Crystal Orientation Drives the Interface Physics at

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2/3-Dimensional Hybrid Perovskites

- 3 Marine E. F. Bouduban^{1,+}, Valentin I. E. Queloz^{2,+}, Valentina M. Caselli³, Kyung Taek Cho²,
- 4 Ahmad R. Kirmani^{4,5}, Sanghyun Paek², Cristina Roldan-Carmona², Lee J. Richter⁴, Jacques E.
- 5 Moser¹, Tom J. Savenije³, Mohammad Khaja Nazeeruddin², Giulia Grancini^{2,*}
- 6 ¹ Photochemical Dynamics Group, Institute of Chemical Sciences and Engineering, EPFL,
- 7 Station 6, CH-1015 Lausanne, Switzerland.
- 8 ² Group for Molecular Engineering of Functional Materials, Institute of Chemical Sciences and
- 9 Engineering, EPFL Valais Wallis, Rue de l'Industrie 17, CH-1951 Sion, Switzerland.
- 10 ³ Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9,
- 11 2629 HZ Delft, The Netherlands
- 12 ⁴ Material Measurement Laboratory, National Institute of Standards and Technology,
- 13 Gaithersburg, MD, USA 20899.
- ⁵Guest researcher.
- 15 Corresponding author: giulia.grancini@epfl.ch

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ABSTRACT. Combining halide perovskites with tailored dimensionality into two/three-18 19 dimensional (2D/3D) systems has revealed a powerful strategy to boost the performances of 20 perovskite photovoltaics (PVs). Despite therecent advances, a clear understanding of the 21 intimate link between interface structure and physics is still missing, leading so far to a blind 22 optimization of the 2D/3D PVs. Here, we reveal the impact of 2D/3D crystal alignment in 23 driving the interface charge-recombination dynamics. The 2D crystal growth and orientation is 24 manipulated by specific fluorination of the phenethylammonium (PEA), used here as the organic 25 cation backbone of the 2D component. By means of time-resolved optoelectronic analysis from 26 femto- to microsecond, we demonstrate a static function of the 2D as an electron barrier and 27 homogeneous surface passivant, together with a dynamic role in retarding back charge 28 recombination. Our results reveal a crucial dependence of such beneficial effects with the 2D 29 crystal orientation, leading to an enhanced open circuit voltage (VOC) if 2D lies parallel on the 30 3D. Such findings provide a deep understanding and delineate precise guidelines for the smart 31 design of multidimensional perovskite interfaces for advanced PV and beyond. 32

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38 TOC GRAPHICS



Since the last ten years, three dimensional (3D) APbI₃ halide perovskites (where A is a small 40 organic cation such as methylammonium) have been dominating the scene of new generation 41 photovoltaics (PVs).¹⁻³ Their intrinsic hybrid organic-inorganic nature enables great versatility in 42 their structural properties, providing an interesting playground for the design of structures with 43 44 desirable physical and optoelectronic parameters.^{4,5} Cutting the 3D framework along specific 45 crystal planes results in layered systems where the [PbI₆] inorganic slabs are spaced by large 46 organic cations. Among them, Ruddlesden-Popper or "quasi-2D" perovskites, R₂A_{n-1}Pb_nI_{3n+1}. 47 with R the organic spacer and n the number of inorganic slabs held together by the small A 48 cation, have recently attracted attention for their key role in addressing the stability issue of 49 perovskite PVs.⁶⁻¹² Within this family, if n=1 they form a R₂PbX₄ structure, called hereafter 2D perovskite. The latest exhibit potential for PVs with power conversion efficiency (PCE) around 50 15 %.¹³ This limit is dictated by the reduced charge transport with respect to the 3D parent, 51 52 intimately linked with the-poor control of the crystal growth kinetics. To encompass this limit, 2D/3D mixed system has been proposed as efficient and stable solutions.¹⁰⁻¹⁶ Either as 2D/3D 53 54 blends, where 2D acts as a bulk passivant, or as 2D/3D interface, where the 2D functionalizes the 55 perovskite/ electron (or hole) transporting layers (ETL/HTM). These mixed solutions have propelled the perovskite device performances;- hHowever, such empirical evolution of devices 56 57 processing prevents a clear control of the interface properties and structure, leading to a poor

