

Perovskite superlattices with efficient carrier dynamics

Sheng Xu (✉ shengxu@ucsd.edu)

University of California, San Diego <https://orcid.org/0000-0002-3120-4992>

Yusheng Lei

University of California San Diego

Yuheng Li

University of California San Diego <https://orcid.org/0000-0002-1865-1122>

Chengchangfeng Lu

University of California San Diego

Qizhang Yan

University of California San Diego <https://orcid.org/0000-0002-3798-642X>

Huaxin Gong

Stanford University

Song Zhang

Stanford University

Jiayun Zhou

University of California, San Diego

Ruiqi Zhang

University of California San Diego

Yimu Chen

University of California, San Diego

Hsinhan Tsai

Los Alamos National Lab <https://orcid.org/0000-0002-1492-1279>

Yue Gu

UC San Diego <https://orcid.org/0000-0003-0437-5339>

Hongjie Hu

University of California, San Diego

Yu-Hwa Lo

University of California, San Diego <https://orcid.org/0000-0003-4602-1627>

Wanyi Nie

Los Alamos National Laboratory <https://orcid.org/0000-0002-5909-3155>

Taeyoon Lee

Yonsei University <https://orcid.org/0000-0002-8269-0257>

Jian Luo

University of California, San Diego

Kesong Yang

University of California San Diego,

Kyung-In Jang

Daegu Gyeongbuk Institute of Science and Technology

Physical Sciences - Article

Keywords: low-dimensional metal halide perovskites, carrier transport, organic spacers

Posted Date: November 12th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1048977/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Nature on August 10th, 2022. See the published version at <https://doi.org/10.1038/s41586-022-04961-1>.

Perovskite superlattices with efficient carrier dynamics

Yusheng Lei^{1,2*}, Yuheng Li^{1*}, Chengchangfeng Lu³, Qizhang Yan¹, Huaxin Gong², Song Zhang², Jiayun Zhou⁴, Ruiqi Zhang¹, Yimu Chen¹, Hsinhan Tsai⁵, Yue Gu⁴, Hongjie Hu¹, Yuhwa Lo³, Wanyi Nie⁵, Taeyoon Lee^{6,7}, Jian Luo^{1,4}, Kesong Yang¹, Kyung-In Jang⁸, Sheng Xu^{1,4,5,9#}.

¹Department of Nanoengineering, University of California San Diego, La Jolla, CA 92093-0448, USA

²Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA

³Department of Electrical and Computer Engineering, University of California San Diego, La Jolla, CA 92093, USA

⁴Material Science and Engineering Program, University of California San Diego, La Jolla, CA 92093-0418, USA

⁵Los Alamos National Laboratory, Los Alamos, NM 87545, USA

⁶School of Electrical and Electronic Engineering, Yonsei University, Seoul 03722, Republic of Korea.

⁷Department of Bio and Brain Engineering, Korea Institute of Science and Technology, Republic of Korea.

⁸Department of Robotics Engineering, Daegu Gyeongbuk Institute of Science and Technology, Daegu 42988, Republic of Korea.

⁹Department of Bioengineering, University of California San Diego, La Jolla, CA 92093-0412, USA

*These authors contributed equally to this work.

#Email: shengxu@ucsd.edu

28 **Abstract**

29 **Compared with their three-dimensional counterparts, low-dimensional metal halide**
30 **perovskites with periodic inorganic/organic structures have shown promising stability**
31 **and hysteresis-free electrical performance, which paves the way for next-generation**
32 **optoelectronic devices. However, when integrated in devices, they have relatively limited**
33 **efficiencies because devices usually require carrier transport through the film thickness**
34 **direction. In conventionally grown single crystals, the carrier transport in the thickness**
35 **direction is hindered by the insulating organic spacers. In addition, the strong quantum**
36 **confinement from the organic spacers limits the generation and transport of free carriers.**
37 **The carrier dynamics is further compromised by the presence of grain boundaries in**
38 **polycrystals. Here, we report a low-dimensional metal halide perovskite superlattice with**
39 **efficient carrier transport in three dimensions by epitaxial growth. Epitaxy on a slightly**
40 **lattice-mismatched substrate compresses the organic spacers in the superlattice, which**
41 **weakens the quantum confinement and further improves carrier dynamics. The**
42 **performance of a low-dimensional perovskite superlattice solar cell has been certified**
43 **under the quasi-steady state for the first time. Moreover, the device shows an unusually**
44 **high open-circuit voltage, due to a unique intra-band exciton relaxation mechanism.**

45 Metal halide perovskites, with a general formula of AMX_3 (e.g., $A = CH_3NH_3^+$ (MA),
46 $HC(NH_2)_2^+$, Cs^+ , Rb^+ ; $M = Pb^{2+}$, Sn^{2+} ; $X = Cl^-$, Br^- , I^-), are emerging as next-generation
47 optoelectronic materials because of their phenomenal performance and processability in low-
48 cost solutions¹⁻³. However, their practical applications have been hindered by three issues:
49 instability⁴, electrical hysteresis⁵, and toxicity⁶. Recently, low-dimensional (two-dimensional
50 (2D) and quasi-2D) metal halide perovskites with a formula of $B_2A_{n-1}M_nX_{3n+1}$ (e.g., $B = R-$
51 NH_3^+) have been invented to mediate the instability and hysteresis issues⁷⁻¹¹. In these materials,
52 the insulating ammonium interlayer spacers divide the semiconductive metal-halide structure
53 into slabs, forming a multiple-quantum-well¹²⁻¹⁵. Existing single crystals are grown with the
54 insulating organic spacers parallel to the substrate surface and cannot support carrier transport
55 in the film thickness direction, which is required for device integration¹⁶. Moreover, the strong
56 confinement of the multiple-quantum-well leads to a large exciton binding energy, which limits
57 the generation and transport of carriers within the inorganic slabs^{16,17}. Polycrystals contain
58 grain boundaries that further compromise carrier dynamics¹⁸. Furthermore, lead-free metal
59 halide perovskites have been developed, but their device performance is limited by their low
60 crystallinity and structural instability¹⁹.

61

62 Here, we report a $BA_2MA_{n-1}Sn_nI_{3n+1}$ (BA: butylammonium; $n = 1, 3, 5$) superlattice with long-
63 range order. The superlattice was epitaxially grown on a 3D perovskite substrate. The inorganic
64 slabs are aligned vertical to the substrate and interconnected in a crisscross 2D network parallel
65 to the substrate, leading to efficient carrier transport both in-plane and out-of-plane. In addition,

66 due to the lattice mismatch with the substrate, the superlattice is under compressive strain,
67 which reduces the width of the organic spacers. This weakens the quantum confinement of the
68 organic spacers and thus further improves the carrier dynamics of the superlattice. The
69 performance of a Bi³⁺ alloyed superlattice solar cell has been certified under the quasi-steady
70 state for the first time, with a stable 12.36% photoelectric conversion efficiency and an
71 unusually high open-circuit voltage.

72

73 We studied the growth process and structure of BA₂SnI₄ ($n = 1$) superlattice on a
74 MAPb_{0.5}Sn_{0.5}Br₃ substrate. The superlattice is formed by a unique epitaxial mechanism
75 (Supplementary Discussion 1). The Sn-I slabs exhibit a favorable epitaxial relationship with
76 the substrate but cannot form a horizontally aligned lattice²⁰⁻²², which would contain
77 thermodynamic unstable high n value structures (Supplementary Fig. 1)¹⁵. A vertically aligned
78 lattice structure is energetically most favorable under experimental conditions in this work.
79 Scanning electron microscopy images reveal that the crystals first grow into crisscross vertical
80 thin plates (Fig. 1a; Supplementary Fig. 2). This is because the crystal structure of the substrate
81 is cubic, and therefore the epitaxial growth behavior along the a and b directions is symmetric.
82 As the growth progresses, they merge into a smooth film (Fig. 1a; Supplementary Fig. 2).
83 Similar growth behavior is observed in other low-dimensional perovskites grown on different
84 3D perovskite substrates (Supplementary Fig. 3). Cryogenic-scanning transmission electron
85 microscope was used to study the structure of a single plate, which exhibits an anisotropic
86 structure (Fig. 1b). The a - c plane image shows a periodic distribution of inorganic Sn-I slabs

87 and organic BA spacers along the a direction (Fig. 1b, middle; Supplementary Fig. 4)²³. The b -
88 c plane image shows a continuous Sn-I slab with a coherent heteroepitaxial interface with the
89 substrate (Fig. 1b, right). Therefore, the crisscross vertical plates on the substrates create a 3D
90 network of Sn-I slabs, unseen in any polycrystals (Supplementary Fig. 5) or conventionally
91 grown single crystals^{7,12}.

