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1 Self-Assembly of Two-Dimensional Perovskite Nanosheet Building 2 Blocks into Ordered Ruddlesden–Popper Perovskite Phase

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14 **S** Supporting Information

15 **ABSTRACT:** The self-assembly of nanoparticles, a
16 process whereby nanocrystal building blocks organize
17 into even more ordered superstructures, is of great interest
18 to nanoscience. Here we report the layer-by-layer
19 assembly of 2D perovskite nanosheet building blocks.
20 Structural analysis reveals that the assembled superlattice
21 nanocrystals match with the layered Ruddlesden–Popper
22 perovskite phase. This assembly proves reversible, as these
23 superlattice nanocrystals can be reversibly exfoliated back
24 into their building blocks via sonication. This study
25 demonstrates the opportunity to further understand and
26 exploit thermodynamics to increase order in a system of
27 nanoparticles and to study emergent optical properties of
28 a superlattice from 2D, weakly attracted, perovskite
29 building blocks.

30 **C**ompared to bulk perovskites, quantum confined perov-
31 skites offer significant improvements, including stronger
32 exciton binding energies, increased photoluminescence quan-
33 tum yield, longer photon lifetime and increased stability.^{1–8}
34 Over the years, various groups have tuned the dimensionality,
35 phase, and composition of perovskite nanocrystals. Typically,
36 we can synthesize perovskites from 0D quantum dots,⁹ 1D
37 nanowires,^{10,11} to 2D nanosheets.^{6,12,13} We can tune the
38 composition of ABX₃ perovskite by substituting various X-
39 anions, A- and B-site cations.^{14,15} We can also tune the
40 arrangement of atoms in a perovskite crystal by tuning the
41 phase,^{16,17} due to the rich phase transitions available in the
42 halide perovskite system. These are all ways to engineer and
43 tune the optical properties at the atomic length scale. However,
44 by systematically arranging the connection between the
45 individual crystals themselves, we gain access to another level
46 of tunability at a greater length scale. It is widely reported that
47 superlattice nanocrystals offer emerging and interesting
48 properties that are not found in their individual building

blocks.^{7,18,19} Typical strategies for creating such layered 49
superlattices rely on complex methods, such as DNA grafting, 50
direct layer-by-layer mechanical stacking, or liquid–air and 51
liquid–liquid interface techniques.^{20–25} A solvent-evaporation- 52
based self-assembly process can produce high uniformity 53
layered superlattices, but often yields an irreversible 54
assembly.^{26,27} In previous work, the intercalation of 2D sheets 55
of metal-halide octahedral [MX₆]^{4–} atomic building blocks 56
with alkylammonium cations offered an approach to produce 57
long-range ordered, well-crystalline 2D layered superlattices.²⁸ 58
These layered structures typically formed Ruddlesden–Popper 59
(RP) phase, an ideal class of perovskite analogues. RP crystals 60
are of special interest due to their intrinsic confinement of the 61
perovskite units and their increased stability.^{29–31} 62

Currently, the most widely adopted method for the 63
preparation of 2D layered perovskites involves a solution- 64
processed crystallization.³² This conventional crystallization 65
technique often relies on either the slow cooling of 66
concentrated solutions or quick solvent evaporation, which 67
makes it difficult to engineer the shape, size, lattice structures 68
and chemical compositions at the nanoscale level. Here, we 69
address this challenge by synthesizing 2D perovskite nano- 70
sheets of precise thickness, which assemble, through a layer by 71
layer process, into 2D layered RP phase superlattice nano- 72
crystals with composition of (C₈H₁₇NH₃)₂Cs_{n–1}Pb_nBr_{3n+1} 73
(where *n* represents the number of [PbBr₆]^{4–} octahedral 74
layers). Figure 1A schematically illustrates the layer-by-layer 75
self-assembly process, from individual perovskite nanosheets 76
with an alkylammonium ligand surface to many superlattices 77
matching the RP phase. The nanosheet building blocks were 78
synthesized by a modified, ligand-assisted, air-free, hot- 79
injection method⁹ (Figures S1 and S2), which is similar to 80
the synthesis reported by Manna et al.¹² 81

