Letter

Dimensional Mixing Increases the Efficiency of 2D/3D Perovskite Solar Cells

Sam Teale,[⊥] Andrew H. Proppe,[⊥] Eui Hyuk Jung, Andrew Johnston, Darshan H. Parmar, Bin Chen, Yi Hou, Shana O. Kelley, and Edward H. Sargent*

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: 2D/3D heterojunction perovskite solar cells have demonstrated superior efficiency and stability compared to their fully 3D counterparts. Previous studies have focused on producing 2D layers containing predominantly $n = 1$ perovskite quantum wells. In this report we demonstrate a technique to introduce dimensional mixing into the 2D layer, and we show that this leads to more efficient devices relative to controls. Simulations suggest that the improvements are due to a reduction in trap state density and superior band alignment between the 3D/2D perovskite and the hole-transporting layer.

Soaking time
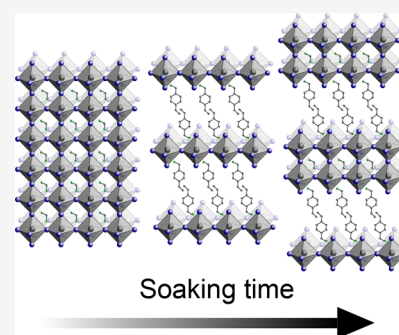
The topic of improving instability in metal halide perovskite solar cells (PSCs) is one of ongoing interest. Reduced-dimensional perovskites (RDPs) have been shown to increase ambient and operating lifetimes of PSCs, and 2D/3D heterostructure PSCs consisting of a thin layer of RDPs atop a 3D active layer improve both stability and efficiency compared to pure 3D counterparts.[1−5]

Studies of 2D/3D interfaces in perovskite solar cells are many and varied, with several reports demonstrating that a 2D interlayer can improve charge extraction.[6−8] Reports have generally focused on creating a thin (5−10 nm) 2D layer to prevent resistive losses. To this end, a dilute solution of ligand is usually employed and is rapidly spin-coated to construct the 2D/3D interface. X-ray diffraction techniques are then used to identify the RDPs formed, with $n = 1$ being dominant in most reports.[7,9,10]

Considering the tunability of RDPs, we posited that it is possible to modify the distribution of quantum wells through materials processing parameters. This could then be used to investigate the effect of $n > 1$ heterostructures on device performance. Initial studies of charge transport through these alternating conductive/insulating layers have shown that high solution concentrations (>5 mM) and thicker 2D layers are detrimental to performance[12,8] and that it is beneficial to produce disordered interlayers having fewer planes oriented parallel with the substrate.[11] We proposed that by using a very dilute solution (1 mM) and prolonging exposure, we could influence the quantum well distribution without a detrimental thickness increase.

We found that prolonging the exposure of 3D perovskite surfaces to a dilute ligand-solution modifies the width distribution of quantum wells in the 2D/3D heterojunction. Tuning this parameter for optimal performance, we were able to improve device power conversion efficiency (PCE) from $19.0(\pm0.4)\%$ to $21.4(\pm0.3)\%$.