92

93 To further study the crystal orientation in the a - b plane, we measured polarization-dependent
94 photocurrent of the superlattice and a conventionally grown single crystal with a linearly
95 polarized excitation source (Fig. 1c). The results in both show a strong dependence on the
96 polarization direction, but the response of the superlattice has a 90° period while that of the
97 conventionally grown single crystal has a 180° period. This is because the inorganic slabs are
98 aligned in two perpendicular orientations in the a - b plane of the superlattice, but in only one
99 orientation of the conventionally grown single crystal (Supplementary Fig. 6). Similar trends
100 can also be observed in the carrier lifetime obtained from orientation-dependent transient
101 photovoltage measurements (Fig. 1d; Supplementary Fig. 7). These results collectively support
102 that the superlattice has Sn-I slabs interconnected, with numerous crisscross thin plates merged
103 in the a - b plane.

104

105 Because of the interconnected Sn-I slabs, carriers in the superlattice does not need to cross any
106 grain boundaries or organic spacers. This allows the superlattice to have more efficient carrier
107 dynamics along the film thickness (c) direction compared to its polycrystalline and

108 conventionally grown single crystal counterparts. Transient photocurrent measurements along
109 the film thickness direction show a much higher carrier mobility in the superlattice than in the
110 polycrystalline or conventionally grown single crystal sample (Fig. 2a). The grain boundaries
111 in the polycrystal act as traps, which significantly reduce carrier mobility (Supplementary Fig.
112 8)²². The conventionally grown single crystal shows the lowest mobility, with only in-plane
113 carrier transport (Supplementary Fig. 9). Power-dependent time-resolved photoluminescence
114 measurements reveal that the superlattice has a longer carrier lifetime than the polycrystal (Fig.
115 2b), indicating minimal restriction of the carriers in the superlattice. Additionally, the
116 superlattice shows better tolerance to high excitation power than the polycrystal, suggesting
117 that better crystallinity can reduce material degradation under high excitation power²⁴.

118

119 The structural advantages of the superlattice are validated with temperature-dependent
120 photovoltaic J - V characteristics of a BA_2SnI_4 solar cell. Solar cell fabrication was conducted
121 on the as-grown film to minimize any possible confounding factors introduced by the
122 fabrication process (Supplementary Fig. 10)²². As the temperature gradually drops, thermal
123 energy becomes too small for the carriers to overcome barriers (e.g., due to ionized impurity
124 scattering), so the fill factor (FF) decreases substantially for both the superlattice and
125 polycrystalline devices (Fig. 2c). However, the decrease is less significant in the superlattice,
126 indicating lower internal energy barriers and a higher charge-collection efficiency²⁵.

127

128 We measured the electron-beam-induced-current to directly visualize carrier transport

129 behaviors. For the polycrystal, the collected currents on the thin film surface heavily depend
130 on the grain orientations, indicating the existence of strong barriers for carrier transport (Fig.
131 2d, left). In contrast, the superlattice yields higher and much more uniform currents due to the
132 well-aligned crystal structure (Fig. 2d, right). Note that the superlattice currents exhibit a
133 crisscross pattern due to the imperfect merging of the crystals during solution growth
134 (Supplementary Fig. 11). Similar observations can also be made in the sample cross-sections
135 (Fig. 2e; Supplementary Discussion 2).

136

137 The improved carrier dynamics of the superlattice allow a higher absorber thickness and thus
138 more efficient light harvesting. The absorber thickness of the polycrystalline devices is usually
139 highly restricted because of the limited carrier diffusion length²⁵. For polycrystalline BA₂SnI₄,
140 the external quantum efficiency (EQE) peaks at an absorber thickness of ~400 nm (Fig. 2f, top).
141 Due to the improved carrier dynamics in the superlattice, the absorber thickness can be
142 increased to ~700 nm with enhanced light absorption and thus EQE (Fig. 2f, bottom).

143

144 We investigated the heteroepitaxial strain in the BA₂SnI₄ superlattice quantitatively by X-ray
145 diffraction. Compared to conventionally grown single crystals, high overall compressive
146 strains are present in the superlattice along the *a* and *b* directions, at ~8.59% and ~1.32%,
147 respectively (Fig. 3a, top); a tensile strain of ~0.99% is present in the *c* direction due to Poisson
148 effect (Fig. 3a, bottom; Supplementary Discussion 3, Supplementary Table 1)²⁶. These strains
149 are validated by calculations using the lattice constants extracted from the scanning

150 transmission electron microscope images (Supplementary Fig. 4, Supplementary Discussion
151 3). Structural computation by density-functional theory (DFT) further reveals that the lattice
152 constant of Sn-I slabs in the a direction is compressed from ~ 6.04 Å to ~ 5.94 Å (Supplementary
153 Fig. 12), yielding a $\sim 1.66\%$ strain, which is close to the 1.32% strain in the b direction; the
154 width of the organic spacer is compressed from ~ 7.00 Å to ~ 5.98 Å (Supplementary Figs. 12
155 and 13), corresponding to a 14.6% strain. Therefore, the high compressive strain is mostly
156 accommodated by the organic spacer. High strain reduces the stability of the superlattice
157 (Supplementary Figs. 14 and 15). For general heteroepitaxial $BA_2MA_{n-1}Sn_nI_{3n+1}$, as n increases,
158 the volume ratio of the Sn-I slabs increases, and the overall lattice strain decreases (Fig. 3b),
159 and the structure is more stable. Moreover, lower strain results in less structural defects and
160 smoother surfaces (Fig. 3b, inset images).

161

162 To avoid potential phase change and achieve reliable measurements of the superlattice, we
163 chose $BA_2MA_2Sn_3I_{10}$ ($n = 3$) to study their strain-controlled optoelectronic properties, and
164 found that the high compressive strain in the a - b plane alters the quantum effects of the
165 superlattice. We used ellipsometry to study the dielectric functions ($\epsilon' + i\epsilon''$) of the superlattice
166 and a conventionally grown single crystal. The higher ϵ' of the superlattice indicates
167 weakened quantum confinement by the compressed organic spacers (Fig. 3c), a larger Bohr
168 radius in the multiple-quantum-well, and therefore a higher rate of free carrier generation
169 (Supplementary Discussion 4)¹⁴. Besides, the shift in ϵ'' , which reflects the absorption
170 wavelength²⁷, suggests a smaller bandgap in the superlattice compared with the conventionally

171 grown single crystal, which is also evident by the longer-wavelength collection edge of the
172 superlattice (Fig. 2f; Supplementary Fig. 16)²⁶. Temperature-dependent photoluminescence
173 measurements also show a much-reduced fitted exciton binding energy in the superlattice
174 compared to the conventionally grown single crystal (Fig. 3d)^{14,26}. In addition, the carrier
175 lifetime in the superlattice is slightly longer than the conventionally grown single crystal at 0°
176 in the transient photovoltage measurements (Fig. 1d)²⁶. All these characteristics can be
177 attributed to the weakened quantum confinement in the superlattice.

178

179 The enhanced carrier dynamics of the superlattice suggest potential improvements in
180 photovoltaic performance. To relieve the compressive strain and create an even more stable
181 structure, we investigated using Bi³⁺ (103 pm in radius²⁸) to partially replace Sn²⁺ (118 pm in
182 radius²⁹). DFT calculations show that the Bi³⁺ tends to aggregate at the interface between the
183 inorganic slab and the organic spacer to relieve the compressive strain (Fig. 4a, top;
184 Supplementary Fig. 17), forming a Bi³⁺ rich atomic layer (Supplementary Fig. 18;
185 Supplementary Discussion 5). This effectively decreases the formation energy of the
186 superlattice and yields a much more stable structure (Supplementary Fig. 19). Furthermore,
187 Bi³⁺ alloying alters the local electronic structure of the superlattice, which substantially
188 decreases the conduction band minimum (CBM) (Fig. 4a, bottom; Supplementary Figs. 20 and
189 21)³⁰. The region without Bi³⁺ alloying remains intact. The result is an inorganic slab with a
190 double-band structure.

