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Ultrafast relaxation of lattice distortion in 2D perovskites

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Direct visualization of ultrafast coupling between charge carriers and lattice degrees of freedom in photo-excited semiconductors has remained a long-standing challenge and is critical for understanding the light-induced physical behavior of materials under extreme non-equilibrium conditions. Here, we obtain a direct visual of the structural dynamics in monocrystalline 2D perovskites. We achieve this by monitoring the evolution of the wave-vector resolved ultrafast electron diffraction intensity following above-bandgap high-density photoexcitation. Our analysis reveals a light-induced ultrafast reduction of antiferro-

35 **distortion resulting from a strong interaction between the electron-hole plasma and the**
36 **perovskite lattice, which induces an in-plane octahedra rotation towards a more symmetric**
37 **phase. Correlated ultrafast spectroscopy performed at the same carrier density as ultrafast**
38 **electron diffraction reveals that the creation of a dense electron-hole plasma triggers the**
39 **relaxation of lattice distortion at short timescales by modulating the crystal cohesive energy.**
40 **Finally, we show that the interaction between the carrier gas and the lattice can be altered**
41 **by tailoring the rigidity of the 2D perovskite by choosing the appropriate organic spacer**
42 **layer.**

43 Organic-inorganic (hybrid) two-dimensional (2D) halide perovskites (2DP) are constructed
44 by a superlattice of interlocking organic and inorganic nanometer-thick layers and have
45 demonstrated unique and non-classical behaviors and are being extensively explored for a wide
46 range of technologies such as photovoltaics, photodetectors, photocatalysts, light emitting diodes,
47 lasers, and quantum emitters.¹⁻⁹ The underlying design principles for each of these devices are
48 strongly correlated to the exact details of how photoexcited or electronically injected charge
49 carriers dissipate their energy via electron-phonon coupling. For example, it has been shown
50 recently, that unusual electron-phonon coupling mechanisms are likely to promote emission of
51 single photons or correlated photon pairs from perovskite quantum sources.¹⁰ There have been
52 only handful experimental studies based on ultrafast or temperature dependent optical
53 spectroscopies to elucidate the carrier dynamics in 2D perovskites. These studies reveal different
54 facets of electron-phonon coupling, which could strongly govern the exciton polaronic effects,¹¹
55 hot-carrier dynamics,¹² vibrational relaxation dynamics,¹³ and carrier trapping and re-combination
56 rates.⁵ Moreover, these measurements also indicate that presence of an organic cation in close
57 proximity to the inorganic perovskite lattice strongly modulates the nature of electron-phonon
58 interactions,^{5,11,13-19} and suggest that electron-phonon scattering in 2D perovskites occurs via, local
59 dynamic disorder.⁶ These short-range carrier-lattice interactions modulate the quantum-well
60 thickness and octahedral tilts, leading to exciton self-trapping and broadband emission, thanks to
61 the lattice softness, as well as the unique photo-physics properties under extreme non-equilibrium.
62 However, there exists no direct ultrafast structural measurement of 2D perovskites, which
63 elucidates the underlying carrier-lattice interaction mechanisms upon optical excitation. Moreover,
64 the exact geometry and dynamics of these lattice distortions are unknown. This is largely due to

65 the challenges in visualizing the carrier-lattice coupling and dynamics that result after optical
66 excitation above the band-gap.

67 Here we report the first direct measurement of structural dynamics in 2D perovskites
68 obtained by monitoring the change in the ultrafast femtosecond electron diffraction (UED) after
69 optical excitation. This technique enables a time-resolved structural evolution of the 2D
70 perovskites by tracking the changes in the diffraction pattern, thus providing a direct visualization
71 of lattice response after photo-doping. Detailed analysis of the Bragg peak intensities and temporal
72 signatures reveals an ultrafast reduction of antiferro-distortion at early times ($\tau \leq 1$ ps), which is
73 attributed to the light-induced in-plane rotation of the perovskite octahedra from a distorted to a
74 symmetrical (ordered) phase. Complementary transient absorption measurements further reveal a
75 high excitation regime (beyond Mott transition),^{20,21} where a dense electron-hole plasma strongly
76 modulates the crystal cohesive energy,²² leading to an ultrafast lattice ordering. In parallel, a
77 classical energy transfer to the whole phonon bath via thermal atomic displacements was observed,
78 which was attributed to the Debye-Waller effect. The Debye-Waller effect was associated with a
79 slower rise time ($\tau \sim 5$ ps) of the thermal dissipation (or lattice heating). Additionally, the observed
80 long-lived coherent acoustic oscillations suggest the long lifetime of the observed lattice response.
81 Concomitant with the Debye-Waller effect, we also observe an increase in the diffused scattering,
82 which confirms the activation of thermal transfer to the phonon bath. Finally, we show that the
83 mechanism and dynamics of the interaction between the charge carriers and the lattice are acutely
84 tunable and sensitive to the initial lattice distortion of the 2D perovskites dictated by the choice of
85 the organic spacer layer. These findings reveal new and distinct carrier-lattice interactions and
86 counterintuitive mechanisms in 2D perovskites at room temperature, which have not been reported
87 in conventional non-polar/weakly-polar semiconductors such as Si and GaAs or even in 3D iodide
88 perovskites.^{23,24}