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58 "trial and error" device optimization. A solid rationalization of the relation between interface 59 structure and physics is thus urgent. For example, how to manipulate crystal growth by material 60 design to drive proper crystallization of the 2D on top of the 3D, or how this impacts the 61 interface charge carrier dynamics in terms of surface trapping, recombination, and device physics 62 are paramount issues to address. Here we consider a stratified nanometer-thick 2D/3D interface 63 based on PEAI-based 2D / Cs_{0.1}Fa_{0.77}Ma_{0.13}PbI_{2.59}Br_{0.41} perovskites, where PEAI is 64 phenethylammonium iodide (see Figure 1a), Fa is formamidinium, and Ma is methylammonium. 65 which, Wwhen -embedded in the device stack (i.e. between the mesoporous oxide ETL and the 66 organic HTM on top), the 2D interface outperforms the standard 3D solar cells pushing device open circuit voltage (Voc). We reveal that the beneficial effect of the 2D on the device 67 performances is strictly related to the orientation of the crystal planes when growing on top of 68 69 the 3D, as determined by grazing- incidence wide-angle X-ray scattering (GIWAXS). 70 Importantly, this is dictated by specific fluorination of the cation, resulting in 71 fluorophenethylammonium (FPEA), which affects the crystal orientation of the 2D, changing 72 from parallel (with respect to the 3D substrate) to a disordered configuration. In turns, this 73 impacts the interface energetics and subsequent dynamics, which we monitored by combining 74 time-resolved optical spectroscopy from femtosecond to microsecond timescales, together with 75 time-resolved photo-conductivity experiments. Our results demonstrate that by modulating the 76 cation either planar or out-of-plane crystal orientation can be achieved. It results in a different 77 interface physics, and a more efficient electron barrier and passivation effect for the ordered 78 planar PEAI-based 2D. Embedded in the device, the PEAI-2D functions as a physical spacer 79 between the 3D and the HTM, being able to retard charge recombination and ultimately 80 explaining the enhanced Voc. Importantly, the functional interface does not inhibit the current

extraction, yielding solar cells with PCE of more than 20%. Our results highlight the importance
of properly choosing the 2D organic cation, providing valuable insights towards the exact control
and understanding of the 2D/3D structure- function relation, paramount for the proper design of
efficient multidimensional perovskite interfaces.







Figure 1. (a) Device stack architecture along with the chemical structure of the two cations used in the 2D layer. (b) Current-voltage characteristic comparing 2D-PEAI/3D, 2D-FPEAI/3D and Ref 3D devices. Zoom close to the Voc in inset. (c) Voc statistic (<u>T</u>turkey boxplot) for the two bilayers and the reference cell over 25 devices of each.

		PCE (%)	Voc (V)	Jsc (mAcm ⁻²)	FF	•
	FPEAI-2D/3D	20.53	1.127	23.21	0.784	
	PEAI-2D/3D	20.62	1.138	23.43	0.774	
	Ref 3D	19.48	1.104	23.25	0.759	
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98 Table 1. Champion Solar cells. Device parameters for the champion solar cell

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100 Figure 1a represents a sketch of the 2D/3D perovskite solar cell architecture, highlighting the 101 chemical structures of the PEAI and fluorinated analogous, FPEAI, obtained by the para-102 substitution of one fluorine atom on the phenyl moiety cations. Recently, similar compounds 103 have been used in "Quasi-2D" based solar cells, showing that the fluorinated version imparts a 104 better alignment of the perovskite sheets stacking, responsible for better PCE (around 14 %). In 105 our work, we develop a stratified 2D/3D interface where the 2D is dynamically grown on top of 106 the 3D (see Methods for details). This results in a few tens of nanometers thick 2D crust (20-60 nm, see scanning electron microscopy images in Figure S1).^{14,15} Devices current-voltage 107 108 characteristics and parameters are presented in Figure 1b and Table 1, while Figure 1c shows the 109 Voc statistics (see Figure S2 for full device statistics). Solar cells involving a 2D/3D interface 110 outperform their 3D reference, with a clear improvement in the device VOC, without causing a 111 detrimental loss of current. Notably, the boost in the VOC appears higher for the PEAI-based 2D 112 with respect to the FPEAI, overall leading to 20.62% PCE for the champion device. Such 113 improvement asks for a deeper understanding on the optoelectronic processes governing the 114 device operation, which is of key importance for device development, often disregarded. The 2D 115 being the core of our system, here we investigate the interface processes at the 2D/3D stack as 116 well as at the HTM/2D/3D interfaces making use of a combined series of light-induced 117 spectroscopic tools to shine light on the interface energetic and carrier dynamics from 118 femtosecond to microsecond timescale.



