0.05 , which is below the detection limit of our XPS system. Figure S 7 d shows the calculated ratio of the O 1 s peak from BrBA to the $\mathrm{I} 3 \mathrm{~d}_{5 / 2}$ peak from $\mathrm{MAPbI}_{3}$ and Figure S 7 e and f show the experimentally measured XPS results on O and I peaks with varying take-off angles. Our experimental results show the presence of oxygen at a $75^{\circ}$ take-off angle, with an $\mathrm{O}: I$ ratio of 0.15 . At this ratio, the surface coverage is calculated to be $69 \pm 10 \%$. The calculation also indicates that with this surface coverage the peak ratios at lower angles should drop to 0.05 , which is below the limit of detection.


Figure S7. Calculated ratios of O 1 s and I $3 \mathrm{~d}_{5 / 2}$ signal intensity vs. surface coverage for (a) OCA and (d) BrBA at 3 different electron take off angles $\left(0^{\circ}, 45^{\circ}\right.$ and $\left.75^{\circ}\right)$ and 3 different molecular tilt angles $\left(0^{\circ}, 30^{\circ}\right.$ and $60^{\circ}$ ). Angle dependent XPS of the (b,e) O 1 s and (c,f) I $3 \mathrm{~d}_{5 / 2}$ regions at $\theta=0^{\circ}$, $45^{\circ}$ and $75^{\circ}$ for (b,c) OCA and (e,f) BrBA treated MAPbI3.

Table S3. Attenuation length and parameters used in the calculations for the various layers.

| Film | Molar Mass (g.mol ${ }^{-1}$ ) | Density (g.cm ${ }^{-3}$ ) | Atomic <br> Number | Element | Kinetic Energy (eV) | Attenuation <br> Length (nm) | Symbol |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{MAPbl}_{3}$ | 619.97 | 3.947 | 260 | 1 | 886.76 | 2.416 | $\lambda^{\prime}$ марыІ3 |
| CA | 45.03 | 1.22 | 25 | 0 | 954 | 2.984 | $\lambda^{0}{ }_{C A}$ |
| OCA | 144.21 | 0.9 | 82 | 1 | 886.76 | 3.658 | $\lambda^{\prime} \mathrm{OCA}$ |
| Heptane | 100.196 | 0.684 | 58 | O | 954 | 4.266 | $\lambda^{\circ}{ }_{\text {Heptyl }}$ |
| BrBA | 201.019 | 1.701 | 100 | 1 | 886.76 | 2.921 | $\lambda^{\prime}{ }_{\text {BrBA }}$ |
| 4-bromophenyl | 156.002 | 1.4 | 77 | O | 954 | 3.362 | $\lambda{ }^{\circ}{ }_{4 \text {-bromophenyl }}$ |

Modeling the C peaks using the equations presented above is difficult, and thus we use a comparative approach to OPA and PPA. Figure S 8 shows the C 1 s peak and the non-MA C to MA C ratios for untreated, PPA treated, and OPA treated $\mathrm{MAPbI}_{3}$. In our experimental data two additional peaks appear in the C region with peak positions of ca. 283 and 285.5, which are satellite peaks from I 4d. Figure S 8 a shows the C 1 s region for untreated $\mathrm{MAPbI}_{3}$. The intensity of the nonMA C peak (ca. 285 eV ) is less than the MA C peak intensity when the probing depth is greater, i.e. take-off angle is smaller, and as the take-off angle increases the non-MA C peak increases until both peaks are close to equal at $75^{\circ}$. This data is reasonable as we expect most of the carbon contamination is located on the surface. Figure S8c shows the C 1 s region of OPA. As discussed in the above section, OPA does not penetrate into the film and is mostly on the surface. By looking at the trends in the ratio of the non-MA C to MA C in part d (red line), the ratio increases more drastically than the un-modified $\mathrm{MAPbI}_{3}$, which is an indication of increased adsorption of hydrocarbons on the $\mathrm{MAPbI}_{3}$ surface. Looking at PPA in part b and d (blue line), we can see the ratio between the non-MA carbon and MA carbon is higher at all angles and increases more slowly compared to OPA as the angle increases, which is due to penetration of PPA into the $\mathrm{MAPbI}_{3}$ film as previously discussed. The $\mathrm{MAPbI}_{3}$ films that were treated with the ammonium salts can be compared to the PPA results, as shown in Figure S9. Here, AnCl shows similar results as PPA with a slightly lower non-MA C to MA C ratio at all angles, indicating that it also penetrates into $\mathrm{MAPbI}_{3}$. Both OAI and PEAI show even higher non-MA C to MA C ratios at all concentrations, indicating a larger amount of these ligands penetrate into the film. These results show that the ammonium salts all penetrate into the $\mathrm{MAPbI}_{3}$ layer.