89

90 **UED experiment on 2D perovskites**

91 The UED experiments are performed in a pump-probe setup in which sub-micron thick 2D hybrid
92 perovskite single crystals are photoexcited with a 75-fs pulse laser and the structural dynamics are
93 probed with a pulsed electron beam with 150 fs temporal width after specific delay times (t) (Fig.
94 1a). A diffraction image is acquired at each delay time after above-gap excitation (Fig. 1b), which

95 reflects the instantaneous 2D perovskite crystal structure. Monitoring the characteristics of the
96 diffraction peaks (or Bragg peaks) on the image allows us to directly probe the dynamic changes
97 in the lattice structure after light excitation, revealing the carrier-lattice interactions during energy
98 relaxation (cooling) to the 2D perovskite semiconductors band-edge. We start with a phase-pure
99 (homogenous perovskite layer thickness) 2D perovskite crystal of Dion-Jacobson 4AMP-MAPb₂I₇
100 (DJ n=2) with thickness of 270 nm (Fig. 1a and Fig. S1), which is excited with 3.1 eV light, i.e.
101 0.9 eV above its ground state optical transition.²⁵ The diffraction pattern of DJ n=2 at rest is
102 consistent with the static crystal structure reported previously (Fig. 1c and 1d, and details in Fig.
103 S2),²⁵ which exhibits antiferro-distortions (clockwise and anticlockwise octahedral rotations
104 around the **c** axis) associated with an in-plane doubling of the unit cell (in-plane is defined by **a**
105 and **b** axes).^{26,27} The diffraction pattern also indicates that the orientation of the crystal layers is
106 parallel to the substrate (see Supplementary discussion 1 and Fig. S2), with both the light excitation
107 and the probe electron beams impinging along the DJ n=2 stacking axis (**c** axis), as depicted in Fig.
108 1a.

109 Fig. 2a shows the differential diffraction map indicating the change in the Bragg peak
110 intensities of the DJ n=2 crystal that occurs within a few picoseconds ($t=2$ ps, averaged from 1 to
111 3 ps) after light excitation with a fluence of 2 mJ/cm² (corresponds to a carrier density of
112 2.5×10^{13} cm⁻², see Supplementary discussion 2). A first visual inspection of this data reveals both
113 an anisotropic response with respect to the in-plane directions in the 2D perovskite lattice and a
114 monotonically decreasing of absolute intensity response with respect to the magnitude of the
115 scattering vector $|q|$. The Bragg peaks that show a detectable increase in their intensity after light
116 excitation are {400} ((400) and (040)), and {220} (Fig. 2a). The {220} belongs to the {hh0} family
117 and corresponds to the d-spacing of 3.2 Å (Pb-I bonds) along the octahedra diagonal (shown as
118 the highlighted yellow rectangle in Fig. 2b), whereas the {400} Bragg peaks are in the {h00}
119 family correlated with the d-spacing of 2.25 Å (half of octahedron length) along the edge of the
120 octahedra (**a** and **b** directions, shown as cyan in Fig. 2b). On the contrary, higher orders of these
121 two Bragg families such as {800}, {330} and {550}, as well as other directions with reasonable
122 signal ({310}, {530}, {750} and {1020}), all exhibit a decrease in their intensities after
123 photoexcitation. Details of these Bragg peak traces are illustrated in Fig. S3. Furthermore, these

124 transient intensity response scales monotonically with the pump fluence ($1\text{mJ}/\text{cm}^2$, estimated
125 carrier density $1.3\times 10^{13}\text{cm}^{-2}$), as shown in Fig. S4 for the representative Bragg peaks.