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Figure 2. (a) Transient absorption (TA) spectra of 3D perovskite, PEAI-2D/3D and FPEAI-120 2D/3D bilayers (excitation wavelength $\lambda ex= 600$ nm, carrier density of 10^{18} cm⁻³) at 1 ps delay 121 122 (spectra up to 1ns in Figure S3). (b) TA dynamic at 755 nm comparing 3D perovskite with 123 PEAI-2D/3D and FPEAI-2D/3D bilayers (excitation wavelength $\lambda ex=600$ nm, carrier density of 124 10¹⁸ cm⁻³). (c) TA spectra of 3D perovskite, PEAI-2D/3D and FPEAI-2D/3D bilayers (excitation wavelength $\lambda ex=390$ nm, carrier density of 10^{18} cm⁻³) at 1 ps delay (spectra up to 1 ns in Figure 125 126 S4). In inset: illustration of band diagram and of the charge transfer from the 2D to the 3D perovskite. (d) TA dynamic of FPEAI-2D/3D and PEAI-2D/3D respectively, at 497 nm and 755 127

128 nm upon excitation at 390 nm (carrier density of 10^{18} cm⁻³). Samples have been excited from the 129 2D side.

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Given the complexity of the 2D/3D system and the paramount importance of the 2D/3D interface 131 132 energy level alignment we have combined X-ray photoelectron spectroscopy (XPS) with 133 broadband transient absorption (TA). In TA, the selective excitation of the components will 134 enable to monitor the photoinduced processes from $3D \rightarrow 2D$ or from $2D \rightarrow 3D$, allowing us to retrieve the energy level alignment. Figures 2a,b displays the TA spectra and dynamics for 3D 135 136 perovskite and 2D/3D systems upon excitation at $\lambda ex=600$ nm (selectively exciting the 3D), while Figures 2 c,d are obtained upon pumping at λ ex=390 nm (exciting both 2D and 3D). 137 138 Exciting only the 3D (Figure 2a), the signal is dominated by a large negative feature peaking at 139 750 nm, which forms with a time constant of 300 fs and persists throughout the investigated time 140 window (1.5 ns). This feature relates to ground state bleaching (GSB) upon state filling at the 3D 141 perovskite band edge.¹⁶ TA spectra of the 2D/3D systems are identical, with no difference in the 142 evolution of the GSB (Figure 2b). Given that the GSB is proportional to the photoexcited carrier 143 density, its evolution reflects the charge dynamics. This indicates that no energy or charge 144 transfer occurs when the 3D only is excited (from $3D \rightarrow 2D$). On the other side Notably, when 145 exciting at λ ex=390 nm, the TA spectra (Figure 2c) for the 2D/3D differ from the only-3D 146 control. Two additional bumps appear in the blue region [500-575 nm]. They arise from the 147 excitation of the 2D layer, and relate to the GSB of the 2D perovskite. Corresponding dynamics 148 of FPEAI-2D/3D and PEAI-2D/3D are presented in Figures 2d, e, compared to the GSB 149 dynamics at 750 nm of the 3D. A clear trend is observed: the GSB at 750nm rises (with a time 150 constant of few ps, see Table S2) while the GSB at 500 nm decays with a similar time constant.