Figure S8. Angle dependent XPS of the C 1 s region at $\theta=0,45$ and $75^{\circ}$ for (a) untreated $\mathrm{MAPbI}_{3}$, (b) with PPA treatment and (c) with OPA treatment. The red peak is fit to the MA carbon and the blue peak is fit to the non-MA carbon. (d) Ratio of non-MA C to MA C for the films as a function of the electron take-off angle.


Figure S9. Angle dependent XPS of the C 1 s region at $\theta=0,45$ and $75^{\circ}$ for (a) AnCl , (b) PEAI, and (c) OAI treated $\mathrm{MAPbI}_{3}$ films. The red peak is fit to the MA carbon and blue is the fit to the non-MA carbon. (d) Ratio of non-MA C to MA C for the films as a function of the electron takeoff angle.

As mentioned, the O 1s peak is not visible for OPA, BrBA and OCA ligands at low take-off angles. We estimated the limit of detection for the O 1 s peak using the following method. First, the signal-to-noise $(\mathrm{S} / \mathrm{N})$ ratio of the O 1 s and $3 \mathrm{~d}_{5 / 2}$ peaks were calculated at different angles. Here, the noise is the standard deviation of at least a 3 eV range of the background signal. For $\theta=0^{\circ}$ and $45^{\circ}$ first we estimated the signal ratios with equation (S8):
$\frac{s_{O}^{\theta}}{s_{I}^{\theta}}=\frac{S_{O}^{75}}{s_{I}^{5}} \times \frac{\frac{I_{O}^{\theta}}{I_{I}^{\theta}}}{\frac{I_{O}^{75}}{I_{I}^{75}}}$
Here $S_{X}{ }^{\theta}$ is the raw signal from the XPS data for element $x$ at take-off angle $\theta$ and $I_{x}{ }^{\theta}$ is the integrated intensity of element $x$ with the sensitivity factor taken into account, so the ratio of $\frac{I_{O}^{\theta}}{I_{I}^{\theta}}$ represents the atomic ratio and not the signal ratio. The experimental spectra recorded at $75^{\circ}$ allows determination of both $\frac{S_{0}^{75}}{S_{I}^{75}}$ and $\frac{I_{O}^{75}}{I_{I}^{75}}$. Comparing this $\frac{I_{O}^{75}}{I_{I}^{75}}$ to the calculated the $\frac{I_{O}^{75}}{I_{I}^{75}}$ as a function of surface coverage allows the surface coverage to be quantified. Based on the calculated surface
coverage, $\frac{I_{O}^{\theta}}{I_{I}^{\theta}}$ is determined (e.g., based on calculated values shown in Figure S7a and d) and plugged into equation (S8) to calculate the expected $\frac{s_{O}^{\theta}}{s_{I}^{\theta}}$ ratio. Based on the measured $S_{I}^{\theta}$ value we can then calculate the expected $S_{O}^{\theta}$. Table S4 details these measured and calculated values. Next we approximate the limit of detection (LOD) in terms of the atomic ratio of the $O$ to I peak at $\theta=$ $0^{\circ}$ and $45^{\circ}$ with equation (S9):
$\operatorname{LOD}\left(\frac{I_{O}^{\theta}}{I_{I}^{\theta}}\right)=\frac{3 N_{O}^{\theta}}{S F_{O}} / \frac{s_{I}^{\theta}}{S F_{I}}$
Here $N_{o}{ }^{\theta}$ is the noise for the O 1s peak for takeoff angle $\theta$, where the noise is taken as the standard deviation of the averaged background signal. The average background signal was determined with two-point boxcar smoothing. Here we take $3 \mathrm{No}^{\theta}$ as the LOD. The LOD values are shown in Table S4 and Table S1.

Table S4. Calculated values of $I_{O} / I_{I}$ and signal of I $3 \mathrm{~d}_{5 / 2}$ and O 1 s peak from XPS data and $\mathrm{S} / \mathrm{N}$ ratio.

| OPA | $I_{0} / I_{1}$ | $S_{I}$ | $S_{0}$ | $N_{0}$ | S/N | $\operatorname{LOD}\left(\frac{I_{O}^{\theta}}{I_{I}^{\theta}}\right)^{b}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\theta=0^{\circ}$ | 0.08 | 19841 | 99a) | 50 | 1.93 | 0.07 |
| $\theta=45^{\circ}$ | 0.13 | 20185 | 163 ${ }^{\text {a }}$ | 37 | 4.01 | 0.05 |
| $\theta=75^{\circ}$ | 0.6 | 9497 | 354 | 33 | 10.87 | 0.09 |