To probe the effect of ligand exposure on RDP formation, we fabricated 2D/3D perovskite thin films and collected grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns. The 2D layer was formed using a solution of 4-vinylbenzylammonium (VBA) ligands, which has been shown to increase the efficiency and ambient stability of PSCs,[6] and the solution was prepared according to ref 7 with a concentration of 1 mM, a protocol that previously has been reported to form a ~10 nm thick conformal layer between the perovskite and the hole-transporting layer (HTL). Rather than spinning immediately after deposition of the solution, we soaked the films for varying amounts of time (Methods in the Supporting Information). The 2D pattern for the 60 s soaked film is shown in Figure 1a, and patterns for the other films may be found in Figure S1. The textured spots along $q_{xy} = 0$ indicate the RDPs are well-oriented parallel with the substrate. Longer exposure is not correlated with a change in orientation or disorder, but rather with the formation of $n = 2$ quantum wells. Integrating radially along q_z and azimuthally between 0 and $\frac{\pi}{2}$, we obtain Figure 1b. We observed that, without soaking,
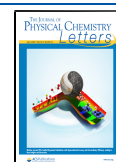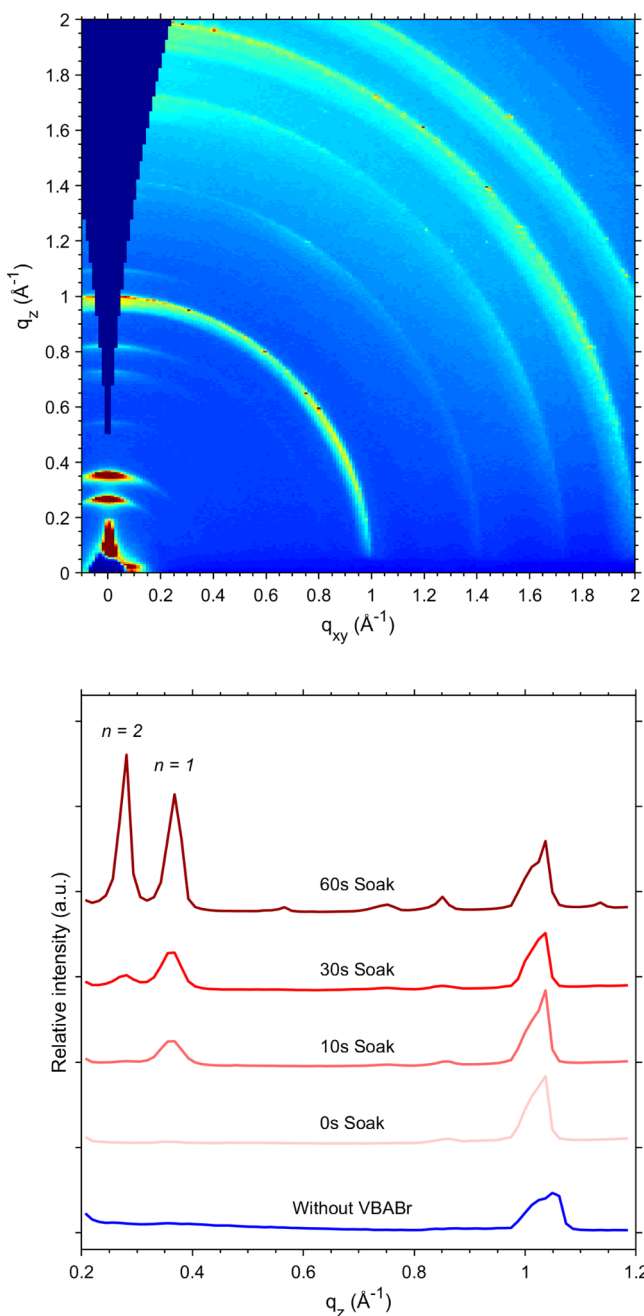
Figure 1. GIWAXS pattern for the 60 s exposure film (upper panel) and azimuthal integrations along q_z for the various conditions (lower panel). Peaks at $q \approx 1.0$, ~0.37, and ~0.25 Å^{-1} correspond to the (110) plane of bulk perovskite and (001) planes of $n = 1$ and $n = 2$, respectively.[12,13]

Table 1. Volume Integration of $n = 1$ and $n = 2$ Diffraction Spots for Each Soaking Time

	relative diffraction intensity normalized to the 3D perovskite ring		
condition	$n = 1$	$n = 2$	$n = 2$ (%)
no VBABr	0	0	N/A
0 s soak	0.03	0	0
10 s soak	0.56	0.02	3
30 s soak	1.06	0.23	18
60 s soak	2.68	2.76	51

photovoltaic figures of merit are shown in Figure 2. We found that increased exposure did indeed lead to improved
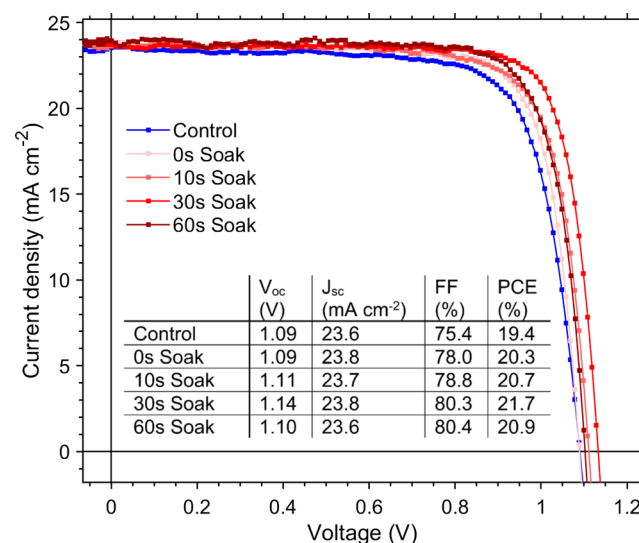