Figure 3. (a) Normalized Photoluminescence (PL) decay of PEAI-2D/3D, FPEAI-2D/3D and Ref 3D sample (excitation wavelength λ exc=635 nm, carrier density of 10¹⁴ cm⁻³). (b) Normalized time resolved microwave conductivity (TRMC) of the same samples (λ exc=650 nm, carrier density of 10¹⁴ cm⁻³). (c) Normalized PL decay of HTM/PEAI-2D/3D, HTM/FPEAI-

2D/3D sample (λexc=635 nm, carrier density of 10¹⁴ cm⁻³). (d) Normalized TRMC of bilayers
of HTM/PEAI-2D/3D, HTM/FPEAI-2D/3D and HTM/3D (λex=650 nm, carrier density of 10¹⁴ cm⁻³). Samples have been excited from the 3D side.

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167 Combing this information with the dynamical picture retrieved from the TA analysis, we can 168 thus conclude that exciton dissociation happens from 2D->3D. In addition, XPS results on the 169 energy band alignment are shown in Figure S8. From XPS and TA analysis, we extracted the 170 energy levels alignment as illustrated in the inset of Figure 2c. The valence band maximum 171 (VBM) of the 2D perovskite is just slightly down shifted by 0.1 eV with respect to the VBM of 172 the 3D perovskite. Given that the band gap of 2D perovskites is around 3 eV, their conduction 173 band minimum (CBM) lies well above the CBM of the 3D perovskite.¹⁴ CAs a result, 174 eonsidering the TA data witheomparing the different excitation energy, used combineding with 175 the PL and XPS analysis, we can conclude that, despite the relatively high fluence used for- tThe 176 TA measurements, (at which higher order processes might happen), the energy levels landscape 177 of the 2D/3D system results into what is as schematically depicted in the cartoon in the inset of 178 Fig. 2c, whewherere 2D perovskites act as a barrier for electrons. To gain insight on the free 179 carrier dynamics at the interfaces, as main goal of our work, we employ time resolved 180 photoluminescence (TRPL) and time-resolved microwave-conductivity (TRMC) targeting the 181 2D/3D interfaces (Figures 3a, b) as well as the 3D/2D/HTL system (Figures 3c, d). Figure 3a shows the TRPL decays at 780 nm, monitoring the 3D emission with or without the 2D layer. 182 Note that in both cases we selectively excite the 3D with an excitation density of 10^{14} 183

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184 carriers/cm³. Decays of 3D and FPEAI-2D/3D perovskite show a similar behaviour behavior 185 (slightly slower for the FPEAI-2D/3D), while the PEAI-2D exhibits a much slower PL decay 186 (see Table S3 for time constants). Figure 3b shows the TRMC signal which monitors the free 187 charges generated within the 3D slab and their dynamical evolution (see Figure S9 for carrier 188 densities dependent dynamics). Notably, the initial amplitude of the TRMC signal is proportional 189 to both the yield of free charges generated upon photoexcitation and their mobility, while the decay mirrors the charge immobilization or recombination.¹⁷ No sizeable differences are 190 191 observed between the initial TRMC amplitudes of the 3D and the 2D/3D-modified surfaces (see 192 figure S10). However, their dynamics are different, as PEAI-2D shows a slower decay with 193 respect to the bare 3D, while it is rather similar in the case of the FPEAI-2D. The combined 194 TRPL and TRMC findings can be rationalized as follows: i) the initial TRMC amplitudes 195 indicate that no significant $3D \rightarrow 2D$ hole transfer is taking place, as this would have lowered the 196 amplitude of the signal at time zero (for instance, as is the case at the HTM/3D interface, see 197 Figure S10), confirming the TA results; ii) the slower decay in both PL and TRMC results for 198 PEAI-2D/3D indicates a delayed electron-hole recombination, possibly related to better surface 199 passivation induced by the structural organization and homogeneity of the PEAI-2D layer, as 200 demonstrated in the following (see Table S3); iii) this does not extend to FPEAI-2D/3D system, 201 which exhibits similar behavior with respect to the bare 3D. To determine the kinetic parameters 202 from the TRMC measurements, we have applied the kinetic model described in the paper by 203 Hutter et al. (see the relevant parameters summarized in Table S5 in the Supplementary 204 Information, together with a description of the model and experimental fits in Figure S11).¹⁸ 205 Interestingly, the bimolecular recombination rate constant, k₂, is halved upon addition of PEAI or 206 FPEAI-2D layers on the 3D perovskite. As previously reported, k2 represents the sum of all