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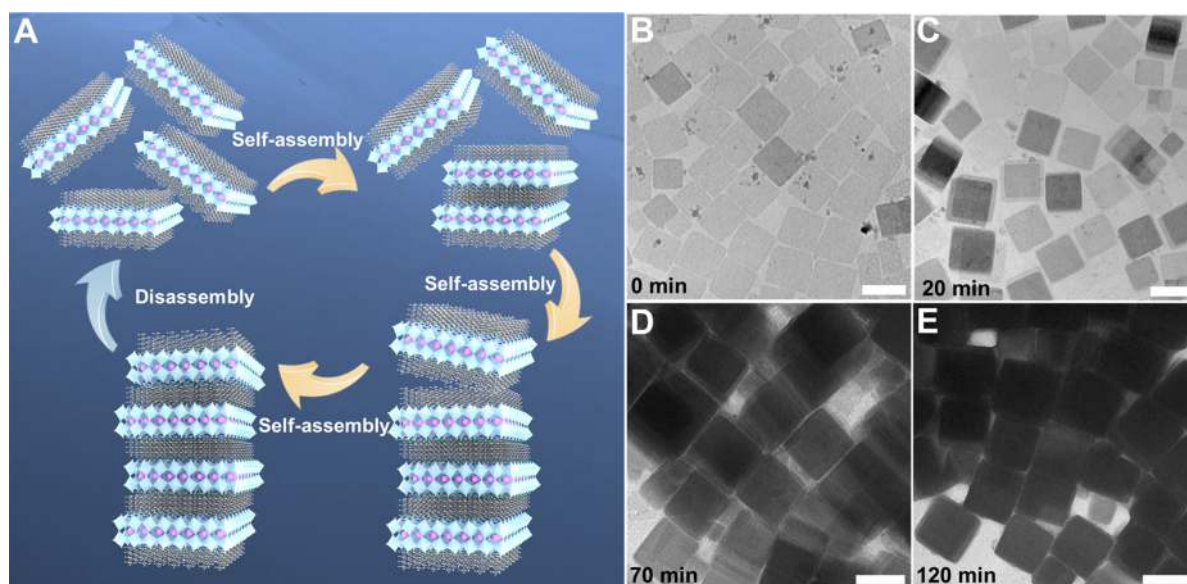


Figure 1. (A) Schematic illustration of the layer-by-layer, self-assembly of $C_8H_{17}NH_3$ -capped $CsPb_2Br_7$ nanosheets into layered $(C_8H_{17}NH_3)_2CsPb_2Br_7$ superlattices. The superlattice nanocrystals can be reversibly exfoliated back into monolayer building blocks by sonication in toluene. (B) Initial $C_8H_{17}NH_3$ -capped $CsPb_2Br_7$ nanosheets. (C, D) Superlattice intermediates. (E) Final $(C_8H_{17}NH_3)_2CsPb_2Br_7$ superlattice nanocrystals. Scale bar, 500 nm.

82 To analyze the self-assembly process, after synthesis, we took
 83 transmission electron microscopy (TEM) images at different
 84 stages of the process (Figure 1B–D and Figures S3–6).
 85 Initially, the $C_8H_{17}NH_3$ -capped $CsPb_2Br_7$ building blocks were
 86 well dispersed in hexane, with limited assembled superlattices
 87 (Figure 1B and Figure S3). After 20 min, many of the crystals
 88 had increased contrast, indicating increased thickness of the
 89 superlattices (Figure 1C–D and Figures S4–7). Tapping-
 90 mode atomic force microscopy (AFM) images (Figure S8)
 91 taken after 30 min show that the thickness of these
 92 superlattices, taken as the assembly progressed, varied from
 93 three (about 6.3 nm), to eight (about 16.8 nm) and
 94 occasionally to tens of layers (25 layers, about 54.3 nm). As
 95 the self-assembly progressed, and the stacking of the building
 96 blocks continued, individual building blocks gradually
 97 decreased, forming many superlattices (Figure 1E). The
 98 overall thickness of the final nanocrystals superlattices were
 99 in the range of 100–400 nm after 4 h of self-assembly. Some
 100 TEM images taken during the assembly process reveal
 101 interlayer slipping between the periodic building blocks,
 102 which indicates the weakness of the force between the layers
 103 (Figure S9).