Figure 2. $J–V$ curves (open-circuit to short-circuit scanning direction) and photovoltaic figures of merit for perovskite solar cells where the 3D perovskite layer was subjected to no ligand exposure (Control), immediate spin-coating of the ligand-solution (0 s), and various soaking times (10, 30, and 60 s) after depositing the solution onto the surface. Forward scans are omitted for clarity and can be found in Figure S3.

we produce a film of predominantly $n = 1$ structures, and with longer soaking time, we observe increasingly strong diffraction from $n = 1$. Alongside this we see an increase in $n = 2$ diffraction with soaking time, growing to exceed the $n = 1$ peak after 60 s of exposure. These results are summarized in Table 1. This represented a new parameter space which we could optimize for device performance.

To investigate the effect of ligand exposure on devices, we fabricated noninverted (n-i-p) planar PSCs with an ITO/SnO$_2$/perovskite/2D-perovskite/spiro-OMeTAD/Au architecture. The 2D layer was once again formed by soaking the films for different times. Reverse scan $J–V$ curves and corresponding

performance, with the greatest improvement for around 30 s of soaking time (21.7% PCE). We also found that over-exposure (greater than 30 s) led to a loss in performance, seen as a reduction in V_{OC}. We note that hysteresis was observed for all devices (reverse and forward scans for each device are shown in Figure S3), but the stabilized power output (SPO) for devices held at their MPP for 60 s were only ~0.7 power points lower than PCEs obtained from the reverse scans. For example, the SPO for control and 30 s soaked devices was 18.5% and 21.2%, respectively. MPP tracking data from these devices can be found in Figure S4.

Yoo et al. have shown that, when preparing 2D/3D perovskites with ligands dissolved in isopropanol (IPA), exposure of the perovskite to IPA results in the formation of a δ-phase that is detrimental to device performance.[9] However, the ligand solution used in the present study was 97% chloroform (a perovskite antisolvent) and contained only 3% IPA to dissolve the VBA ligand, making solvent-related degradation unlikely.

V_{OC} initially increases with prolonged soaking time, which correlates with increasing diffraction from $n = 1$ planes. V_{OC} is

then reduced by longer soaking, corresponding to stronger diffraction from both structures and the dominance of the $n = 2$ peak. However, the performance of the 60 s soaked film still exceeds that of the 0 s soak and the control, and the fill factor continues to increase with all soaking times. This contrasts with RDP-only absorber layers, in which dimensional mixing results instead in lower fill factors.[14,15] It has been proposed that a layer of RDPs above a 3D absorber layer increases efficiency via passivation of traps and thus a reduction in surface recombination.[10] These improvements manifest themselves largely as an improvement in V_{OC}, which is also seen here. It has also been shown that a 2D interlayer results in a higher flat-band potential across the interface between the perovskite and the HTL, which is also related to an increase in V_{OC}.[7]

The peaks for both $n = 1$ and $n = 2$ become more intense and slightly narrower with longer exposure time, which could indicate a greater number of diffracting planes.[16] Previous reports have found that overly thick 2D layers lead to lower performance, but this is usually due to a reduction in current or fill factor, rather than photovoltage.[6,8] The fill factor for the 60 s soaking film remains as high as 80%, suggesting excellent carrier extraction and indicating that other factors are responsible for the lower V_{OC}.

To understand further how altering the 2D layer affects device performance, we simulated perovskite solar cells using the heterojunction solar cell simulator SCAPS-1D. The simulations (Figure 3) show that reducing the surface trap state density between the perovskite layer and HTL increases both V_{OC} (+34 mV) and fill factor (+5.6%) and that the introduction of a thin (5 nm) 2D layer increases V_{OC} (+8 mV) if well-aligned with the 3D perovskite and HTL through a slight increase to the Fermi-level splitting. Misalignment of the 2D layer, however, leads to a significant reduction in V_{OC} (−44 mV), with only a small change in fill factor (−1.5%). These trends suggest the misalignment of the 2D perovskite as a potential explanation for the performance drop of the 60 s soaked films.