bimolecular recombination processes.¹⁹ Therefore bimolecular recombination processes occurring at the 3D surface is considerably retarded by introducing the 2D perovskite. The enhanced lifetimes in the case of PEAI-2D/3D samples are related to the significantly reduced number of background charges in the material, which slows down the bimolecular recombination. In light of this, and in agreement with the energy level alignment previously discussed, we conclude that PEAI-2D/3D interface can retard the electron-hole recombination and passivate the 3D surface much more efficiently compared to FPEAI- based system.

214 Figures 3c and 3d, shows the TRPL and TRMC signals for 3D/2D/HTM systems. From Figure 215 3c, the PL shows similar decays, with a slower tail component for the PEAI-2D/3D system (see 216 Table S3 for the time constants). From TRMC measurements in Figure 3d (see also Figure S10) 217 we can observe that the initial amplitudes drop, and the dynamics get faster if the HTM is 218 deposited on top. This is indicative of a reduction of the charge density due to hole transfers and 219 faster decay due to interfacial recombination. Comparing the TRMC signals of the 3D/HTM with 220 3D/2D/HTML samples, we observe that the addition of a 2D layer does not hinder the charge 221 transfer to the HTM (initial amplitude reduction, see Figure S10), but recombination is slowed 222 down, more visibly for the PEAI based system. As a physical spacer, holes can be easily 223 delocalized at the 2D/3D interface, given the low energetic barrier perceived by the holes at the 224 2D phase, thus favoring charge transfer to the HTM. Therefore, the 2D layer can act as a 225 physical spacer where, especially in the case of PEAI-2D, where back electron-hole 226 recombination is retarded.

227 Overall, our results point to a beneficial effect of the 2D layer by reducing surface 228 recombination, which can explain the improvement in the device Voc. As an important remark, 229 we observe that this statement does not hold a general validity but strongly depends on the





Figure. 4 (a) GIWAXS map of PEAI-2D/3D showing a parallel preferred orientation in low-q region below the 3D bulk perovskite peak of qz = qxy = 1.0 Å⁻¹. (b) GIWAXS map of FPEAI-2D/3D showing more random orientation. (c) 2D GIWAXS sector average for PEAI-2D and FPEAI-2D layers atop 3D bulk. The 2D (n=1) features are noted in green while quasi 2D (n=2) features are noted in purple. PEAI-2D layer clearly-shows relatively more intermixing of lower

dimensionalities compared to the FPEAI-2D. (d) Cartoon representing preferred orientation ofthe 2D on top of the 3D bulk.

242 To address the reason behind such different behavior, we investigate the structural properties 243 of the interfaces and the crystal plan orientation by grazing-incidence wide-angle X-ray 244 scattering (GIWAXS). This technique is extremely surface-sensitive at incident angles below the 245 critical angle, allowing one to directly probe the 2D perovskite layer. GIWAXS maps and 246 corresponding sector averages are shown in Figure 4. Diffraction peaks associated with the lamella structure of the 2D phase are clearly visible for $q < 1.0 \text{ Å}^{-1}$ and correspond to the (0k0) 247 248 planes. Both the PEAI and FPEAI layers show a major diffraction peak for the pure 2D phase (n=1), with first order at 0.36 Å⁻¹ and higher orders at 0.74 Å⁻¹ and 1.08 Å⁻¹. We also 249 observereport a minor intermixing phase resulface ting in a weak n=2 diffraction peak (first order 250 251 at 0.25 Å⁻¹, higher orders at 0.52 Å⁻¹ and 0.80 Å⁻¹). Interestingly, the PEAI-2D layer exhibits a larger extent of n=2 phase compared to FPEAI-2D with a stronger first-order 0.25 Å⁻¹ peak. This 252 253 assignment is also supported by the PL and TA spectra. PL spectra (Figure S3-5) shows a weak 254 shoulder at 550 nm assigned to n=2 quasi-2D perovskite emission; and TA spectra ($\lambda ex=390$ nm, 255 Figure 2a) exhibit a second peak at 540 nm associated to the GSB of the n=2 qQuasi-2D 256 perovskite, as previously discussed. The first-order peak at 0.36 Å⁻¹ belonging to the n=1 lattice 257 was integrated with respect to the azimuthal angle (χ) to glean information regarding the 258 orientation of the 2D perovskite planes. Results are reported in Figure S12 comparing the 259 FPEAI-2D- and the PEAI-2D-based interfaces. From Figure S12, it is clear that the PEAI-2D 260 peak integral is almost entirely in a range of $\chi = 0^{\circ}$ to 5°, suggesting that the PEAI-2D-layers 261 assume a parallel orientation with respect to the underlying 3D phase and the substrate (as observed in other 2D-based systems).²⁰ On the contrary, the formation of FPEAI-3D layers is 262