104 The square nanosheet building block has a lateral size of
 105 around ~ 500 nm (Figure 2A). Energy-dispersive X-ray (EDX)
 106 analysis of single nanosheets (Figure S10A,B) shows an atomic
 107 ratio of Cs:Pb:Br of approximately 1:1.9:7.2. A high resolution
 108 TEM (HR-TEM) image of a single monolayer reveals a single-
 109 crystalline structure matching with an orthorhombic crystal
 110 phase (Figure 2B and Figure S11). The best matching from a
 111 series of simulated images is overlaid in Figure 2B, showing
 112 agreement with the experimental HR-TEM images. The
 113 average in-plane lattice constants of the monolayer were
 114 calculated to be $a \approx 8.2$ Å and $b \approx 8.4$ Å from selected-area
 115 electron diffraction (SAED) (Figure 2C). The well-dispersed
 116 monolayers in hexane exhibit a strong exciton absorption peak
 117 at 427 nm (inset of Figure 2D). Confocal photoluminescence
 118 (PL) of a single monolayer showed an emission peak centered
 119 at 431 nm (Figure 2D). The corresponding height profile

obtained by tapping-mode AFM confirms the monolayers have
 a thickness around 2.2 nm (Figure 2E,F and Figure S10C,D).

After the self-assembly process is complete, uniform
 superlattice nanocrystals with an average lateral size of around
 500 nm were formed (Figure 3A and Figure S12). After
 examining more than 10 individual assembled superlattices by
 EDX analysis (Figure S13 and Table S1), we found that the
 superlattices have an atomic ratio of Cs:Pb:Br of approximately
 1:2:7. This ratio matches well with the 2D layered
 $(C_8H_{17}NH_3)_2CsPb_2Br_7$ RP phase crystal stoichiometry. The
 SAED images taken on a single nanocrystals superlattice
 confirm a crystalline structure with in-plane lattice
 constants of $a \approx 8.1$ Å and $b \approx 8.2$ Å, which are slightly smaller
 than those of the nanosheets measured by SAED. Powder X-
 ray diffraction (XRD) measurement of a drop-casted film of
 assembled crystals show characteristic periodic diffraction
 peaks of textured RP crystals: the (002), (004), (006) and
 (008) diffractions (Figure S14). Because of the nature of the
 textured sample, it is challenging to clarify the crystal structure
 of the superlattice. To further confirm the detailed crystal
 structure, we grounded the assembled crystals into a powder
 and loaded them on a glass substrate for grazing incidence
 wide angle X-ray scattering (GIWAXS) measurements (Figure
 S15). For comparison, we also synthesized the micron-sized
 $(C_8H_{17}NH_3)_2CsPb_2Br_7$ RP phase single crystals by solution-
 processed crystallization with the same organic ligands and
 inorganic perovskite precursors (Figures S16 and S17, crystal
 data summarized in Tables S2–4). Figure 3C shows that the
 in-plane diffraction peaks of the assembled superlattice
 nanocrystals match well with the crystal structure calculated
 from the $(C_8H_{17}NH_3)_2CsPb_2Br_7$ RP phase micrometer-sized
 single crystals. The diffraction peaks from the powder XRD
 matches the d -spacing of the $(C_8H_{17}NH_3)_2CsPb_2Br_7$ RP
 nanocrystals captured with GIWAXS (Figure S15). Compared
 to the nanosheet's emission peak at 431 nm, the superlattice
 nanocrystals show a slightly red-shifted emission peak at 440
 nm (Figure 3D). Our previous work demonstrated that such 156