126 We note that opposite to our results, conventional well-studied bulk semiconductors (such
127 as Si and GaAs), as well as inorganic 2D materials (for example, transition metal dichalcogenides
128 such as MoS_2 and MoSe_2), exhibit in most cases a decrease in Bragg peak intensities after
129 photoexcitation.^{23,28,29} An increase of Bragg peaks has been reported, resulting from suppression
130 of charge density waves,³⁰ however no such signatures have been reported in our material system.
131 We also exclude the other unlikely reasons that could induce the Bragg peak increase, based on
132 investigations on temperature-dependent XRD, differential scanning calorimetry, and diffraction
133 modeling from kinematical scattering theory (SI discussion 4). In conventional well-studied
134 materials, the UED signal is attributed to a typical Debye-Waller response, which corresponds to
135 an energy transfer from hot carriers to the low-frequency vibrational density of states, which scale
136 as $|q|^2$.^{23,31} A recent study on hybrid three-dimensional (3D) perovskites (MAPbI_3) also suggests a
137 Debye-Waller like response, where octahedral rotational disorder induces additional structural
138 deformations.²⁴ The counterintuitive and opposite behavior of light-induced ordering in some
139 specific crystal directions in DJ $n=2$ crystals implies that there must exist another competing
140 mechanism, via which the photogenerated carriers strongly interact with the lattice resulting in
141 transient structural change, instead of thermal activation of the phonon bath leading to lattice
142 heating. The increase in the intensities of specific Bragg peaks, thereby counteracting the Debye-
143 Waller effect at short time scale and reducing the lattice distortion (enhanced order) in specific
144 directions.

145 **Mechanism of transient lattice ordering**

146 Qualitative analysis of the diffraction peaks in Fig. 2a suggests that the light-induced
147 transformation may be related to the in-plane lattice reorganization along specific directions.
148 Therefore, we hypothesize that this observed anisotropic lattice ordering originates from the
149 reduction of antiferro-distortions, a specific type of structural deformation involving the rotations
150 of octahedra, which are widely expected in perovskites materials.^{9,24,32} To quantify this distortion,
151 we define an order parameter θ as the half of the interlayer Pb-I bonds tilt (Fig. 2b), where θ is
152 around 12° for the intrinsic structural distortion.²⁵ To test this hypothesis, we reduced the
153 distortions by decreasing the order parameter θ to match the extent of Bragg peak increase in Fig.

154 2a, and simulated the differential diffraction pattern with respect to the crystal structure in the dark
155 ($\theta_0 = 12^\circ$, Fig. 2b). The estimated optimal tilt ($\Delta\theta$) is found to be 0.25° (details of simulation shown
156 in Supplementary discussion 5 and Fig. S5), and the simulated differential diffraction map is
157 shown in Fig. 2c. Compared to the distorted crystal structure at rest, the new structure reduces the
158 adjacent octahedral tilt along the stacking axis (antiferro-distortion), and better aligns the iodine
159 atoms for both octahedral edge $\{h00\}$ and diagonal directions $\{hh0\}$, especially at the distance
160 spacings of Pb-I bonds $\{220\}$ and half of octahedral edge lengths $\{400\}$ (yellow and cyan in Fig.
161 2b). This structural change intensifies the in-plane Bragg peaks including $\{400\}$ and $\{220\}$,
162 consistent with the experimental observations at short time (Fig. 2a). Furthermore, we note that
163 the expected intensity increase is not observed for the higher orders of the Bragg peaks in these
164 two families, such as $\{800\}$, $\{330\}$ and $\{550\}$. We attribute this deviation to the combination of
165 both the light-induced reduction of antiferro-distortion (ordering) and the Debye-Waller response.
166 However, because of its $|q|^2$ dependence, the Debye-Waller effect dominates and thus neutralizes
167 the effect of ordering for the higher order Bragg peaks. To quantitatively compare these intensity
168 changes, we perform an angular integration at constant $|q|$ of these differential diffraction images
169 ($t = 2\text{ps}$ and the simulated one after octahedral re-ordering) (Fig. 2d). The experimental and
170 simulated results are in fair agreement, especially in the low q -value region ($1 \text{ \AA}^{-1} < |q| < 3 \text{ \AA}^{-1}$)
171 where the Debye-Waller effect is weaker. Therefore, these observations support the hypothesis
172 that the light-induced ultrafast lattice dynamics in DJ $n=2$, is due to the collective lattice
173 reorganization that reduces the octahedral rotations (Fig. 2b). This hypothesis is further confirmed
174 by our calculations of vibrational modes (SI discussion 5).

175 Next, in order to gain a deeper insight into the time evolution of the light-induced structural
176 dynamics in 2D hybrid perovskites, we performed a full analysis (up to 100 ps) of the time-
177 dependent intensity changes of the diffraction images after optical excitation. The time traces of
178 the two Bragg peaks $\{400\}$ and $\{530\}$ are displayed in Fig. 3a, where the $\{400\}$ peaks exhibit a
179 significant faster rise-time ($\tau \approx 1\text{ps}$, Fig. S3), revealing a diverse response in Bragg peak dynamics
180 besides the intensity change. Furthermore, an overall increase of diffuse scatterings in-between the
181 Bragg peaks spots is visualized, in the differential diffraction images as shown in Fig. 3b.
182 Compared between short-time ($t = 2\text{ps}$) and long-time delays ($t = 65\text{ps}$), the regions in-between
183 the Bragg peaks spots appear redder as most of the Bragg peaks intensifies toward a negative
184 response. The evolution of the integrated diffuse scattering intensities yields an average increase

185 with 0.5% (Fig. S3), suggesting a broad energy transfer process to the phonon bath, along with the
186 Debye Waller effect specified at Bragg peak locations.