more random: a majority of these layers have a 40° to 45° orientation with respect to the 3D 263 264 phase and the substrate (see Figure 4d). We suggest that the different crystallites orientation of 265 PEAI-2D and FPEAI-2D is the reason behind the different interfacial physics observed. In the case of the parallel orientation of PEAI-2D the slowing down of the TRMC dynamics proves that 266 267 back electron hole recombination (between holes in the HTM and electrons in the 3D perovskite) 268 is retarded, with a direct positive impact on the charge carrier lifetime and thus on the device 269 Voc. The intimate reason behind lies on the structural orientation of the PEAI-2D and uniformity 270 of this layer enabling to be a more perfect homogeneous physical spacer in between the 3D 271 perovskite and the HTM. On the contrary, the random orientation of FPEAI-2D compromises 272 the beneficial effect of the 2D interlayer in terms of enhanced charge lifetime. In addition, 273 disorder in the 2Dthis may would allow partial interpenetration of the HTM, leading to similar 274 behaviourbehavior of the FPEAI-2D/3D to the only 3D system. Our finding put forwards a 275 different picture with respect to common knowledge: while much effort has been put to orient 276 the 2D planes perpendicular to the substrate in a way to maximize charge transport and extraction^{21–23}, here we reveal that, contrarily, planar orientation is needed for the case of 2D/3D 277 278 interfaces, to optimize interface processes and device performances. A similar finding has been 279 only-revealed for Sn-based 2D/3D interfaces where planar growth of the 2D is essential for devices operation.²⁰ Further analysis, beyond the scope of the presented work, will be needed to 280 281 clarify the transport mechanism through the organic barrier.

To conclude, we elucidate the optoelectronic properties and carrier dynamics at 2D/3D interfaces leading to highly efficient solar cells. Our results provide compelling evidence of the crucial role of the crystal alignment of the 2D perovskite on top of 3D perovskite. If the 2D perovskite orients "flat" with respect to the substrate, it can effectively passivate the surface Commented [MOU5]: Val, among this references, please add the J. Am. Chem. Soc. 2019, 141, 5972–5979

286	while retarding charge recombination. This re <u>sultfleets</u> into an enhanced Voc of the solar cells
287	and overall improved performances. On the other side, a more disordered 2D perovskite
288	alignment limits such beneficial effect. We demonstrate that such alignment can be controlled by
289	fine-tuning the chemical composition of the 2D cation, i.e. by simple atomic substitution,
290	providing a new guideline for material and interface design. Our finding provides a deeper
291	understanding on the main parameters governing the 2D/3D interface physics with important
292	reverberation on interface development for solar cells, and opto-electronics devices.

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- 296 Methods.