191

192 We grew 10% Bi^{3+} -alloyed $\text{BA}_2\text{MA}_4\text{Sn}_5\text{I}_{16}$ ($n = 5$) superlattices with a textured surface and
193 fabricated solar cells directly on the substrate (Supplementary Figs. 22 and 23). We chose
194 $\text{BA}_2\text{MA}_4\text{Sn}_5\text{I}_{16}$ due to its relatively weak quantum confinement, stable structure, and small
195 bandgap. Indene-C60 bisadduct was used as the electron transport layer (ETL) because its
196 CBM level (Supplementary Fig. 24) is higher than that of the Bi/Sn-I but lower than the Sn-I
197 slabs (Supplementary Table 2). Because Bi^{3+} ions are distributed along the vertical slab
198 direction, the Bi/Sn-I and the Sn-I regions are both in contact with the ETL. It is the first low-
199 dimensional metal halide perovskite based solar cell to pass the quasi-steady state test
200 (Supplementary Fig. 25). It exhibits a certified stable 12.36% photoelectric conversion
201 efficiency—the highest in lead-free low-dimensional perovskite solar cells^{19,31}. Moreover, the
202 certified quantum efficiency plot of the solar cell (Fig. 4b; Supplementary Fig. 25) shows a
203 carrier collection cutoff at ~ 1190 nm, which gives a bandgap of ~ 1.042 eV and a V_{OC} of at most
204 0.802 V according to Shockley-Queisser-limit^{32,33}. However, the certified V_{OC} is 0.967 V, which
205 is much higher than what detailed balance would allow.

206

207 Figure 4c shows the schematic band diagram of the solar cell. Because Bi^{3+} alloying in single-
208 crystal perovskites will not lead to a high density of traps or band tail states, nor does it cause
209 macroscale phase-separation between Bi^{3+} and Sn^{2+} regions (Supplementary Fig. 19)³⁴⁻³⁶, the
210 high V_{OC} is not attributed to any defect levels in the bandgap of the superlattice. The carrier
211 collection cutoff of the solar cell is determined by the component of the lowest bandgap, i.e.,
212 1.042 eV of the Bi/Sn-I region in this case. However, this low bandgap region does not seem

213 to affect the overall V_{OC} of the final device.

214

215 We performed wavelength-dependent J - V measurements of the solar cell to investigate the
216 carrier transport process (Figs. 4d-4e). Under short incident wavelengths ($< \sim 1000$ nm), most
217 electrons are excited into energy states higher than the CBM of both Sn-I and Bi/Sn-I regions.
218 Those electrons from the Sn-I region naturally relax to the CBM of the Sn-I region.
219 Additionally, a substantial portion of the electrons from the Bi/Sn-I region can also diffuse to
220 the CBM of the Sn-I region through intra-band relaxation (solid blue arrows in Fig. 4c). This
221 intra-band transition is possible because the ETL layer favors electron collection from the Sn-
222 I region (solid red arrow in Fig. 4c). Moreover, the atomic-thin Bi/Sn-I region is easy for
223 carriers to diffuse across. Therefore, most of carriers are in the Sn-I region, yielding a high V_{OC}
224 and a high FF (Fig. 4d and 4e). Under long incident wavelengths ($> \sim 1000$ nm), electrons can
225 only be excited in the Bi/Sn-I region. The relatively low-energy electrons cannot transit to the
226 Sn-I region; they can only relax to the CBM of the Bi/Sn-I region, and then to the ETL via
227 inter-band transition (dashed red arrows in Fig. 4c). Therefore, most of carriers are in the Bi/Sn-
228 I region, yielding a low V_{OC} (Fig. 4d and 4e). The energy barrier between the Bi/Sn-I region
229 and the ETL can cause serious charge accumulation and recombination (Supplementary
230 Discussion 6)³⁷, which results in inefficient carrier transport and a low FF (Fig. 4d and 4e).
231 When the device is excited under mixed incident wavelengths, the high-energy electrons
232 excited in both Bi/Sn-I and Sn-I regions by the short wavelengths facilitate the quasi-fermi-
233 level splitting in the Sn-I region. The low-energy electrons excited by the long wavelengths

234 will have a relatively small influence on the overall V_{OC} , because the long-wavelength portion
235 (between ~1000 nm and ~1200 nm) of the solar radiation spectrum is small (~9 %) ^{38,39}, so the
236 quantity of the low-energy electrons is low. Therefore, the overall outcome is an unusually high
237 V_{OC} that is predominantly determined by the bandgap of the Sn-I region (Supplementary Fig
238 26, Supplementary Discussion 6).

239

240 Besides the unique intra-band relaxation mechanism discussed here, other carrier transport
241 processes may also be possible. More studies are needed to fully understand this intriguing
242 phenomenon. Further device performance improvements are possible with optimizations of the
243 design of the electrode patterns, the resistivity of the top electrode, and the band alignment of
244 the ETL/hole transport layer. The low-dimensional perovskites are intrinsically flexible without
245 any additional mechanical packaging because of the low bending stiffness of the inorganic
246 slabs (Supplementary Fig. 27) ⁴⁰⁻⁴³. Therefore, these materials can be promising candidates for
247 large-area flexible solar cells as power sources for flexible devices that can be integrated with
248 non-planar surfaces. The strategy demonstrated here can be applied to general low-dimensional
249 perovskites, which may pave the way for exploring solution-based superlattice optoelectronics
250 with high efficiencies.

251

252 **METHODS**

253 **Materials.** The materials used in this study were as-purchased without further purification,
254 which included lead iodide (PbI₂, 99.99%, Tokyo Chemical Industry), lead bromide (PbBr₂

255 (98%, Alfa Aesar), hydrobromic acid (HBr, 48 wt% in water, Sigma Aldrich), methylamine
256 (CH_3NH_2 , 40% in methanol, Tokyo Chemical Industry), tin (II) oxide (SnO , 97%, Sigma
257 Aldrich), hydroiodic acid (HI, 57% in water, Sigma Aldrich), hypophosphorous acid (H_3PO_2 ,
258 50 wt% in water, Sigma Aldrich), methylammonium iodide (MAI, 99.9%, Greatcell Solar), n-
259 butylammonium iodide (BAI, 99.9%, Greatcell Solar), cesium chloride (CsCl , 99.9%, Sigma
260 Aldrich), silver chloride (AgCl , 99%, Sigma Aldrich), antimony (III) chloride (SbCl_3 , 99%,
261 Sigma Aldrich), bismuth (III) iodide (BiI_3 , 99%, Sigma Aldrich), indene-C60 Bisadduct (ICBA,
262 LT-S9030, Luminescence Technology), poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]
263 (PTAA, LT-N168, Luminescence Technology), chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$, TCI America),
264 anhydrous dimethylformamide (DMF, $\text{C}_3\text{H}_7\text{NO}$, 99.8%, Sigma Aldrich), anhydrous gamma-
265 butyrolactone (GBL, $\text{C}_4\text{H}_6\text{O}_2$, 99% Sigma Aldrich), anhydrous dimethyl sulfoxide (DMSO,
266 $\text{C}_2\text{H}_6\text{OS}$, 99.9%, Sigma Aldrich), isopropanol (IPA, $\text{C}_3\text{H}_8\text{O}$, 99.5%, Sigma Aldrich), and
267 methanol (99.8%, CH_3OH , Sigma Aldrich).

268

269 **Preparation of single-crystal perovskites.** MAPbBr_3 : Flat and smooth centimeter-sized bulk
270 MAPbBr_3 single crystals were prepared by solution-based growth²⁰. The MAPbBr_3 were used
271 as the 3D perovskite substrate to grow the low-dimensional perovskite superlattice without any
272 further treatment. MAPbI_3 : MAPbI_3 single crystals were prepared by solution-based growth²².
273 The as-obtained crystals were ultrasonically cleaned in an anhydrous IPA solvent for 5 mins.
274 Then, the crystals were crushed into powers for growth precursor preparation.