Ultraviolet photoelectron spectroscopy (UPS) experiments on 2D ($n = 1$) perovskites have determined the valence band maximum (VBM) to be as low as −5.8 eV,[17] and another study found that the VBM became shallower with increasing n,[18] which would suggest a type I band alignment between 2D and 3D perovskites (both the conduction and valence band of the 3D perovskite sit within the band gap of $n = 1$). However, another report showed that when a 5 mM VBABr solution was used to form an RDP layer, the VBM was measured to be ~ −5.4 eV, which is similar to the VBM of low bromine content perovskite,[6] enabling a type II alignment (only one of the conduction or valence band of the 3D perovskite sits within the band gap of $n = 1$). The position of the VBM for RDPs therefore can vary over hundreds of millielectronvolts. It has been shown that the band alignment of RDPs is dependent on not only their bandgap (~2.3 eV for $n = 1$, ~2 eV for $n = 2$) but also ligand coverage, where a correlation between increased ligand content and shallower VBMs has been observed.[18,19] As shown in Figure 3, an energy level shift of ~0.4 eV causes the 2D layer to move from the superior type-I alignment with the 3D perovskite (type-II with the HTL), to the inferior type-II alignment with the 3D perovskite (type-I with the HTL). We posit that longer soaking times may lead to increased ligand coverage that upshifts the valence band of RDP layers into a favorable alignment with the 3D layer and
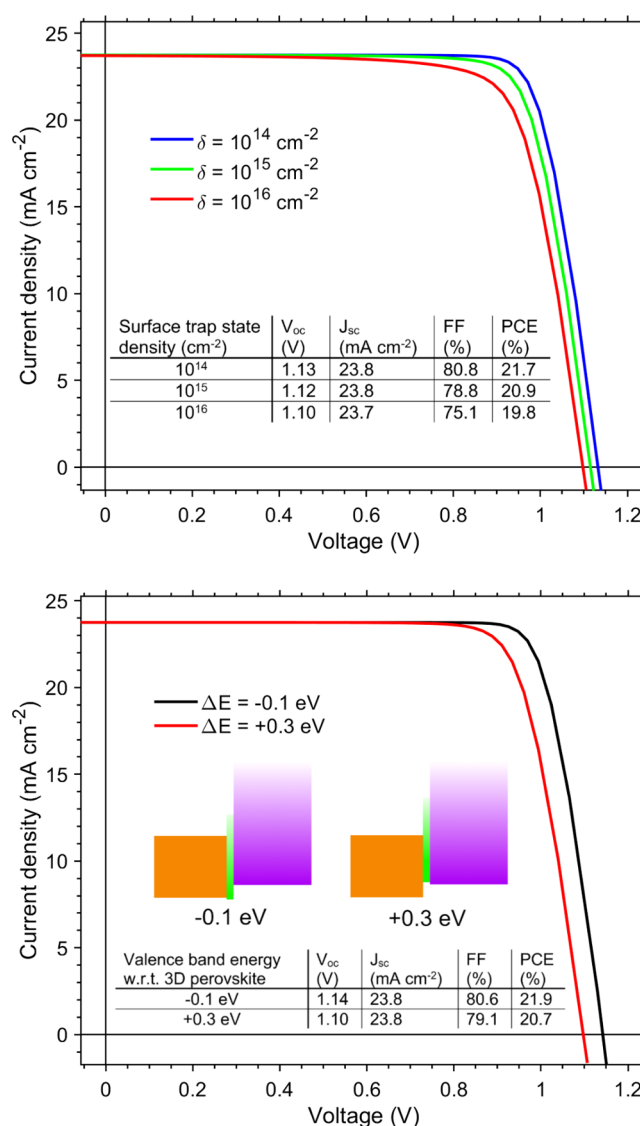

Figure 3. Simulation results. $J-V$ curves and photovoltaic figures of merit calculated using SCAPS-1D. (upper) Effect of surface trap state density between the perovskite and HTL on performance. (lower) Effect of band alignment between the perovskite/2D perovskite layer/HTL on performance. Inset: schematic of band structure used in simulation (orange, 3D perovskite; green, 2D perovskite; purple, Spiro-OMeTAD).

the HTL, and increasing the relative amount of $n = 2$ in the composition would also upshift the valence band with its narrower bandgap and shallower VBM compared to $n = 1$. Our observations here can be explained if after 30 s of soaking, increased dimensional mixing and ligand coverage lead to a more favorable band alignment, and after 60 s the valence band is further upshifted into inferior alignment.