297 Device Fabrication and Testing.

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299	Fluorine doped tin oxide (FTO) glass substrates (Nippon ²⁵ sheet glass) were sequentially
300	cleaned with the detergent solution, deionized water, acetone, and ethanol. A compact TiO_2 layer
301	was coated on the cleaned FTO substrate heated at 450 °C by spray pyrolysis deposition. A
302	precursor solution is prepared by diluting titanium diisopropoxide (Sigma-Aldrich) with
303	isopropanol (0.6 mL; 10 mL). Thereafter, we prepared a bilayer electron transport layer with
304	mesoporous TiO_2 and SnO_2. Mesoporous TiO_2 films were prepared using a diluted TiO_2 paste
305	(Dyesol 30 NR-D) solution. Films were prepared by spin-coating and sintered on a hot plate at
306	500 °C for 30 min. SnO2 layer was prepared by spin-coating a precursor solution of SnCl4
307	(Acros) dissolved in water. 0.1 M of SnCl4 aqueous solution was spin-coated and sintered on a

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308 hot plate at 180 °C for 1 h. The lead excess (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} precursor solution was 309 prepared by mixing FAI (1.1 M), PbI₂ (1.15 M), MABr (0.2 M), and PbBr₂ (0.2 M) in a mixed 310 solvent of DMF:DMSO = 4:1 (volume ratio). Another solution of CsPbI₃ was also prepared as 311 1.15 M solution in DMF:DMSO (same volume ratio). For triple cations mixed perovskite 312 solution, (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} and CsPbI₃ solutions were mixed as 10:1 vol% ratio. The 313 perovskite precursor solution was spin coated at 33 x 2π rad s⁻¹ (2000 rpm) for 10 s, followed by 314 83 x 2π rad s⁻¹ (5000 rpm) for 30 s. Trifluorotoluene (110 µL) was dropped on the spinning substrate at the 10 s during the second step. The films were annealed at 100 °C for 60 min in the 315 316 glove box. For forming an additional 2D perovskite film on top of this perovskite film, substrates 317 were treated with a PEAI (or FPEAI) isopropanol solution. 100 ml of PEAI (or FPEAI) solution 318 (10 mg/mL) were spin-coated on the 3D perovskite films at <u>83 x 2π rad s⁻¹ (5000 rpm)</u>. 5000 rpm, 319 which is similar to the anti-solvent dropping method. The films were annealed once more at 320 100 °C for 10 min to make 2D perovskite layer on the 3D perovskite film. Spiro-OMeTAD was 321 spin-coated at <u>67 x 2π rad s⁻¹ (4000 rpm)</u> for 20 s. A 70 mM spiro-OMeTAD solution was 322 prepared by dissolving in chlorobenzene with 4-tert-butylpyridine, Li-TFSI in acetonitrile, and 323 Co[t-BuPyPz]₃[TFSI]₃ (FK209) in acetonitrile at a molar ratio of Spiro : FK209 : Li-TFSI : TBP 324 of 1: 0.03: 0.5: 3.3. Finally, 70 nm of Au was deposited by thermal evaporation as the back 325 electrode.

The solar cell measurement was done using commercial solar simulators (Oriel, 450 W, Xenon, AAA class). The light intensity was calibrated with a Si reference cell equipped with an IR-cutoff filter (KG3, Newport) and it was recorded before each measurement. Current–voltage characteristics of the cells were obtained by applying an external voltage bias while measuring the current response with a digital source meter (Keithley 2400/2604). The voltage scan rate was Formatted: Superscript

 $50 \text{ mV} \cdot \text{s}^{-1}$ and no device preconditioning such as light soaking or forward voltage bias was applied before starting the measurement. The cells were masked with the active area of 0.16 cm² to fix the active area and reduce the influence of the scattered light.