275

276 **Synthesis of low-dimensional perovskites.** 0.3 g SnO powder was dissolved into a mixture of
277 3 ml hydroiodic acid solution and 0.5 ml hypophosphorous acid solution in a glass vial by
278 heating to 180 °C under constant stirring until a bright yellow precursor solution was obtained.
279 BA₂SnI₄ crystals were synthesized by injecting 1 mL BAI solution (2.5 mmol BAI in 1 mL
280 methanol) into the precursor solution. BA₂MA₂Sn₃I₁₀ crystals were synthesized by injecting 1
281 mL MAI/BAI solution (1.67 mmol MAI and 0.83 mmol BAI in 1 mL methanol) into the
282 precursor solution. BA₂MA₄Sn₅I₁₆ crystals were synthesized by injecting 1 mL MAI/BAI
283 solution (2 mmol MAI and 0.5 mmol BAI in 1 mL methanol) into the precursor solution. Then,
284 the vial was transferred into a nitrogen-filled glove box at room temperature. The as-formed
285 crystals were then isolated by removing the solution, then quickly washed using IPA for three
286 times. Then, the crystals were dried and then directly dissolved in GBL to form the growth
287 solution (0.5 M) for low-dimensional perovskites. For the Bi³⁺ alloyed superlattice, 10% molar
288 ratio of BiI₃ was also dissolved into the growth solution.

289

290 **Preparation of precursors for mixed perovskites and double perovskites.** The
291 MAPb_{0.5}Sn_{0.5}Br₃ was prepared by mixing MABr, PbBr₂, and SnBr₂ with a 2:1:1 molar ratio in
292 DMF (1.5 M). The double perovskites Cs₂AgSbCl₆ precursor solution was prepared by directly
293 mixing CsCl, AgCl, and SbCl₃ with a 2:1:1 molar ratio in DMSO (0.4 M). The as-prepared
294 solution was stirred under 60 °C until the solution became clear. Then, 0.4 M MAPbI₃ single
295 crystal powder is added to the solution to complete precursor solution preparation for achieving
296 a suitable lattice constant with minimal lattice mismatch between the substrate and the

297 inorganic slab of the epitaxial layer.

298

299 **Device fabrication.** MAPbBr₃ bulk crystals were used as the three-dimensional (3D) substrates
300 as their synthesis is well-established. To further reduce the lattice mismatch, the mixed
301 perovskite (or double perovskite) precursor was casted onto the MAPbBr₃ layer while hot to
302 form a smooth epitaxial layer, which was the actual surface for growing the low-dimensional
303 perovskites. The thickness of the smooth epitaxial layer does not influence the subsequent
304 superlattice growth or device fabrication. Polyimide films (12.7 μm thick) were pre-patterned
305 (with an opening size of 1 μm by 1 μm) to serve as the growth mask by following a reported
306 method²². Then, a layer of Au was deposited by sputtering to serve as the bottom electrode.
307 Later, the PTAA solution (1.5 mg/mL in anhydrous toluene) was directly spin-coated onto the
308 patterned polyimide/Au films at 2500 rpm for 30 s, followed by annealing at 80 °C for 3 min.
309 Then the growth substrate was laminated with the polyimide/Au/PTAA mask and then spin-
310 coated by supersaturated mixed perovskite (or double perovskite) precursor at 4000 rpm for 30
311 s followed by annealing at 100 °C for 5 min. Subsequently, low-dimensional perovskite growth
312 solution (0.5 M in GBL) was spin-coated on the substrate at 1500 rpm for 60 s followed by
313 annealing at 180 °C for 2 min to form the superlattice absorber layer. After that, ICBA (20
314 mg/mL in chlorobenzene) was spin-coated onto the epitaxial layer, followed by annealing at
315 100 °C for 5 min. Finally, a layer of ITO was deposited by sputtering to serve as the transparent
316 top electrode.

317

318 **DFT calculations.** First-principles DFT calculations were performed using the Vienna *Ab*
319 *initio* Simulation Package⁴⁴. The Projector Augmented Wave pseudopotential was used for
320 describing electron-ion interactions⁴⁵. The Generalized Gradient Approximation parametrized
321 by Perdew, Burke, and Ernzerhof was used to treat the electron-electron exchange-correlation
322 functional⁴⁶. The van der Waals functional DFT-D3 was applied to properly describe the long-
323 range dispersion interactions between the organic molecules in the hybrid materials⁴⁷. The
324 hybrid functionals within Heyd-Scuseria-Ernzerhof formalism with 70% Hartree-Fock
325 exchange were employed to calculate band gaps for the Sn-based perovskites^{48,49}. The wave
326 functions were expanded in a plane-wave basis set with a cutoff energy of 400 eV. The
327 structures for conventionally grown single crystal Ruddlesden-Popper perovskites and
328 epitaxially grown perovskites were built based on experimental results of the lattices. The
329 atomic positions were fully optimized until all components of the residual forces were smaller
330 than 0.03 eV/Å. The convergence threshold for self-consistent-field iteration was set at 10^{-5} eV.
331 Γ -centered $2 \times 1 \times 4$ and $4 \times 4 \times 1$ k-point grids were used for superlattice and conventionally grown
332 single crystals, respectively. Due to the limited computational resources, we could only
333 simulate the $n = 3$ structure, but this will not influence the device ($n = 5$) because the formation
334 mechanism of the double-bandgap structure is the same.

335

336 **Morphology characterization.** All scanning electron microscope (SEM) images were taken
337 using a Zeiss Sigma 500 SEM. All optical images were taken using a Zeiss Axio Imager Optical
338 Microscope.

339

340 **Structure characterization.** X-ray diffraction was measured by a Rigaku 393 Smart lab
341 diffractometer equipped with a Cu K α 1 radiation source ($\lambda = 0.15406$ nm) and a Ge 394 (220
342 $\times 2$) monochromator. The scanning transmission electron microscopy (STEM) images were
343 taken using a cryo-FEI 200 kV Sphera microscope. Samples for the STEM were prepared using
344 a frozen focused ion beam (FEI Scios Dual Beam FIB/SEM). The conventionally grown single
345 crystal was hard to be imaged by STEM since the sample without an epitaxial substrate curled
346 quickly due to its instability in the STEM. X-ray photoelectron spectroscopy (XPS)
347 measurements were carried out using Kratos AXIS Supra with a He I (21.22 eV) source under
348 10^{-8} torr chamber pressure.

349

350 **Optical characterizations.** Photoluminescence (PL) and time-resolved PL (TRPL)
351 measurements were performed with a confocal microscope system focusing a monochromatic
352 6 ps-pulsed laser with a $\times 4$ objective lens (numerical aperture 0.13). Optical functions were
353 measured by ellipsometry (J.A. Woollam M-2000D Spectroscopic Ellipsometer). Ultraviolet
354 photoelectron spectroscopy (UPS) measurements were carried out using Kratos AXIS Supra
355 with a He I (21.22 eV) source under 10^{-8} torr chamber pressure. Ultraviolet-visible
356 spectroscopy (UV-vis) and absorption spectra were collected using a Perkin Elmer Lambda
357 1050 UV-vis system under the reflection mode.

358

359 **Electrical characterizations.** Polarized photocurrent was measured with a polarizer. Time-of-

360 flight was measured by extracting the decay time of the transient photocurrent to calculate the
361 carrier mobility. An external bias of 0.5 V was used to power the devices with a resistor
362 connected in series. Orientation-dependent transient photovoltages were measured with an
363 oscilloscope (Agilent MSO6104A Channel Mixed Signal) to study the carrier lifetime. A pulsed
364 laser with a pulse width of less than 10^{-10} s was used as the light source. The electron beam
365 induced photocurrent (EBIC) was collected using a FEI Scios Dual Beam microscope with a
366 Mighty EBIC 2.0 controller (Ephemeron Labs) and a Femto DLPCA-200 preamplifier. Lateral
367 Au electrodes were deposited by electron-beam evaporation for surface measurements; a pre-
368 patterned Au-coated polyimide film was used as the bottom electrode for cross-section
369 measurements; the top surface was deposited with a layer of Au by electron-beam evaporation
370 to serve as the top electrode. The EBIC and SEM images of the same region of interest were
371 collected simultaneously. The samples were several micrometers in thickness, while EBIC
372 could penetrate up to several micrometers into the samples⁵⁰.

373

374 **Photovoltaic characterizations.** Current density-voltage (J - V) measurements were carried out
375 using a Keithley 2400 source meter under a simulated air mass of 1.5 irradiation (100 mW/cm^2)
376 and a xenon-lamp-based solar simulator (Oriel LCS-100). Temperature-dependent J - V
377 measurements were performed with the sample in a liquid nitrogen cooled metal tank, where
378 one side was glass to allow illumination. The same configuration was used for both epitaxial
379 and polycrystalline devices. External quantum efficiency (EQE) data were collected by
380 illuminating the device under monochromatic light using a tungsten source (chopped at 150

381 Hz) while collecting the photocurrent by a lock-in amplifier in the alternating current mode.
382 The 2D mapping of the thickness-dependent EQE was generated from the Contour-Color Fill
383 function. Wavelength-dependent J - V measurements were carried out by applying a series of
384 bandpass filters (Newport) under the solar simulator to measure both the polycrystalline and
385 epitaxial devices.