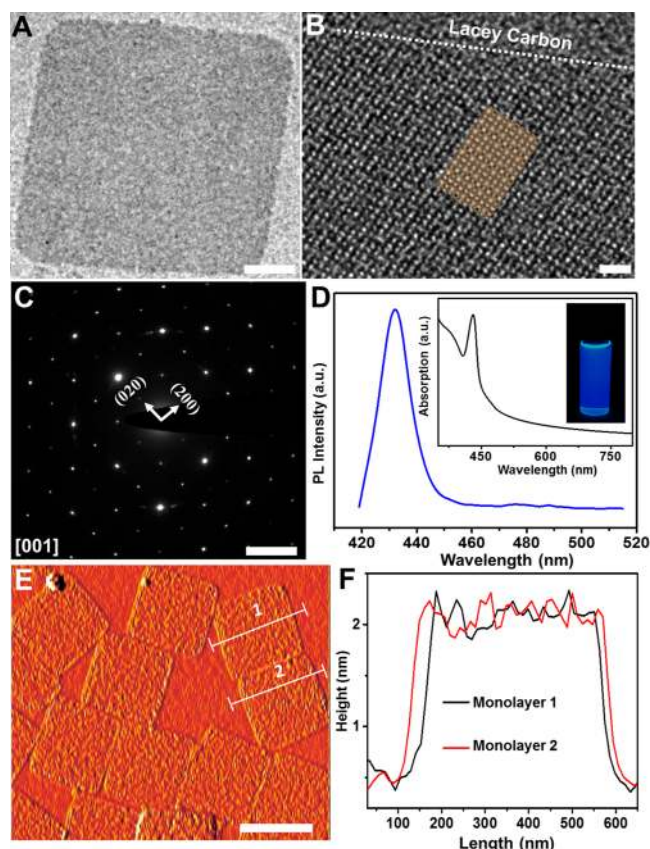


Figure 2. (A) TEM image of $C_8H_{17}NH_3$ -capped $CsPb_2Br_7$ nanosheets. Scale bar, 100 nm. (B) HR-TEM image of a single $C_8H_{17}NH_3$ -capped $CsPb_2Br_7$ nanosheet. Inset of panel B shows simulated TEM image. Scale bar, 1 nm. (C) SAED pattern taken from a single $C_8H_{17}NH_3$ -capped $CsPb_2Br_7$ nanosheet. Scale bar, 5 nm^{-1} . (D) Confocal PL of a single $C_8H_{17}NH_3$ -capped $CsPb_2Br_7$ nanosheet. Inset of panel D shows optical absorption of $C_8H_{17}NH_3$ -capped $CsPb_2Br_7$ nanosheets dispersed in hexane solution. (E) AFM image. Scale bar, 500 nm. (F) Height profile of the $C_8H_{17}NH_3$ -capped $CsPb_2Br_7$ nanosheets.

157 slight PL red-shift could be induced by the lattice contraction
158 upon assembly.¹³

159 Next, we used *in situ* synchrotron-based small-angle X-ray
160 scattering (SAXS), in combination with *ex situ* small-angle
161 XRD to monitor the self-assembly kinetics. Directly after
162 synthesis, we loaded the fresh solution into a 2 mm capillary
163 tube; we then took a SAXS scan periodically. At first, a weak
164 scattering pattern was observed. As the reaction time
165 progressed past 40 min, the weak diffraction peak at $q_{(002)} =$
166 0.289 \AA^{-1} increased (Figure 4A). The $q_{(002)}$ matches with the
167 (002) peak from the GIWAXS and powder XRD. The
168 increased intensity of the (002) peak indicates that as the
169 self-assembly progresses, the building blocks became more
170 ordered and stacked face-to-face, along the [001] crystallo-
171 graphic direction. After 90 min, higher order diffraction planes
172 appeared (Figure 4A). From the (002) and (004) peaks, we
173 can confirm the lamellar nature of the superlattices, with a
174 lattice parameter of 2.2 nm, matching the thickness of the
175 ligand covered building blocks. Figure 4B shows the peak
176 intensity evolution of the (002) and (004) diffraction as a
177 function of growth time. The strong periodicity along the [001]
178 direction from *in situ* SAXS and *ex situ* XRD indicates a highly
179 ordered lamellar structure. Since we performed the *in situ*