187 To further quantify the different types of lattice dynamics, we fit each Bragg peak intensity
188 curve with a single exponential function, and the fitting details and results are listed in Fig. S3 and
189 Fig. S7, respectively. The maximum positive change (increase in intensity) is 4% and the negative
190 change (decrease in intensity) is 12% (detailed plots in Fig. S3a). The time-constant map (Fig. S7b)
191 shows a clear disparity between the dynamics from different Bragg peak groups. The Bragg peaks
192 with positively changing intensity for which the light-induced lattice ordering mechanism
193 dominates ((400) and (040)), exhibit a very fast time constant of 1 ps or shorter, whereas the peaks
194 with negative intensity response yield a longer time constant on the order of 5 ps. Similar time
195 constants have also been reported in 3D perovskites and have been attributed to the Debye-Waller
196 like response originating from the rotational disorder of the iodine atoms in the perovskite
197 octahedra, leading exclusively to a decrease in peak intensities.²⁴ A modification of our model
198 including the Debye-Waller effect at long time scale is shown to give a better prediction of
199 intensity changes at large q range than the lattice ordering effect (Fig. S8), confirming the existence
200 of multiple energy transfer processes in 2D perovskites.

201 All these observations from UED suggest that there are multiple competing mechanisms at
202 play, which attest to the different origins and time scales of carrier-lattice interactions, as illustrated
203 in Fig. 3c. Therefore, we propose that the light-induced lattice ordering, which was attributed to
204 the reduction of the in-plane lattice antiferro-distortion at ultrafast time scale ($\tau \leq 1$ ps), and at
205 longer timescales ($\tau \sim 5$ ps) a Debye-Waller like response.

206 **Lattice transients triggered by dense electron-hole plasma**

207 In order to gain a complete picture of energy transfer and understand the structural dynamics
208 observed in UED measurements, we performed transient absorption (TA) measurements in the
209 same temporal window with similar excitation fluences as the UED experiments on DJ n=2 crystal,
210 (SI discussion 6 and Methods). By monitoring the transmission changes following above-band
211 optical pump at 3.1eV, we estimated the evolution of the effective temperature (T_c) of hot-carrier
212 gas, by fitting the high-energy tail near the band edge with a Maxwell-Boltzmann distribution
213 (analysis details in supplementary discussion 6 and Fig. S11).³³ The hot-carrier dynamics for

214 various fluences are displayed in Fig. 3d. We observe a fast build-up time of the initial carrier
215 temperature within 0.5 ps (Fig. S11b), corresponding to carrier thermalization via carrier-carrier
216 scattering before quasi-equilibrium distribution of hot-carriers, which is typically consistent with
217 the values reported in iodide perovskites.³⁴ To ensure the carriers reach an effective temperature
218 with quasi-Boltzmann distribution, we perform the analysis of carrier cooling process after 0.5ps.
219 As suggested in Fig. 3d, the evolution of hot carrier distribution reveals a combination of fast (τ
220 \sim 1ps) and slow ($\tau \sim$ 5ps) cooling processes. This complex carrier cooling behavior is consistent
221 with previous TA report on DJ n=1 perovskite poly-crystalline films (4AMP-PbI₄).³⁵ The observed
222 fast time scale (sub-ps to 1ps) from both UED and ultrafast spectroscopy may suggest a correlated
223 process that governs the structural change and the carrier response. Furthermore, we attribute the
224 slow cooling process ($\tau \sim$ 5ps) to the typical time of Debye-Waller effect (Fig. 3c), which reflects
225 the relaxation of carrier energy towards the phonon bath and phonon-phonon scatterings, resulting
226 in a lattice heating at similar time scale.

227 To elucidate the microscopic origin of ultrafast relaxation of lattice distortion, we gave an
228 estimation of the saturated densities (N_{2D}) for both carrier and excitonic responses at different
229 carrier temperatures, as is plotted in Fig. 3e (detailed computation in supplementary discussion
230 7).^{20,36} At a fluence of 1mJ/cm² in UED experiment, a high electron-hole pair density of
231 1.3×10^{13} cm⁻² is generated, with effective temperature of $T_c \approx$ 3300K, extrapolated from the carrier
232 temperature in Fig. 3d. This high plasma pair density exceeds the saturation densities for both hot
233 electron-hole plasma (solid line) and cold exciton gas (dashed line, Mott transition density)
234 regimes by one order of magnitude (Fig. 3e). Therefore, we conclude that the observed energy
235 transfer at short time in the UED experiment is rather related to the coupling of a dense carrier
236 plasma to the lattice, instead of exciton polaronic couplings as reported in optical studies on n=1
237 2D perovskites at low temperature and low excitation fluences.¹⁹