386

387 **FIGURE CAPTIONS**

388 **Fig. 1 | Structural characterizations of the BA_2SnI_4 superlattice.** (a) Scanning electron
389 microscope images showing the crisscross epitaxial BA_2SnI_4 superlattice before and after
390 merging into a thin film. (b) Schematics and atomic-resolution cryogenic-scanning
391 transmission electron microscopy images showing the superlattice structure of a single plate.
392 Cryogenic-scanning transmission electron microscope is essential to minimize the damage of
393 beam-sensitive materials. The epitaxial layer has a well-aligned anisotropic structure without
394 grain boundaries or dislocations. The insets are fast Fourier transform (FFT) patterns from the
395 epitaxial layer in the a - c plane, which show a two-dimensional diffraction pattern of the
396 superlattice and is different from that of the substrate. The inset FFT images in the b - c plane
397 show the structural similarity between the inorganic slab and the substrate. Organic atoms are
398 usually invisible under electron diffraction. (c) Photocurrent measurements with a linearly
399 polarized excitation source showing that the response of the epitaxial layer (top) exhibits a
400 period that is half of a conventionally grown single crystal (bottom). (d) Transient photovoltage
401 measurements showing the orientation-dependent carrier lifetime in the a - b plane. The inset

402 optical image shows the measurement setup. The error bars are from measurements of five
403 different devices.

404

405 **Fig. 2 | Carrier transport properties of the BA₂SnI₄ superlattice.** (a) Transient photocurrent
406 measurements along the film thickness (*c*) direction. The superlattice shows the highest carrier
407 mobility. The carrier mobility in the polycrystal is limited by grain boundaries and lattice
408 misalignments between grains. The conventionally grown single crystal shows the lowest
409 carrier mobility because of the energy barriers caused by the organic spacers along the film
410 thickness direction. The inset shows the schematic measurement setup. The error bars are from
411 measurements of five different devices. (b) Time-resolved photoluminescence measurements
412 showing a longer carrier lifetime in the superlattice than the polycrystal. The lifetime-power
413 relationship in the polycrystal tends to deviate from a linear fit (the dashed lines) at high
414 excitation power due to absorber degradation. The error bars are from measurements of five
415 different devices. (c) Temperature-dependent *J-V* measurements on solar cells
416 (ITO/ICBA/perovskite/PTAA/Au; active size, 1 mm²) fabricated on as-grown films. The
417 current density values are normalized. As temperature drops, the *F.F.* of the superlattice device
418 does not change as dramatically as the polycrystal device, indicating a lower internal energy
419 barrier in the superlattice. (d) Scanning electron microscope images and corresponding EBIC
420 mapping of the top surface of BA₂SnI₄ films. The polycrystal exhibits grain-dependent current
421 signals. The superlattice exhibits stronger current signals with a crisscross pattern even with a
422 smooth film surface. (e) Scanning electron microscopy images and corresponding EBIC

423 mapping of the cross-section of BA_2SnI_4 films. The polycrystal exhibits grain-dependent
424 current signals. The superlattice exhibits stronger current signals with a linear pattern. (f)
425 Thickness-dependent EQE measurements. The superlattice device exhibits a higher EQE with
426 a larger optimum absorber thickness, indicating the carrier diffusion length in the superlattice
427 is longer than that in the polycrystal. A broader collection range also indicates a smaller
428 bandgap in the superlattice.

429

430 **Fig. 3 | Strain properties of $\text{BA}_2\text{MA}_{n-1}\text{Sn}_n\text{I}_{3n+1}$ superlattices.** (a) X-ray diffraction
431 measurements of the BA_2SnI_4 superlattice and conventionally grown BA_2SnI_4 single crystals.
432 A compressive strain in the a - b plane and a tensile strain along the c direction are observed in
433 the superlattice. (b) DFT computed and experimentally calculated lattice strain with different
434 n in low-dimensional $\text{BA}_2\text{MA}_{n-1}\text{Sn}_n\text{I}_{3n+1}$ perovskites. Crystals with larger n will have smaller
435 strain. Inset scanning electron microscope images show that a larger n will result in a smoother
436 surface, which is attributed to less defects under smaller epitaxial strain. (c) Ellipsometry
437 measurements of the dielectric function ($\epsilon' + i\epsilon''$) of the $\text{BA}_2\text{MA}_2\text{Sn}_3\text{I}_{10}$ superlattice and
438 conventionally grown $\text{BA}_2\text{MA}_2\text{Sn}_3\text{I}_{10}$ single crystals. The larger ϵ' in the superlattice
439 indicates that the compressive strain can increase the dielectric constant and the Bohr radius in
440 the superlattice. A redshift in the ϵ'' reveals that the compressive strain decreases the bandgap
441 of the superlattice. (d) Estimated exciton binding energies obtained from temperature-
442 dependent photoluminescence measurements. The smaller fitted exciton binding energy in the
443 superlattice than the polycrystal indicates a weaker quantum confinement effect because of the

444 smaller width of the organic barrier. In the inset equation, I is the integrated photoluminescent
445 intensity, I_0 is the integrated intensity at room temperature, A is an arbitrary constant, E_B is
446 the exciton binding energy, k_B is the Boltzmann constant, and T is the temperature.

447

448 **Fig. 4 | Photovoltaic studies of Bi³⁺-alloyed BA₂MA₂Sn₃I₁₀ superlattice.** (a) Structure of the
449 Bi³⁺-alloyed BA₂MA₂Sn₃I₁₀ superlattice computed by DFT. The Bi³⁺ ions preferentially
450 aggregate at the interface between the organic and inorganic slabs to relieve the lattice strain
451 (top). The Bi³⁺ alloying alters the electronic band structure, resulting in a substantially
452 decreased CBM. Combined with the region without Bi³⁺, they form a double-band structure in
453 the inorganic slab (bottom). (b) Certified photovoltaic performance measurement, showing a
454 bandgap of 1.042 eV and a V_{OC} of 0.967 V, beyond the Shockley-Queisser-limit. (c) Unusual
455 carrier transport processes with intra-band relaxation, resulting in beyond-band quasi-fermi-
456 level splitting, and therefore, the high V_{OC} . Note that both Sn-I and Bi/Sn-I regions are in direct
457 physical contact with the ETL. (d) Single-wavelength excited $J-V$ measurements of a
458 polycrystalline solar cell with a uniform Bi³⁺ distribution and therefore, a single bandgap (left)
459 and a superlattice (right) solar cell. In the polycrystalline device, reasonably small variations
460 in the FF and V_{OC} are observed, indicating that the carrier transport and the collection
461 efficiency are almost wavelength-independent. In the superlattice device, when the incident
462 wavelength is shorter than ~ 900 nm, neither FF nor V_{OC} exhibits an obvious wavelength-
463 dependency. However, once the excitation wavelength is longer than ~ 900 nm, both FF and
464 V_{OC} drop substantially. (e) Extracted FF and V_{OC} from (d).