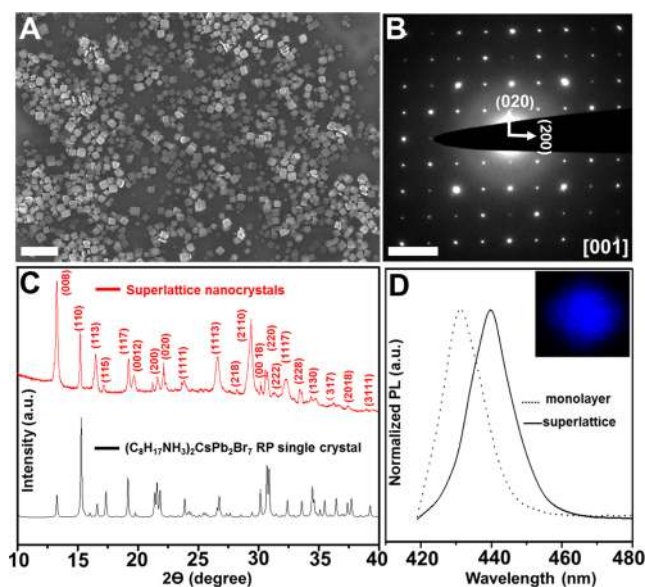


Figure 3. (A) SEM image of the 2D $(C_8H_{17}NH_3)_2CsPb_2Br_7$ superlattice nanocrystals, Scale bar, 2 μm . (B) SAED pattern taken from a single $(C_8H_{17}NH_3)_2CsPb_2Br_7$ nanocrystal. Scale bar, 2 nm^{-1} . (C) Comparison of wide-angle XRD pattern of $(C_8H_{17}NH_3)_2CsPb_2Br_7$ nanocrystals with $(C_8H_{17}NH_3)_2CsPb_2Br_7$ single crystals. (D) Confocal PL comparison of a single $(C_8H_{17}NH_3)_2CsPb_2Br_7$ superlattice nanocrystal and a single nanosheet building block. Inset shows confocal mapping of a single $(C_8H_{17}NH_3)_2CsPb_2Br_7$ superlattice nanocrystal.

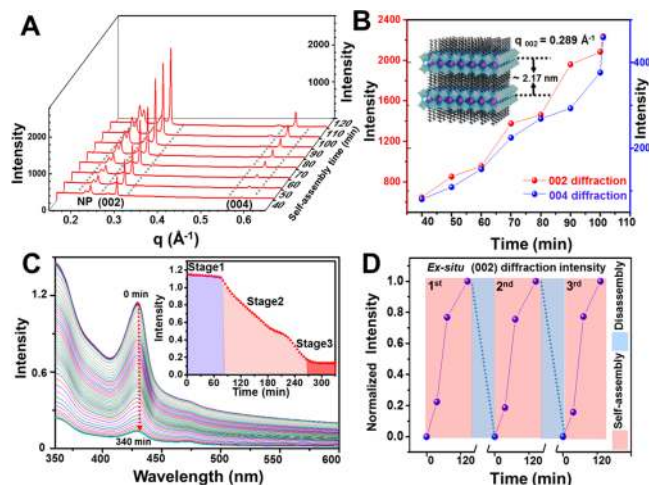


Figure 4. (A) *In situ* circularly averaged SAXS patterns taken at different self-assembly stages in hexane. (B) *In situ* SAXS diffraction peak intensity of the (002) and (004) reflection as a function of self-assembly time. (C) *In situ* UV-vis spectrum taken at different self-assembly stages in hexane. Inset shows evolution of the absorption peak intensity as a function of self-assembly time. (D) *Ex situ* XRD intensity of (002) diffraction peak as a function of self-assembly and disassembly cycles.

SAXS experiment directly after synthesis, there inevitably exists 180 other nanoparticles (NP) in the solution. We attribute the q - 181 vector at 0.228 \AA^{-1} to the assembly of these coexisting 182 nanoparticles (Figure S18). These nanoparticles can generally 183 be separated through centrifugation. 184

The *in situ* UV-vis spectrum complements the *in situ* SAXS 185 and *ex situ* XRD data, showing similar kinetics (Figure 4C,D). 186 Within the first 60 min, the absorption intensity at 427 nm did 187

188 not change much. The lack of change in attenuation of the
189 light indicates that the nanosheets stay at relatively similar
190 concentration, while suspended in hexane. After 60 min, as
191 shown in the inset of Figure 4C, the absorption intensity
192 begins to decrease and the absorption position slightly red-
193 shifts (from 427 to 429 nm) as a function of self-assembly
194 time. The decrease in attenuation of the light indicates that the
195 nanosheet concentration begins to decrease in solution. We
196 can attribute this decrease in concentration to assembled
197 crystals precipitating out of the solution. The settling down of
198 these crystals is likely due to the increasing mass and
199 decreasing surface area with ligand coverage as the assembly
200 progresses. At the final stage, the weak absorption intensity at
201 429 nm remained unchanged for a continuous 4 h (inset of
202 Figure 4C), indicating that the assembly has plateaued, and the
203 process is in equilibrium.