| OCA | $I_{0} / I_{l}$ | $S_{I}$ | $S_{0}$ | $N_{0}$ | S/N | $\left.\operatorname{LOD}\left(\frac{I_{\theta}^{\theta}}{I_{I}^{\theta}}\right)^{\mathrm{b}}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\theta=0^{\circ}$ | 0.03 | 21137 | $41^{\text {a) }}$ | 45 | 0.7 | 0.06 |
| $\theta=45^{\circ}$ | 0.05 | 20114 | $66^{\text {a) }}$ | 46 | 1 | 0.06 |
| $\theta=75^{\circ}$ | 0.15 | 14268 | 140 | 33 | 4.29 | 0.06 |


| BrBA | $I_{0} / I_{I}$ | $S_{I}$ | $S_{0}$ | $N_{0}$ | S/N | $\operatorname{LOD}\left(\frac{I^{\left(\frac{\theta}{\theta}\right.} I_{I}^{\theta}}{}\right)^{\mathrm{b}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\theta=0^{\circ}$ | 0.03 | 18226 | 53a) | 73 | 0.55 | 0.1 |
| $\theta=45^{\circ}$ | 0.05 | 15700 | $76^{\text {a }}$ | 87 | 0.63 | 0.14 |
| $\theta=75^{\circ}$ | 0.15 | 13051 | 188 | 55 | 3.41 | 0.11 |

${ }^{\text {a) }}$ calculated from equation (S8); ${ }^{\text {b }}$ calculated from equation (S9).


Figure S10. UPS (black) and IPES (blue) spectra of an $\mathrm{MAPbI}_{3}$ film showing the Gaussian fits that were used to determine the IE and EA, respectively. Following work by Endres, et al., ${ }^{7}$ 2.9 ${ }^{1}$ is subtracted from, or added to, the Gaussian peak location to determine the IE or EA, respectively, where $\sigma$ is the width of the Gaussian ( $\mathrm{FWHM}=2.35 \sigma$ ).


Figure S11. PCE distribution of PV devices with untreated, BrBA treated, and $p$-TA treated $\mathrm{MAPbI}_{3}$.


Figure S12. External quantum efficiency and integrated current densities for PV devices with untreated, BrBA treated, and $p-\mathrm{TA}$ treated $\mathrm{MAPbI}_{3}$.

Table S5. Photovoltaic parameters of $\mathrm{MAPbI}_{3}$ based PV devices treated with different surface ligands.

| Surface ligand | $V_{\text {oc }}(\mathrm{V})$ | $J_{\mathrm{sc}}(\mathrm{mA} \mathrm{cm}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $-2)$ | $F F$ | PCE $(\%)$ | Best PCE $(\%)$ |  |  |
| Control | $0.997 \pm 0.037$ | $21.02 \pm 0.46$ | $0.728 \pm 0.014$ | $15.26 \pm 0.65$ | 16.45 |
| PTS | $0.998 \pm 0.033$ | $21.16 \pm 0.21$ | $0.724 \pm 0.017$ | $15.29 \pm 0.42$ | 16.13 |
| PPA | $0.858 \pm 0.095$ | $18.21 \pm 1.85$ | $0.713 \pm 0.031$ | $11.04 \pm 0.45$ | 12.07 |
| OPA | $0.949 \pm 0.076$ | $18.02 \pm 1.71$ | $0.730 \pm 0.030$ | $12.42 \pm 0.89$ | 13.48 |
| BrBA | $0.989 \pm 0.043$ | $21.92 \pm 0.54$ | $0.763 \pm 0.011$ | $16.56 \pm 0.85$ | 17.92 |
| $p-$ TA | $1.047 \pm 0.010$ | $21.29 \pm 0.40$ | $0.763 \pm 0.009$ | $17.03 \pm 0.52$ | 18.00 |
| OCA | $1.023 \pm 0.010$ | $20.11 \pm 0.40$ | $0.769 \pm 0.021$ | $15.84 \pm 0.78$ | 17.05 |
| AnCl | $1.023 \pm 0.033$ | $19.60 \pm 0.44$ | $0.758 \pm 0.014$ | $15.21 \pm 0.48$ | 15.80 |
| PEAI | $0.909 \pm 0.083$ | $15.39 \pm 1.27$ | $0.680 \pm 0.061$ | $9.49 \pm 1.17$ | 11.87 |
| OAI | $1.029 \pm 0.029$ | $15.04 \pm 1.42$ | $0.582 \pm 0.042$ | $9.05 \pm 1.37$ | 11.11 |
| TP | $0.909 \pm 0.059$ | $21.27 \pm 0.53$ | $0.683 \pm 0.038$ | $13.20 \pm 0.80$ | 14.75 |
| OT | $0.966 \pm 0.080$ | $19.81 \pm 0.59$ | $0.722 \pm 0.026$ | $13.81 \pm 0.84$ | 14.48 |

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