466 **REFERENCES**

- 467 1 Zhang, W. et al. Metal halide perovskites for energy applications. *Nat. Energy* **1**, 1-8
468 (2016).
- 469 2 de Arquer, F. P. G. et al. Solution-processed semiconductors for next-generation
470 photodetectors. *Nat. Rev. Mater.* **2**, 1-17 (2017).
- 471 3 Lei, Y. et al. Single-crystal halide perovskites: Opportunities and challenges. *Matter* **4**,
472 2266-2308 (2021).
- 473 4 Meng, L. et al. Addressing the stability issue of perovskite solar cells for commercial
474 applications. *Nat. Commun.* **9**, 1-4 (2018).
- 475 5 Park, N. G. Research direction toward scalable, stable, and high efficiency perovskite
476 solar cells. *Adv. Energy Mater.* **10**, 1903106 (2020).
- 477 6 Ke, W. et al. Prospects for low-toxicity lead-free perovskite solar cells. *Nat. Commun.*
478 **10**, 965 (2019).
- 479 7 Tsai, H. et al. High-efficiency two-dimensional Ruddlesden–Popper perovskite solar
480 cells. *Nature* **536**, 312-316 (2016).
- 481 8 Blancon, J.-C. et al. Extremely efficient internal exciton dissociation through edge
482 states in layered 2D perovskites. *Science* **355**, 1288-1292 (2017).
- 483 9 Yang, X. et al. Efficient green light-emitting diodes based on quasi-two-dimensional
484 composition and phase engineered perovskite with surface passivation. *Nat. Commun.*
485 **9**, 1-8 (2018).
- 486 10 Qin, C. et al. Stable room-temperature continuous-wave lasing in quasi-2D perovskite
487 films. *Nature* **585**, 53-57 (2020).
- 488 11 Kumar, A. et al. Excitons in 2D perovskites for ultrafast terahertz photonic devices. *Sci.*
489 *Adv.* **6**, eaax8821 (2020).
- 490 12 Chen, A. Z. et al. Origin of vertical orientation in two-dimensional metal halide
491 perovskites and its effect on photovoltaic performance. *Nat. Commun.* **9**, 1-7 (2018).
- 492 13 Fang, H.-H. et al. Long-lived hot-carrier light emission and large blue shift in
493 formamidinium tin triiodide perovskites. *Nat. Commun.* **9**, 1-8 (2018).
- 494 14 Cheng, B. et al. Extremely reduced dielectric confinement in two-dimensional hybrid
495 perovskites with large polar organics. *Commun. Phys.* **1**, 1-8 (2018).
- 496 15 Soe, C. M. M. et al. Structural and thermodynamic limits of layer thickness in 2D halide
497 perovskites. *Proc. Natl. Acad. Sci.* **116**, 58-66 (2019).
- 498 16 Blancon, J.-C. et al. Scaling law for excitons in 2D perovskite quantum wells. *Nat.*
499 *Commun.* **9**, 1-10 (2018).
- 500 17 Gélvez-Rueda, M. C. et al. Overcoming the exciton binding energy in two-dimensional
501 perovskite nanoplatelets by attachment of conjugated organic chromophores. *Nat.*
502 *Commun.* **11**, 1-9 (2020).
- 503 18 Grancini, G. et al. Dimensional tailoring of hybrid perovskites for photovoltaics. *Nat.*
504 *Rev. Mater.* **4**, 4-22 (2019).

- 505 19 Ke, W. et al. Prospects for low-toxicity lead-free perovskite solar cells. *Nat. Commun.*
506 **10**, 1-4 (2019).
- 507 20 Lei, Y. et al. Controlled Homoepitaxial Growth of Hybrid Perovskites. *Adv. Mater.* **30**,
508 1705992 (2018).
- 509 21 Chen, Y. et al. Strain engineering and epitaxial stabilization of halide perovskites.
510 *Nature* **577**, 209-215 (2020).
- 511 22 Lei, Y. et al. A fabrication process for flexible single-crystal perovskite devices. *Nature*
512 **583**, 790-795 (2020).
- 513 23 Rothmann, M. U. et al. Atomic-scale microstructure of metal halide perovskite. *Science*
514 **370** (2020).
- 515 24 Tsai, H. et al. Light-induced lattice expansion leads to high-efficiency perovskite solar
516 cells. *Science* **360**, 67-70 (2018).
- 517 25 Tsai, H. et al. Design principles for electronic charge transport in solution-processed
518 vertically stacked 2D perovskite quantum wells. *Nat. Commun.* **9**, 1-9 (2018).
- 519 26 Liu, S. et al. Manipulating efficient light emission in two-dimensional perovskite
520 crystals by pressure-induced anisotropic deformation. *Sci. Adv.* **5**, eaav9445 (2019).
- 521 27 Fujiwara, H. *Spectroscopic ellipsometry: principles and applications*. (John Wiley &
522 Sons, 2007).
- 523 28 Chatterjee, S. et al. Influence of metal substitution on hybrid halide perovskites:
524 towards lead-free perovskite solar cells. *J. Mater. Chem. A* **6**, 3793-3823 (2018).
- 525 29 Abdel-Shakour, M. et al. High - Efficiency Tin Halide Perovskite Solar Cells: The
526 Chemistry of Tin (II) Compounds and Their Interaction with Lewis Base Additives
527 during Perovskite Film Formation. *Sol. RRL* **5**, 2000606 (2021).
- 528 30 Hasegawa, H. et al. Effective band gap tuning by foreign metal doping in hybrid tin
529 iodide perovskites. *J. Mater. Chem. C* **5**, 4048-4052 (2017).
- 530 31 Liao, Y. et al. Highly oriented low-dimensional tin halide perovskites with enhanced
531 stability and photovoltaic performance. *J. Am. Chem. Soc.* **139**, 6693-6699 (2017).
- 532 32 Ruppel, W. et al. Upper limit for the conversion of solar energy. *IEEE Trans. Electron*
533 *Devices* **27**, 877-882 (1980).
- 534 33 De Vos, A. et al. On the thermodynamic limit of photovoltaic energy conversion. *Appl.*
535 *Phys.* **25**, 119-125 (1981).
- 536 34 Li, C. et al. Highly conductive n-type CH₃NH₃PbI₃ single crystals doped with
537 bismuth donors. *J. Mater. Chem. C* **8**, 3694-3704 (2020).
- 538 35 Bartolomé, J. et al. Huge Photostability Enhancement in Bismuth-Doped
539 Methylammonium Lead Iodide Hybrid Perovskites by Light-Induced Transformation.
540 *Chem. Mater.* **31**, 3662-3671 (2019).
- 541 36 Kang, Y. et al. Influence of Bi doping on physical properties of lead halide perovskites:
542 a comparative first-principles study between CsPbI₃ and CsPbBr₃. *Mater. Today Adv.*
543 **3**, 100019 (2019).
- 544 37 He, T. et al. Reduced-dimensional perovskite photovoltaics with homogeneous energy
545 landscape. *Nat. Commun.* **11**, 1-11 (2020).
- 546 38 Huang, X. et al. Enhancing solar cell efficiency: the search for luminescent materials

- 547 as spectral converters. *Chem. Soc. Rev.* **42**, 173-201 (2013).
- 548 39 Kruse, O. et al. Photosynthesis: a blueprint for solar energy capture and biohydrogen
549 production technologies. *Photochem. Photobiol. Sci.* **4**, 957-970 (2005).
- 550 40 Quan, L. N. et al. Ligand-stabilized reduced-dimensionality perovskites. *J. Am. Chem.*
551 *Soc.* **138**, 2649-2655 (2016).
- 552 41 Spanopoulos, I. et al. Uniaxial expansion of the 2D Ruddlesden–Popper perovskite
553 family for improved environmental stability. *J. Am. Chem. Soc.* **141**, 5518-5534 (2019).
- 554 42 Smith, I. C. et al. A layered hybrid perovskite solar - cell absorber with enhanced
555 moisture stability. *Angew. Chem.* **126**, 11414-11417 (2014).
- 556 43 Stoumpos, C. C. et al. Ruddlesden–Popper hybrid lead iodide perovskite 2D
557 homologous semiconductors. *Chem. Mater.* **28**, 2852-2867 (2016).
- 558 44 Kresse, G. et al. Efficient iterative schemes for ab initio total-energy calculations using
559 a plane-wave basis set. *Phys. Rev. B* **54**, 11169 (1996).
- 560 45 Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953 (1994).
- 561 46 Perdew, J. P. et al. Generalized gradient approximation made simple. *Phys. Rev. Lett.*
562 **77**, 3865 (1996).
- 563 47 Grimme, S. et al. A consistent and accurate ab initio parametrization of density
564 functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**,
565 154104 (2010).
- 566 48 Heyd, J. et al. Hybrid functionals based on a screened Coulomb potential. *J. Chem.*
567 *Phys.* **118**, 8207-8215 (2003).
- 568 49 Yang, D. et al. Functionality-directed screening of Pb-free hybrid organic–inorganic
569 perovskites with desired intrinsic photovoltaic functionalities. *Chem. Mater.* **29**, 524-
570 538 (2017).
- 571 50 Powell, K. M. et al. Depth-dependent EBIC microscopy of radial-junction Si
572 micropillar arrays. *Appl. Microsc.* **50**, 1-9 (2020).