We correlate higher performance in 2D/3D PSCs for films with more $n = 1$ structures and some dimensional mixing at the perovskite−HTL interface and lower performance for films with majority $n = 2$ structures. Modulation of 2D/3D interfaces influences the device performance through alterations to the energy landscape via bandgap tuning and shifting of energy levels with varying ligand coverage, improving V_{OC} and fill factor. These results suggest this may be a parameter space warranting further exploration in the field of 2D/3D perovskites.

This report is limited to examining the structure and orientation of RDPs using GIWAXS and comparing with device performance. Questions remain, such as the influence of 2D layer thickness;[8] whether prolonged ligand exposure promotes RDP formation only at the film surface or also at grain boundaries; if the band levels of RDPs are altered by ligand exposure time;[18] the true extent of dimensional mixing at the 2D/3D interfaces, and how this affects carrier dynamics and long-term stability.[14] We have shown previously that GIWAXS and XRD are often unable to probe the true n distribution of RDPs because of limited spatial coherence between wells, and optical probes are required instead. Future studies should include a wider suite of characterizations to examine changes in carrier dynamics induced by the modified quantum well structure.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c01444.

Methods and materials, Figures S1−S5, and Tables S1 and S2 (PDF)

AUTHOR INFORMATION

Corresponding Author

Edward H. Sargent − The Edward S. Rogers Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario, Canada M5S 3G4; orcid.org/0000-0003-0396-6495; Email: ted.sargent@utoronto.ca

Authors

Sam Teale − The Edward S. Rogers Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario, Canada M5S 3G4; orcid.org/0000-0001-9638-3453

Andrew H. Proppe − The Edward S. Rogers Department of Electrical and Computer Engineering and Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3G4; orcid.org/0000-0003-3860-9949

Eui Hyuk Jung − The Edward S. Rogers Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario, Canada M5S 3G4; orcid.org/0000-0002-2833-522X

Andrew Johnston − The Edward S. Rogers Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario, Canada M5S 3G4; orcid.org/0000-0002-4545-532X

Darshan H. Parmar − The Edward S. Rogers Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario, Canada M5S 3G4

Bin Chen − The Edward S. Rogers Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario, Canada M5S 3G4

Yi Hou − The Edward S. Rogers Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario, Canada M5S 3G4; orcid.org/0000-0002-1532-816X

Shana O. Kelley − Department of Chemistry and Department of Pharmaceutical Sciences, Leslie Dan Faculty of Pharmacy, University of Toronto, Toronto, Ontario, Canada M5S 3G4; orcid.org/0000-0003-3360-5359

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpclett.0c01444

REFERENCES

(1) Wang, Z.; Lin, Q.; Chmiel, F. P.; Sakai, N.; Herz, L. M.; Snaith, H. J. Efficient Ambient-Air-Stable Solar Cells with 2D−3D Heterostructured Butylammonium-Caesium-Formamidinium Lead Halide Perovskites. Nat. Energy 2017, 2, 17135.

(2) Tsai, H.; Nie, W.; Blancon, J.-C.; Stoumpos, C. C.; Asadpour, R.; Harutyunyan, B.; Neukirch, A. J.; Verduzco, R.; Crochet, J. J.; Tretiak, S.; et al. High-Efficiency Two-Dimensional Ruddlesden−Popper Perovskite Solar Cells. Nature 2016, 536, 312−316.

(3) Grancini, G.; Roldán-Carmona, C.; Zimmermann, I.; Mosconi, E.; Lee, X.; Martineau, D.; Narbey, S.; Oswald, F.; De Angelis, F.; Graetzel, M.; et al. One-Year Stable Perovskite Solar Cells by 2D/3D Interface Engineering. Nat. Commun. 2017, 8, 15684.

(4) Rodríguez-Romero, J.; Sanchez-Diaz, J.; Echeverría-Arrondo, C.; Masi, S.; Esparza, D.; Barea, E. M.; Mora-Seró, I. Widening the 2D/3D Perovskite Family for Efficient and Thermal-Resistant Solar Cells by the Use of Secondary Ammonium Cations. ACS Energy Lett. 2020, 5, 1013−1021.

(5) Sutanto, A. A.; Drigo, N.; Queloz, V. I. E.; Garcia-Benito, I.; Kirmani, A. R.; Richter, L. J.; Schouwink, P. A.; Cho, K. T.; Paek, S.; Nazeeruddin, M. K.; et al. Dynamical Evolution of the 2D/3D Interface: A Hidden Driver behind Perovskite Solar Cell Instability. J. Mater. Chem. A 2020, 8, 2343−2348.