238 In the case of a dense electron-hole plasma, strong transient lattice distortions different
239 from Debye-Waller effects can be induced in semiconductors, generating supersonically
240 propagating strain pulses,^{37,38} and more complex lattice reorganizations such as the suppression of
241 the ferroelectric instability in KTaO₃,³⁹ and the activation of the antiferro-distorsive rotation of
242 octahedra in SrTiO₃.⁴⁰ The last case, which was interpreted on the basis of a photodoping-induced
243 modification of the structural soft-mode potential, might be closely related to our present study on

244 2D perovskites. Furthermore, it was shown that the ultrafast dynamics ($\tau \sim 0.2$ ps) of the observed
245 antiferro-distortion in SrTiO₃ is non-thermally driven by changes of the phonon potential.⁴⁰ Thus,
246 we propose a picture where, the electron-hole plasma produces a strong modification of the lattice
247 dielectric properties. On the one hand it results in screening bound electron-hole (exciton) pair
248 formation, and on the other hand modifies the interatomic force constants. This last mechanism of
249 plasma-induced modulation of the interatomic force must be considered because halide perovskites
250 are strongly ionic materials like SrTiO₃. The resulting modification of the crystal cohesive energy,
251 manifests as a strong lattice reorganization with antiferro-distortive rotation of octahedra in 2D DJ
252 perovskites. In parallel, a more classical decay of the plasma energy occurs through electron-
253 phonon interactions and observed in structural dynamics associated with a Debye-Waller effect.
254 This classical process is mainly associated with an initial activation of optical phonons, that decay
255 later in time to form acoustic phonons.³⁵ Additionally, the activation of long-lived acoustic
256 oscillations has been observed from TA measurements (Fig. S12), suggesting a long equilibration
257 time (hundreds of ps) of phonon bath, which is consistent with the long recovery time of the lattice
258 response in UED (Fig. 3a). Such oscillations have been attributed in RP phases to below band gap
259 resonant optical excitation of longitudinal acoustic waves.^{41,42} Furthermore, the persistence of the
260 reduction of antiferro-distortion can be attributed to the long-lived electron-hole plasma. Indeed,
261 a high density of carriers persists after reduction of its effective temperature as shown by the long-
262 time bleaching the exciton resonance over 100 to 200ps (Fig. S11f).

263 **Organic cations alter the carrier-lattice interactions**

264 Finally, in order to understand if the mechanism of light-induced transformation is generally
265 applicable to other 2D perovskites with different organic cations and structural phases, we perform
266 UED experiments on three other hybrid 2D perovskites: 4AMP-MA₂Pb₃I₁₀ (DJ n=3) exhibiting
267 the same composition as DJ n=2 but a thicker perovskite layer, BA₂MAPb₂I₇ (RP n=2) of
268 Ruddlesden-Popper (RP) phase type with same perovskite layer as DJ n=2 but different spacer
269 organic cations (with BA butylammonium), and BA₂MA₃Pb₄I₁₃ (RP n=4) with a different
270 perovskite layer and spacer organic cations. The structures of these 2D perovskites are illustrated
271 in Fig. 4a and Fig. 4b, respectively. The experimental UED static diffraction pattern of DJ n=3
272 (shown in Fig. S13) resembles that of DJ n=2, suggesting that changing the perovskite layer
273 thickness for the DJ 2D perovskites has a negligible effect on the in-plane diffraction pattern.²⁵

274 In order to quantify the different behaviors between the DJ and the RP phase 2D
275 perovskites we evaluated the differential intensity and the time constant of the relevant Bragg
276 peaks. First, we compared the differential intensity between DJ n=2 and DJ n=3 as illustrated in
277 Fig. 4c (detailed diffraction map in Fig. S14), where both samples exhibit similar behaviors. We
278 observed an increase in the intensity of the in-plane Bragg peaks for DJ n=2 {400} and DJ n=3
279 {040}, and a decrease for the intermediate peaks {310}, {330}, {510} and {530}, consistent with
280 the Debye-Waller effect. These positive changing peaks of DJ crystals exhibit rapid increase with
281 similar time scale of 1ps (Fig. S15). These similarities between the DJ n=2 and n=3 indicate that
282 the phenomena of light-induced ordering at short time scales is generally applicable to the DJ type
283 2D perovskites. However, in sharp contrast to the DJ case, all the observed Bragg peaks in RP n=2
284 and n=4 yield a global decrease in intensity (Fig. 4c, detailed time traces and diffraction maps in
285 Fig. S15-S16). Furthermore, comparison of the time constants τ (Fig. 4d, see also SI discussion 3)
286 suggests a generally slower response (up to 15 ps) for RP perovskites than the DJ system. As
287 similarly observed in DJ n=2, an increased diffuse scattering at longer time scales (Fig. S14, Fig.
288 S16 and Fig. S17) indicates a thermal energy transfer to phonon populations, with similar time
289 constant as the Debye-Waller decrease.