573

574 **Acknowledgements** We thank S. Xiang for constructive feedback on preparing the manuscript
575 and D. Fenning for inspiring discussions on the data analysis. **Funding:** This work was
576 supported by a Sloan Research Fellowship from the Alfred P. Sloan Foundation and a Lattimer
577 Faculty Research Fellowship from the University of California San Diego. The
578 microfabrication involved in this work was performed at the San Diego Nanotechnology
579 Infrastructure (SDNI) of UCSD, a member of the National Nanotechnology Coordinated
580 Infrastructure, which was supported by the National Science Foundation (Grant No. ECCS-

581 1542148); This work was performed, in part, at the Center for Integrated Nanotechnologies, an
582 Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of
583 Science at Los Alamos National Laboratory, Stanford Nano Shared Facilities (SNSF, supported
584 by the National Science Foundation under award ECCS-1542152), and Stanford Synchrotron
585 Radiation Laboratory (SSRL, a national user facility operated by Stanford University on behalf
586 of the U.S. Department of Energy, Office of Basic Energy Sciences). The computational work
587 used the Extreme Science and Engineering Discovery Environment (XSEDE), which is
588 supported by the National Science Foundation grant number OCI-1053575.

589

590 **Author contributions** S.X. and Y.Lei conceived the idea. Y.Li carried out the DFT
591 calculations. Y.Lei and C.C.F.L. synthesized the materials, prepared the substrates, and
592 fabricated the devices. Y.Lei, Q.Y., S.Z., H.G., and Y.C. contributed to the structural
593 characterizations. J.Z. contributed to the optical and electrical characterizations. R.Z. carried
594 out the FTIR characterizations and the simulations. All authors contributed to analyzing the
595 data and commenting on the manuscript. **Competing interests:** The authors declare no
596 competing interests. **Data and materials availability:** All data are available in the manuscript
597 or supplementary materials.

Figures

Figure 1

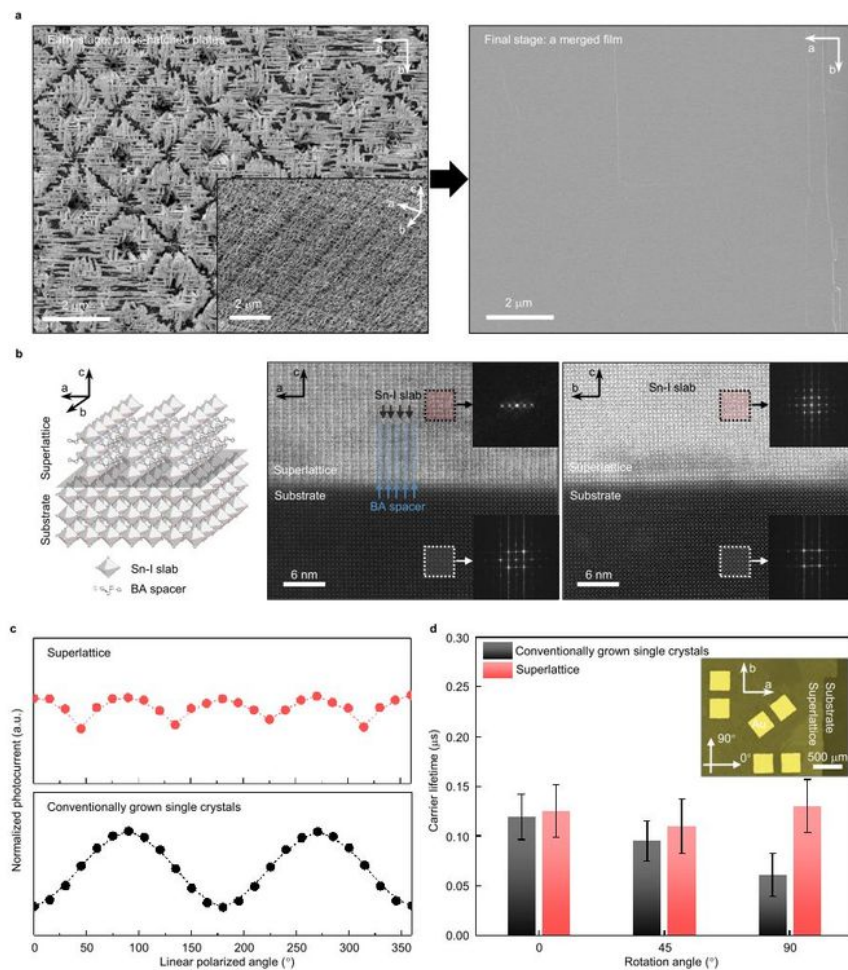


Figure 1

Structural characterizations of the BA₂SnI₄ superlattice. (a) Scanning electron microscope images showing the crisscross epitaxial BA₂SnI₄ superlattice before and after merging into a thin film. (b) Schematics and atomic-resolution cryogenic-scanning transmission electron microscopy images

showing the superlattice structure of a single plate. Cryogenic-scanning transmission electron microscope is essential to minimize the damage of beam-sensitive materials. The epitaxial layer has a well-aligned anisotropic structure without grain boundaries or dislocations. The insets are fast Fourier transform (FFT) patterns from the epitaxial layer in the a-c plane, which show a two-dimensional diffraction pattern of the superlattice and is different from that of the substrate. The inset FFT images in the b-c plane show the structural similarity between the inorganic slab and the substrate. Organic atoms are usually invisible under electron diffraction. (c) Photocurrent measurements with a linearly polarized excitation source showing that the response of the epitaxial layer (top) exhibits a period that is half of a conventionally grown single crystal (bottom). (d) Transient photovoltage measurements showing the orientation-dependent carrier lifetime in the a-b plane. The inset 20 optical image shows the measurement setup. The error bars are from measurements of five different devices.

Figure 2

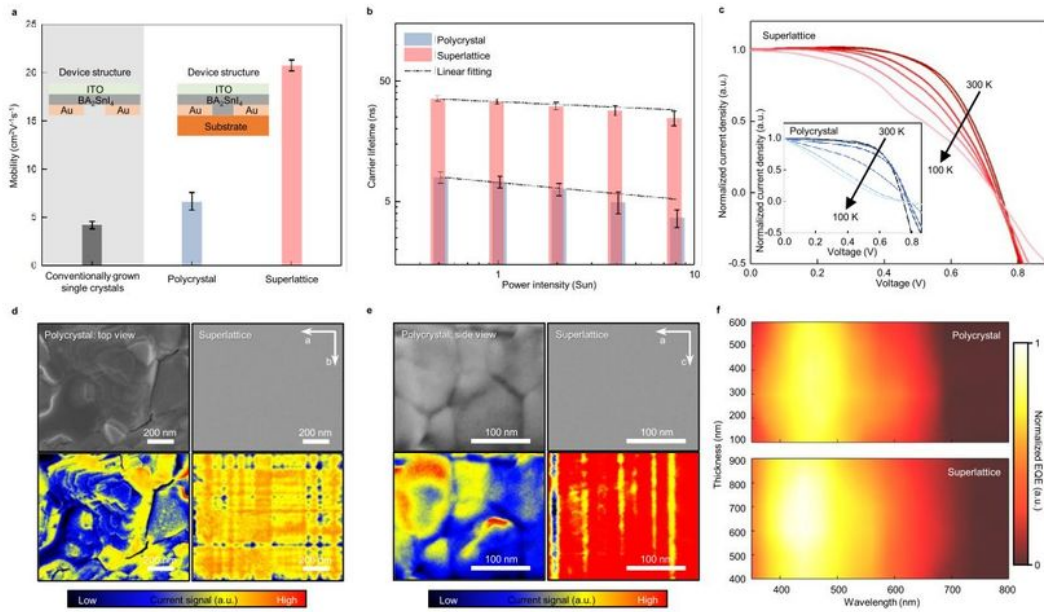


Figure 2

Carrier transport properties of the BA₂SnI₄ superlattice. (a) Transient photocurrent measurements along the film thickness (c) direction. The superlattice shows the highest carrier mobility. The carrier mobility in the polycrystal is limited by grain boundaries and lattice misalignments between grains. The conventionally grown single crystal shows the lowest carrier mobility because of the energy barriers caused by the organic spacers along the film thickness direction. The inset shows the schematic

measurement setup. The error bars are from measurements of five different devices. (b) Time-resolved photoluminescence measurements showing a longer carrier lifetime in the superlattice than the polycrystal. The lifetime-power relationship in the polycrystal tends to deviate from a linear fit (the dashed lines) at high excitation power due to absorber degradation. The error bars are from measurements of five different devices. (c) Temperature-dependent J-V measurements on solar cells (ITO/ICBA/perovskite/PTAA/Au; active size, 1 mm²) fabricated on as-grown films. The current density values are normalized. As temperature drops, the F.F. of the superlattice device does not change as dramatically as the polycrystal device, indicating a lower internal energy barrier in the superlattice. (d) Scanning electron microscope images and corresponding EBIC mapping of the top surface of BA₂SnI₄ films. The polycrystal exhibits grain-dependent current signals. The superlattice exhibits stronger current signals with a crisscross pattern even with a smooth film surface. (e) Scanning electron microscopy images and corresponding EBIC mapping of the cross-section of BA₂SnI₄ films. The polycrystal exhibits grain-dependent current signals. The superlattice exhibits stronger current signals with a linear pattern. (f) Thickness-dependent EQE measurements. The superlattice device exhibits a higher EQE with a larger optimum absorber thickness, indicating the carrier diffusion length in the superlattice is longer than that in the polycrystal. A broader collection range also indicates a smaller bandgap in the superlattice.