334 Transient Absorption measurements

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336 Ultrafast transient absorbance (TA) spectra were acquired using femtosecond pump-probe 337 spectroscopy with two different pump wavelengths: $\lambda_{ex} = 390$ nm and $\lambda_{ex} = 600$ nm. The 390 nm 338 pump beam was obtained by frequency doubling the output of a chirped pulse amplified (CPA) 339 Ti:Sapphire laser (CPA-2001, Clark-MXR, 778 nm fundamental central wavelength, 120 fs pulse 340 duration, 1 kHz repetition rate) in a BBO crystal, yielding 200 fs pulses. In turn, the 600 nm 341 excitation beam was generated by directing the CPA output into a non-collinear parametric 342 amplifier (NOPA), and then compressed by a pair of SF_6 prisms, yielding 100 fs pulses. The 343 probe beam was generated by directing a portion of the CPA fundamental output into a 344 CaF₂ crystal, yielding a white light continuum measured over a (400 to -780) nm spectral 345 domain. The probe fluence at the sample was much lower than that of the pump (39 μ J cm⁻²). 346 Similarly, the diameter of the probe beam was smaller to ensure homogeneous excitation of the 347 probed area. The dynamics of the phot-induced signals were obtained with a computer-controlled 348 delay-line on the pump path. The probe beam was split before the sample into a beam going 349 through the sample (signal beam) and a reference beam. Both signal and reference beams were 350 directed to respective spectrographs (Princeton Instruments, Spectra Pro 2150i) and detected 351 pulse-to-pulse with 512x58 pixels back-thinned charge-coupled-device CCD cameras 352 (Hamamatsu S07030-0906). The pump beam was chopped at half of the laser frequency

(500 Hz) and a satisfying signal-to-noise ratio was obtained by typically averaging 3000
spectra. The time resolution of the experiment was 250 fs.

355 Steady State Optical Measurement

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357 Steady-state absorption spectra were acquired with a Perkins Elmer lambda 950s
 <u>ultravioletUV</u>/Vis spectrophotometer using an integrating sphere to account for optical losses
 outside of the active layer.

360 Steady state and time resolved photoluminescence measurement where carried out on Horiba a 361 Fluorolog-3, with a <u>photomultiplier tubePMT</u> as detector. The excitation source for the TCSPC 362 is a Horiba nanoLED-370 with an excitation wavelength of 369nm, a pulse duration of 1.3_ns 363 and a repetition rate of 1 MHz.

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365 Time-Resolved Photoluminescence Measurements

For TRMC measurements the samples have been loaded into air-tight resonant cavity (low intensity measurements) and open cell (high intensities) holders in a N₂ filled glovebox. The traces have been measured upon pulsed (10 Hz, 3 ns <u>full-width at half-maximumFWHM</u>) photoexcitation at 650 nm from a Q-switched Nd:YAG laser ("Infinity 15-30", Coherent).²⁴ Excitation intensities have been varied in the range $10^9 to -10^{12}$ photons/cm².

371 GIWAXS Measurements

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GIWAXS measurements were carried out in reflection geometry at beamline 7.3.3 of the
 Advanced Light Source, Lawrence Berkeley National Laboratory. Samples were measured at a

375	detector distance of 0.249 m using X-ray wavelength of 1.240 Å, at 0.18° angle of incidence with				
376	respect to the substrate plane. Calibration was performed with a silver behenate standard.				
377	Scattering intensity was detected by a PILATUS 2M detector. ¹ Nika software package was used				
378	to sector average the 2D GIWAXS images. ² Data plotting was done in Igor Pro (Wavemetrics,				
379	Inc., Lake Oswego, OR, USA).				
380					
381	Supporting Information. Additional data are included in the material supplied as Supporting				
382	Information.				
383	Notes				
384	The authors declare no competing financial interest.				
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386					
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reported in Figure 3a,c.

Author contributions

397	M.E.F.B performed and analyzed the TAS data under the supervision of J.E.M. and G.G.					
398	V.I.E.Q carried out the PL and TRPL measurements under the supervision of G.G. V.C.					
399	performed the TRMC measurements and their analysis, under the supervision of T.J.S. A.R.K					
400	realized the GIWAXS measurements and their analysis, under the supervision of L. J. R. The					
401	samples and devices were prepared and characterized by K.T.C and S.P. supervised by M. K. N.					
402	C. R-C. performed the SEM and XRD characterization of the sample. G.G conceived the idea of					
403	the work. All the authors contributed in writing the manuscript. J.E.M and M.K.N contributed in					
404	the discussion and analysis of the data.					
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483	recommendation or endorsement by the National Institute of Standards and Technology, nor is it	
484	intended to imply that the materials or equipment identified are necessarily the best available for	
485	the purpose.	Commented [RLJD(7]: Please properly insert this citation.