(6) Proppe, A. H.; Wei, M.; Chen, B.; Quintero-Bermudez, R.; Kelley, S. O.; Sargent, E. H. Photochemically Cross-Linked Quantum Well Ligands for 2D/3D Perovskite Photovoltaics with Improved Photovoltage and Stability. J. Am. Chem. Soc. 2019, 141, 14180.

(7) Jung, E. H.; Jeon, N. J.; Park, E. Y.; Moon, C. S.; Shin, T. J.; Yang, T.-Y.; Noh, J. H.; Seo, J. Efficient, Stable and Scalable Perovskite Solar Cells Using Poly(3-Hexylthiophene). Nature 2019, 567, 511.

(8) La-Placa, M.-G.; Gil-Escrig, L.; Guo, D.; Palazon, F.; Savenije, T. J.; Sessolo, M.; Bolink, H. J. Vacuum-Deposited 2D/3D Perovskite Heterojunctions. ACS Energy Lett. 2019, 4, 2893−2901.

(9) Yoo, J. J.; Wieghold, S.; Sponseller, M. C.; Chua, M. R.; Bertram, S. N.; Hartono, N. T. P.; Tresback, J. S.; Hansen, E. C.; Correa-Baena, J.-P.; Bulović, V.; et al. An Interface Stabilized Perovskite Solar Cell with High Stabilized Efficiency and Low Voltage Loss. Energy Environ. Sci. 2019, 12, 2192−2199.

(10) Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J. Surface Passivation of Perovskite Film for Efficient Solar Cells. Nat. Photonics 2019, 13, 460−466.

(11) Abbas, M. S.; Hussain, S.; Zhang, J.; Wang, B.; Yang, C.; Wang, Z.; Wei, Z.; Ahmad, R. Orientationally Engineered 2D/3D Perovskite for High Efficiency Solar Cells. Sustain. Energy Fuels 2020, 4, 324−330.

(12) Quintero-Bermudez, R.; Gold-Parker, A.; Proppe, A. H.; Munir, R.; Yang, Z.; Kelley, S. O.; Amassian, A.; Toney, M. F.; Sargent, E. H. Compositional and Orientational Control in Metal Halide Perovskites of Reduced Dimensionality. Nat. Mater. 2018, 17, 900.

(13) Cao, D. H.; Stoumpos, C. C.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G. 2D Homologous Perovskites as Light-Absorbing Materials for Solar Cell Applications. *J. Am. Chem. Soc.* **2015**, *137*, 7843−7850.

(14) Proppe, A. H.; Quintero-Bermudez, R.; Tan, H.; Voznyy, O.; Kelley, S. O.; Sargent, E. H. Synthetic Control over Quantum Well Width Distribution and Carrier Migration in Low-Dimensional Perovskite Photovoltaics. *J. Am. Chem. Soc.* **2018**, *140*, 2890−2896.

(15) He, T.; Li, S.; Jiang, Y.; Qin, C.; Cui, M.; Qiao, L.; Xu, H.; Yang, J.; Long, R.; Wang, H.; et al. Reduced-Dimensional Perovskite Photovoltaics with Homogeneous Energy Landscape. *Nat. Commun.* **2020**, *11*, 1−11.

(16) Patterson, A. L. The Scherrer Formula for X-Ray Particle Size Determination. *Phys. Rev.* **1939**, *56*, 978−982.

(17) Silver, S.; Yin, J.; Li, H.; Brédas, J.-L.; Kahn, A. Characterization of the Valence and Conduction Band Levels of n = 1 2D Perovskites: A Combined Experimental and Theoretical Investigation. *Adv. Energy Mater.* **2018**, *8*, 1703468.

(18) Quintero-Bermudez, R.; Proppe, A. H.; Mahata, A.; Todorović, P.; Kelley, S. O.; De Angelis, F.; Sargent, E. H. Ligand-Induced Surface Charge Density Modulation Generates Local Type-II Band Alignment in Reduced-Dimensional Perovskites. *J. Am. Chem. Soc.* **2019**, *141*, 13459−13467.

(19) Mahata, A.; Mosconi, E.; Meggiolaro, D.; De Angelis, F. Modulating Band Alignment in Mixed Dimensionality 3D/2D Perovskites by Surface Termination Ligand Engineering. *Chem. Mater.* **2020**, *32*, 105−113.