204 A unique aspect of this colloidal system is the reversibility of
205 the assembly, which has yet to be achieved with alkylammo-
206 nium hybrid RP phase, or solvent-evaporation and Langmuir–
207 Blodgett assembly techniques. The weak van der Waals forces
208 between the building blocks allows for separation using
209 mechanical force. By sonication in a weak polar solvent, the
210 assembled superlattice can be disassembled back into its
211 building blocks. We have tried several different solvents and
212 found that sonication in toluene works the best. Under
213 sonication, for around 15 to 25 min, the building blocks begin
214 to detach from the assembled superlattice (Figure S19). We do
215 note that at intense powers, sonication can break the
216 monolayers due to the soft nature of the halide perovskite
217 lattice. We can see signs of such structural damage in Figure
218 S19E. Within 25 min, most superlattice are exfoliated back into
219 their individual building blocks. The disassembled nanosheets
220 were isolated from toluene by centrifugation, and then
221 redispersed in hexane. Intriguingly, as shown in Figure 4D
222 and Figure S20, these disassembled building blocks will
223 reassemble back into a similar superlattice structure within
224 120 min, and such self/dis-assembly process can be well
225 recycled for three times in the experiment.

226 The layer-by-layer self-assembly process exhibited in this
227 system is a simple yet robust approach to generate large-scale
228 2D layered halide perovskite superlattices with atomic scale
229 precision. Furthermore, the reversibility of this system gives us
230 a way to systematically test properties that arise as a result of a
231 more ordered system. This system may offer a general pathway
232 for synthesizing other 2D layered superlattice nanomaterials
233 for novel electronic and photonic applications.

234 ■ ASSOCIATED CONTENT

235 ● Supporting Information

236 The Supporting Information is available free of charge on the
237 ACS Publications website at DOI: 10.1021/jacs.9b06889.

238 Detailed experimental procedures, supporting results
239 and additional figures (PDF)

240 ■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Wang, N.; Cheng, L.; Ge, R.; Zhang, S.; Miao, Y.; Zou, W.; Yi, C.; Sun, Y.; Cao, Y.; Yang, R.; Wei, Y.; Guo, Q.; Ke, Y.; Yu, M.; Jin, Y.; Liu, Y.; Ding, Q.; Di, D.; Yang, L.; Xing, G.; Tian, H.; Jin, C.; Gao, F.; Friend, R. H.; Wang, J.; Huang, W. Perovskite light-emitting diodes based on solution-processed self-organized multiple quantum wells. *Nat. Photonics* **2016**, *10*, 699–704.
- (2) Swarnkar, A.; Marshall, A. R.; Sanhira, E. M.; Chernomordik, B. D.; Moore, D. T.; Christians, J. A.; Chakrabarti, T.; Luther, J. M. Quantum dot-induced phase stabilization of alpha-CsPbI₃ perovskite for high-efficiency photovoltaics. *Science* **2016**, *354*, 92–95.
- (3) Grancini, G.; Nazeeruddin, M. K. Dimensional tailoring of hybrid perovskites for photovoltaics. *Nature Rev. Mater.* **2019**, *4*, 4–22.
- (4) Yang, S.; Niu, W. X.; Wang, A. L.; Fan, Z. X.; Chen, B.; Tan, C. L.; Lu, Q. P.; Zhang, H. Ultrathin two-dimensional organic-inorganic hybrid perovskite nanosheets with bright, tunable photoluminescence and high stability. *Angew. Chem., Int. Ed.* **2017**, *56*, 4252–4255.
- (5) Akkerman, Q. A.; Rainò, G.; Kovalenko, M. V.; Manna, L. Genesis, challenges and opportunities for colloidal lead halide perovskite nanocrystals. *Nat. Mater.* **2018**, *17*, 394–405.
- (6) Bekenstein, Y.; Koscher, B. A.; Eaton, S. W.; Yang, P.; Alivisatos, A. P. Highly luminescent colloidal nanoplates of perovskite cesium lead halide and their oriented assemblies. *J. Am. Chem. Soc.* **2015**, *137*, 16008–16011.
- (7) Rainò, G.; Becker, M. A.; Bodnarchuk, M. I.; Mahrt, R. F.; Kovalenko, M. V.; Stöferle, T. Superfluorescence from lead halide perovskite quantum dot superlattices. *Nature* **2018**, *563*, 671–675.
- (8) Imran, M.; Caligiuri, V.; Wang, M.; Goldoni, L.; Prato, M.; Krahn, R.; De Trizio, L.; Manna, L. Benzoyl halides as alternative precursors for the colloidal synthesis of lead-based halide perovskite nanocrystals. *J. Am. Chem. Soc.* **2018**, *140*, 2656–2664.
- (9) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of cesium lead halide perovskites (CsPbX₃, X = Cl, Br, 309