290 These results demonstrate that there is a fundamental difference in the mechanism of
291 carrier-lattice coupling and structural dynamics between the DJ and RP 2D perovskite phases,
292 which implies that the competing mechanism of ultrafast lattice ordering during an antiferro-
293 distortive phase transformation is mitigated in the RP phase. As described in Fig. 4b, the diffraction
294 patterns of RP n=2 and n=4 at rest are consistent with the static crystal structures reported
295 previously, which exhibit almost no antiferro-distortions in plane,⁴³ contrary to DJ n=2 and n=3
296 (Fig. 1d and 4a).²⁵ Therefore, in the RP case the initial ordering step (Fig. 3d) is by-passed and the
297 energy of the hot carriers is directly released to the lattice without the initial energy transfer. We
298 also note that the RP n=4 case is more consistent with the results on 3D MAPbI₃, which only shows
299 the Debye-Waller like effect with similar time scales ($\tau \sim 10$ ps).²⁴ We also note that MAPbI₃
300 indeed exhibit similar intensity variations as RP phases (detailed comparison in SI discussion 8),
301 providing clear evidence of the distinct lattice dynamics in 2D DJ perovskites. These results
302 comparing the nature of carrier-lattice interactions in 2D perovskites with different organic spacer

303 layers provides clear design principle for controlling carrier dynamics in 2D perovskites-based
304 devices.

305

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323

324 **Author contributions**

325 A.D.M. and J-C. B. conceived and designed the experiment. J.H. and S.S. synthesized the
326 perovskite single crystals, and W.L. prepared samples with the help of J.H. and H.Z; H.Z.
327 performed optical absorbance characterizations. W.L., H.Z., S.S. and A.F. performed the UED
328 experiments with the help of. A.A, M.-F.L, A.B., X.Z., X.W. and U.B.; H.Z. performed data
329 analysis under the help of J.Essman and I.M, with guidance from J.-C.B., J.Even. and M.G.K.
330 Phonon modeling was carried out by C.Q. with guidance from J. Even and C.K.; W.Y. performed
331 TA measurements with guidance from S.L. J.-C. B. and A. D. M. wrote the manuscript with inputs

332 from everyone. All authors read the manuscript and agree to its contents, and all data are reported
333 in the main text and supplemental materials.

334

335 **Competing Interests**

336 The authors declare no competing interests.

337

338 Figure Legends/Captions

339

340 **Fig. 1 | UED measurements on 4AMP-MAPb₂I₇ (DJ n=2) 2D perovskite. a,** Schematics of
341 UED apparatus. The directions of light pump and electron probe with respect to crystal orientation
342 is illustrated. (inset) Optical microscopic top-view image of DJ n=2 single crystal. The dashed
343 yellow line indicates the transmission window for the electron beam. Scale bar is 50 μ m. **b,** Electron
344 diffraction pattern of DJ n=2 crystal at different pump-probe delay time: $t = 0$ ps, 1 ps and 35 ps.
345 **c,** Static diffraction pattern ($t \leq 0$) and indexing of Bragg planes (hk0). Diffraction peaks circled
346 with white, brown, cyan, green, and yellow colors belong to {200}, {110}, {400}, {310}, and
347 {220} Bragg peak families, respectively. The diffraction peaks {110} are partially blocked by the
348 direct beam filter ($q < 1 \text{ \AA}^{-1}$). **d,** Crystal structure of DJ n=2 viewing at [110] and [001] directions,
349 showing intrinsic antiferro-distortion (in-plane octahedral rotations). The corresponding Bragg
350 plane directions are displayed for {400} (cyan), {310} (green) and {220} (yellow).

351

352 **Fig. 2 | Reduction of lattice distortion observed from UED response of DJ n=2 crystal. a,**
353 Differential diffraction map at $t = 2 (\pm 1)$ ps, acquired by subtracting the averaged response of 1 – 3
354 ps after light excitation by the response at rest ($t \leq 0$ ps). The intensity change ΔI (increase and
355 decrease) of each specific Bragg peak (hk0) is indicated by red and blue colors, respectively. The
356 map is zoomed in to the first quadrant ($0 < q_x, q_y < 6 \text{ \AA}^{-1}$). **b,** Crystal structure at rest showing intrinsic
357 antiferro-distortion (top) and simulated structure reducing the distortion (bottom), with order
358 parameter θ defined as half of the interlayer octahedral rotations. For clarity the organic cations
359 are omitted. **c,** Simulated differential diffraction map between the two crystal structures in Fig. 2b,
360 showing intensity change (ΔI) of each Bragg peak after reducing the antiferro-distortion angle θ .
361 **d,** Angular-integrated differential diffraction (filtering out diffuse scattering regions), comparing
362 the experimental data ($t = 2 (\pm 1)$ ps) (gray solid line and shadow), the expected Debye-Waller
363 response (gray dashed line), and simulated signal acquired from Fig. 2c (black solid line). Note
364 that the {110} peaks are partially filtered by the direct beam blocker (Fig. 1c).