Figure 3

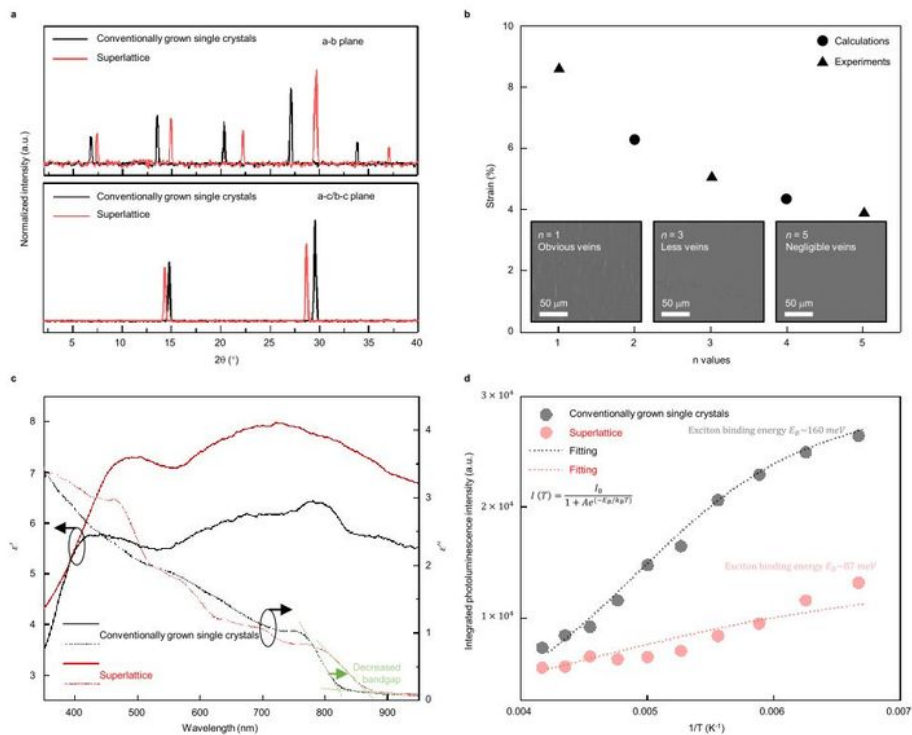


Figure 3

Strain properties of $\text{BA}_2\text{MAn-1Snn13n+1}$ superlattices. (a) X-ray diffraction measurements of the BA_2Sn_4 superlattice and conventionally grown BA_2Sn_4 single crystals. A compressive strain in the a-b plane and a tensile strain along the c direction are observed in the superlattice. (b) DFT computed and experimentally calculated lattice strain with different n in low-dimensional $\text{BA}_2\text{MAn-1Snn13n+1}$ perovskites. Crystals with larger n will have smaller strain. Inset scanning electron microscope images

show that a larger n will result in a smoother surface, which is attributed to less defects under smaller epitaxial strain. (c) Ellipsometry measurements of the dielectric function ($\epsilon' + i\epsilon''$) of the BA2MA2Sn3I10 superlattice and conventionally grown BA2MA2Sn3I10 single crystals. The larger ϵ' in the superlattice indicates that the compressive strain can increase the dielectric constant and the Bohr radius in the superlattice. A redshift in the ϵ'' reveals that the compressive strain decreases the bandgap of the superlattice. (d) Estimated exciton binding energies obtained from temperature dependent photoluminescence measurements. The smaller fitted exciton binding energy in the superlattice than the polycrystal indicates a weaker quantum confinement effect because of the smaller width of the organic barrier. In the inset equation, I is the integrated photoluminescent intensity, I_0 is the integrated intensity at room temperature, A is an arbitrary constant, E_b is the exciton binding energy, k_B is the Boltzmann constant, and T is the temperature.

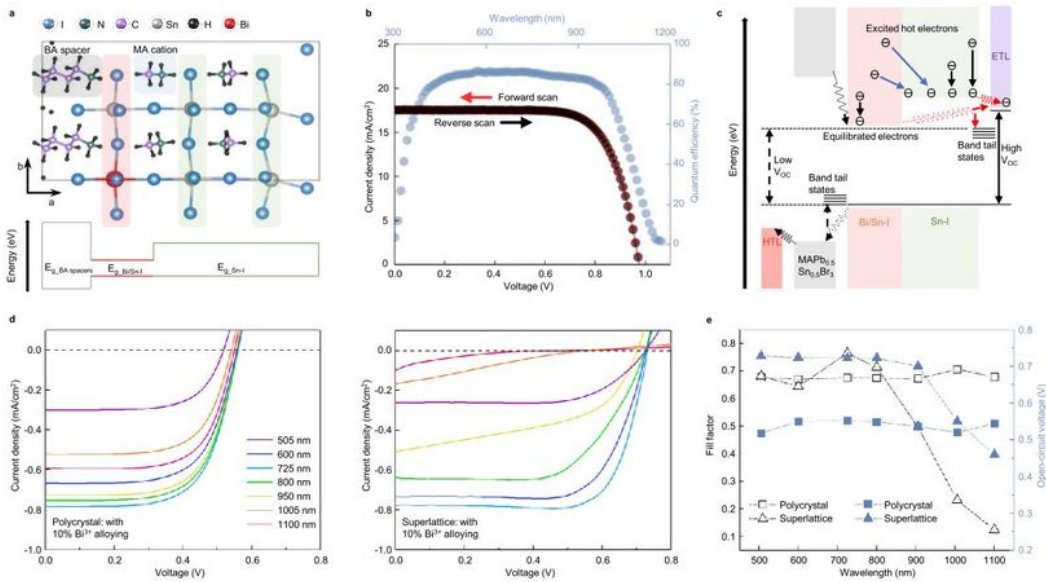


Figure 4

Photovoltaic studies of Bi³⁺-alloyed BA₂MA₂Sn₃I₁₀ superlattice. (a) Structure of the Bi³⁺-alloyed BA₂MA₂Sn₃I₁₀ superlattice computed by DFT. The Bi³⁺ ions preferentially aggregate at the interface between the organic and inorganic slabs to relieve the lattice strain (top). The Bi³⁺ alloying alters the electronic band structure, resulting in a substantially decreased CBM. Combined with the region without Bi³⁺, they form a double-band structure in the inorganic slab (bottom). (b) Certified photovoltaic

performance measurement, showing a bandgap of 1.042 eV and a VOC of 0.967 V, beyond the Shockley-Queisser-limit. (c) Unusual carrier transport processes with intra-band relaxation, resulting in beyond-band quasi-fermi level splitting, and therefore, the high VOC. Note that both Sn-I and Bi/Sn-I regions are in direct physical contact with the ETL. (d) Single-wavelength excited J-V measurements of a polycrystalline solar cell with a uniform Bi³⁺ distribution and therefore, a single bandgap (left) and a superlattice (right) solar cell. In the polycrystalline device, reasonably small variations in the F.F. and VOC are observed, indicating that the carrier transport and the collection efficiency are almost wavelength-independent. In the superlattice device, when the incident wavelength is shorter than ~900 nm, neither F.F. nor VOC exhibits an obvious wavelength dependency. However, once the excitation wavelength is longer than ~900 nm, both F.F. and VOC drop substantially. (e) Extracted F.F. and VOC from (d).

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Leisupplement.pdf](#)