- 310 and I): novel optoelectronic materials showing bright emission with
311 wide color gamut. *Nano Lett.* **2015**, *15*, 3692–3696.
- 312 (10) Zhang, D.; Eaton, S. W.; Yu, Y.; Dou, L.; Yang, P. Solution-
313 phase synthesis of cesium lead halide perovskite nanowires. *J. Am.*
314 *Chem. Soc.* **2015**, *137*, 9230–9233.
- 315 (11) Zhang, D.; Yu, Y.; Bekenstein, Y.; Wong, A. B.; Alivisatos, A. P.;
316 Yang, P. Ultrathin colloidal cesium lead halide perovskite nanowires. *J.*
317 *Am. Chem. Soc.* **2016**, *138*, 13155–13158.
- 318 (12) Shamsi, J.; Dang, Z.; Bianchini, P.; Canale, C.; Di Stasio, F.;
319 Brescia, R.; Prato, M.; Manna, L. Colloidal synthesis of quantum
320 confined single crystal CsPbBr₃ nanosheets with lateral size control up
321 to the micrometer range. *J. Am. Chem. Soc.* **2016**, *138*, 7240–7243.
- 322 (13) Dou, L.; Wong, A. B.; Yu, Y.; Lai, M.; Kornienko, N.; Eaton, S.
323 W.; Fu, A.; Bischak, C. G.; Ma, J.; Ding, T.; et al. Atomically thin two-
324 dimensional organic-inorganic hybrid perovskites. *Science* **2015**, *349*,
325 1518–1521.
- 326 (14) Wong, A. B.; Lai, M.; Eaton, S. W.; Yu, Y.; Lin, E.; Dou, L.; Fu,
327 A.; Yang, P. Growth and anion exchange conversion of CH₃NH₃PbX₃
328 nanorod arrays for light-emitting diodes. *Nano Lett.* **2015**, *15*, 5519–
329 5524.
- 330 (15) Dou, L.; Lai, M.; Kley, C. S.; Yang, Y.; Bischak, C. G.; Zhang,
331 D.; Eaton, S. W.; Ginsberg, N. S.; Yang, P. Spatially resolved
332 multicolor CsPbX₃ nanowire heterojunctions via anion exchange.
333 *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 7216–7221.
- 334 (16) Kong, Q.; Lee, W.; Lai, M.; Bischak, C. G.; Gao, G.; Wong, A.
335 B.; Lei, T.; Yu, Y.; Wang, L.-W.; Ginsberg, N. S.; Yang, P. Phase-
336 transition-induced p–n junction in single halide perovskite nanowire.
337 *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 8889–8894.
- 338 (17) Lai, M.; Obliger, A.; Lu, D.; Kley, C. S.; Bischak, C. G.; Kong,
339 Q.; Lei, T.; Dou, L.; Ginsberg, N. S.; Limmer, D. T.; Yang, P. Intrinsic
340 anion diffusivity in lead halide perovskites is facilitated by a soft
341 lattice. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 11929–11934.
- 342 (18) Nie, Z.; Petukhova, A.; Kumacheva, E. Properties and emerging
343 applications of self-assembled structures made from inorganic
344 nanoparticles. *Nat. Nanotechnol.* **2010**, *5*, 15–25.
- 345 (19) Nagaoka, Y.; Tan, R.; Li, R.; Zhu, H.; Eggert, D.; Wu, Y. A.;
346 Liu, Y.; Wang, Z.; Chen, O. Superstructures generated from truncated
347 tetrahedral quantum dots. *Nature* **2018**, *561*, 378–382.
- 348 (20) Dong, A.; Chen, J.; Vora, P. M.; Kikkawa, J. M.; Murray, C. B.
349 Binary nanocrystal superlattice membranes self-assembled at the
350 liquid–air interface. *Nature* **2010**, *466*, 474–477.
- 351 (21) Wang, C.; He, Q.; Halim, U.; Liu, Y.; Zhu, E.; Lin, Z.; Xiao, H.;
352 Duan, X.; Feng, Z.; Cheng, R. Monolayer atomic crystal molecular