365

366 **Fig. 3 | Lattice (in-plane) and carrier response of DJ n=2 crystal under light excitation. a,**
367 Intensity dynamic plots of peak families {400} and {530}. **b,** 2D differential diffraction map
368 averaged at $t = 2$ ps (left half) and $t = 65$ ps (right half), with blue for intensity decrease and red for
369 increase. The dashed region indicates the area with the most increase of diffuse scatterings. **c,**
370 Schematics of light-induced reduction of antiferro-distortion and thermally activated atomic
371 displacement from Debye-Waller effect. **d,** Evolution of carrier temperatures (T_c) as a function of
372 delay times at different excitation densities ($1.1, 3.4, 5.6$ and $8.4 \times 10^{12} \text{ cm}^{-2}$), showing fast and slow
373 cooling processes. **e,** Estimation of saturation densities (N_{2D}) for DJ n=2 (red) and RP n=2 (blue)

374 crystals at different temperatures. The saturation densities due to electron-hole plasma and exciton
375 gas are shown in solid and dashed lines, respectively. For $1\text{mJ}/\text{cm}^2$, a hot e-h plasma is generated
376 ($1.3\times 10^{13}\text{ cm}^{-2}$), as indicated by the gray dashed arrow.

377

378 **Fig. 4 | Comparison between different 2D perovskite structures with different organic cations.**
379 Crystal structures of the **a**, DJ $n=3$ and **b**, RP $n=2$ and $n=4$ perovskites. **c**, Angular integrated
380 differential diffraction plot (20 – 40ps) for the DJ $n=2$, DJ $n=3$, RP $n=2$ and RP $n=4$ perovskites.
381 The yellow and cyan colors label the Bragg peaks showing positive responses in DJ systems. **d**,
382 Histogram of rise-time constants of DJ $n=2$, DJ $n=3$ and RP $n=4$ structures.

383

384

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488 implementation in the CRYSTAL code. *Journal of Computational Chemistry* **25**, 888–897 (2004).

489
490

491 **Methods**

492 **Materials**

493 The materials used for 2D perovskites (DJ and RP) precursors were purchased from Sigma Aldrich,
494 including methylamine hydrochloride (MACl), lead oxide (PbO), 4-aminomethyl piperidine
495 (4AMP), butylamine (BA), hypophosphorous acid (H₃PO₂), and hydroiodic (HI). Methylamine
496 iodide (MAI) was purchased from Greatcell Solar.

497 **Single crystal synthesis and transfer**

498 *Single Crystal Synthesis:* BA n=2,4 perovskites solution was synthesized by adopting the
499 previously reported procedure, using 0.4 times the scale.²⁵ 4AMP n=2,3 perovskites solution was
500 synthesized by adopting the previously reported procedure, using 0.5 times the scale.⁴³ Glass was
501 used as the substrate for the 2D perovskite growth. Glass substrates were cut into 2.5 cm × 2.5 cm
502 squares, then cleaned in soapy water, isopropanol, and acetone by ultrasonication for 20 min each,
503 and then were dried using an argon gun. The substrates were transferred into a UV-Ozone cleaner,

504 and cleaned for 20 min. 10 μ L of the diluted solution was deposited dropwise onto the glass surface.
505 Another glass was put on top to fully cover the bottom glass and dried overnight at 80 $^{\circ}$ C for BA
506 and 75 $^{\circ}$ C for 4AMP. A thin single crystal grew spontaneously as the solvent evaporated.

507 *Crystal Exfoliation and Transfer:* Large-flake single-crystal perovskites were mechanically
508 exfoliated and then transferred onto 100 \times 100 μ m TEM transmission windows with silicon nitride
509 membranes. All samples were prepared and sealed in Argon gas until UED measurements. A
510 comparison of diffraction images between first and last scans suggests no new peaks arising,
511 confirming no degradation during the measurement period (Fig. S19).

512 **Sample characterization**

513 *Optical absorbance:* The optical absorbance of the single crystals was determined based on
514 confocal microscopy, by focusing a broad-spectrum white light beam (Thorlabs SOLIS-3C) into a
515 50 μ m spot and measuring the transmission spectrum through a TEM window. The spectrum was
516 acquired using a spectrometer (Andor Kymera 328i) and CCD (Andor iDus 416).