353 superlattices. *Nature* **2018**, *555*, 231–236.
- 354 (22) Haigh, S.; Gholinia, A.; Jalil, R.; Romani, S.; Britnell, L.; Elias,
355 D.; Novoselov, K.; Ponomarenko, L.; Geim, A.; Gorbachev, R. Cross-
356 sectional imaging of individual layers and buried interfaces of
357 graphene-based heterostructures and superlattices. *Nat. Mater.* **2012**,
358 *11*, 764–767.
- 359 (23) Yu, W. J.; Li, Z.; Zhou, H.; Chen, Y.; Wang, Y.; Huang, Y.;
360 Duan, X. Vertically stacked multi-heterostructures of layered materials
361 for logic transistors and complementary inverters. *Nat. Mater.* **2013**,
362 *12*, 246–252.
- 363 (24) Srivastava, S.; Nykypanchuk, D.; Fukuto, M.; Halverson, J. D.;
364 Tkachenko, A. V.; Yager, K. G.; Gang, O. Two-Dimensional DNA-
365 Programmable Assembly of Nanoparticles at Liquid Interfaces. *J. Am.*
366 *Chem. Soc.* **2014**, *136*, 8323–8332.
- 367 (25) Lee, C.-H.; Lee, G.-H.; Van Der Zande, A. M.; Chen, W.; Li, Y.;
368 Han, M.; Cui, X.; Arefe, G.; Nuckolls, C.; Heinz, T. F.; et al.
369 Atomically thin p–n junctions with van der Waals heterointerfaces.
370 *Nat. Nanotechnol.* **2014**, *9*, 676–681.
- 371 (26) Geuchies, J. J.; Van Overbeek, C.; Evers, W. H.; Goris, B.; De
372 Backer, A.; Gantapara, A. P.; Rabouw, F. T.; Hilhorst, J.; Peters, J. L.;
373 Kononov, O.; et al. In situ study of the formation mechanism of two-
374 dimensional superlattices from PbSe nanocrystals. *Nat. Mater.* **2016**,
375 *15*, 1248–1254.
- 376 (27) Weidman, M. C.; Smilgies, D.-M.; Tisdale, W. A. Kinetics of
377 the self-assembly of nanocrystal superlattices measured by real-time in
378 situ X-ray scattering. *Nat. Mater.* **2016**, *15*, 775–781.
- (28) Mitzi, D. B.; Feild, C.; Harrison, W.; Guloy, A. Conducting tin
379 halides with a layered organic-based perovskite structure. *Nature* **1994**, *369*,
380 467–469.
- (29) Tsai, H.; Nie, W.; Blancon, J.-C.; Stoumpos, C. C.; Asadpour,
381 R.; Harutyunyan, B.; Neukirch, A. J.; Verduzco, R.; Crochet, J. J.;
382 Tretiak, S.; et al. High-efficiency two-dimensional Ruddlesden–
383 Popper perovskite solar cells. *Nature* **2016**, *536*, 312–316.
- (30) Yuan, M.; Quan, L. N.; Comin, R.; Walters, G.; Sabatini, R.;
384 Voznyy, O.; Hoogland, S.; Zhao, Y.; Beauregard, E. M.; Kanjanaboos,
385 P.; et al. Perovskite energy funnels for efficient light-emitting diodes.
386 *Nat. Nanotechnol.* **2016**, *11*, 872–877.
- (31) Heinz, H.; Vaia, R.; Krishnamoorti, R.; Farmer, B. Self-
387 assembly of alkylammonium chains on montmorillonite: effect of
388 chain length, head group structure, and cation exchange capacity.
389 *Chem. Mater.* **2007**, *19*, 59–68.
- (32) Stoumpos, C. C.; Cao, D. H.; Clark, D. J.; Young, J.; Rondinelli,
390 J. M.; Jang, J. I.; Hupp, J. T.; Kanatzidis, M. G. Ruddlesden-Popper
391 Hybrid Lead Iodide Perovskite 2D Homologous Semiconductors. **392**
Chem. Mater. **2016**, *28*, 2852–2867. **393**