517 *Differential scanning calorimetry (DSC):* Differential scanning calorimetry was performed from
518 room temperature to 150 $^{\circ}$ C with a ramp rate of 15 $^{\circ}$ C/min. The heat capacity of the sample was
519 calculated from the heat flow (W/g) and was calibrated using a sapphire sample as a reference.

520 **Ultrafast electron diffraction (UED)**

521 UED experiments were performed at SLAC National Accelerator Laboratory. Electrons were
522 accelerated to 3.7 MeV by Klystron with temporal width of 150fs. Normal incident pulses were
523 diffracted by the sample in transmission geometry on TEM transmission window, and diffracted
524 intensities were captured by an EMCCD. The electron pulses were synchronized with a laser beam
525 (3.1eV, $\tau_{\text{width}} \approx 75$ fs) at the frequency of 180Hz, with temporal delay typically from -20ps to 100ps.
526 The delay time was tuned by adjusting the relative path length difference using a delay stage. To
527 reduce the confounding effect of mechanical shift and possible crystal structural change during
528 time evolution ($T_{\text{total}} \sim \text{hrs.}$), the sequence of stage locations was configured randomly during each
529 scan. Each typical UED run contained 20 – 30 pump-probe scans and each diffraction image was
530 averaged over approximately 8000 shots to reduce statistical fluctuations.

531 *UED Bragg peaks indexing*: The Bragg peaks of the measured samples (DJ n=2, DJ n=3, RP n=2
532 and RP n=4) were indexed by comparing the diffraction patterns with the simulated diffraction
533 images calculated via SingleCrystal software (<http://crystalmaker.com/singlecrystal/>), using
534 structure files (.cif) from Mao et al.²⁵ These comparisons are shown in Fig. S2 (DJ n=2), Fig. S13
535 (DJ n=3), Fig. S20 (RP n=2) and Fig. S21 (RP n=4).

536 *UED data processing*: A stack of diffraction maps at different time steps was collected for each
537 sample measurement. Each diffraction image was background-removed by CCD dark counts and
538 normalized by total diffraction intensity. To extract the time traces of relative intensity response
539 of each Bragg peak ($\Delta I(t)/I_0$), we first integrated the intensity within a ROI centered at each peak
540 (0.2Å in diameter), and then normalized the intensity curve by averaging over negative delays
541 ($t < 0$). Time traces of Bragg peaks were fitted globally by a single exponential curve:

$$542 \quad \Delta I(t)/I_0 = \begin{cases} 0 & , t < t_0 \\ \Delta \left(\exp\left(\frac{t - t_0}{\tau}\right) - 1 \right) & , t \geq t_0 \end{cases}$$

543 Where Δ stands for intensity change (%), τ for time constant (ps), and t_0 for time zero offset
544 (calibrated by the response of bismuth crystal and fixed globally). Fitting results are plotted in Fig.
545 S7 (DJ n=2) and Fig. S18 (DJ n=3 and RP n=4). Results of selected peak families of DJ n=2 are
546 displayed in Fig. S3. Error intervals of the fitting parameters Δ and τ were estimated from one
547 standard deviation calculated from the square root of the covariance matrix diagonal. Fitting
548 methods were based on least squares optimization performed by ‘curve_fitting’ function using
549 Python (version 3.7.4).

550 **Transient absorption spectroscopy (TA)**

551 Transient absorption (TA) experiments for 2D perovskites were done by using a 400 nm pump
552 beam and a supercontinuum white light probe beam ranging from 450 to 750 nm. The pump laser
553 was obtained from a 2nd harmonic generator (Ultrafast System) derived by a fundamental 60 fs-
554 pulsed laser (Coherent, Inc.) at 800 nm with a repetition rate of 1 kHz. The 1 kHz pump laser
555 passed through a chopper to yield a 500 Hz modulation frequency. The pump fluence was
556 controlled within 0.1 – 0.75 mJ/cm². The supercontinuum white light laser was generated by
557 introducing the fundamental laser into a nonlinear crystal, CaF₂ (Ultrafast System). Pump and
558 probe beam pulses were temporally and spatially overlapped and focused on the 2D perovskites.

559 2D perovskites were measured in ambient air condition with DJ n=2 sample sealed with 50nm
560 thick PMMA on top.

561 **Phonon simulation methods**

562 *Phonon modes simulation:* These simulations were based on periodic Density Functional Theory
563 (DFT) calculations, performed within Linear Combination of Atomic Orbital (LCAO) formalism,
564 as implemented in the CRYSTAL17 code.⁴⁴ Electronic ground state was computed within the
565 GGA approximation, employing the PBE exchange-correlation functional,⁴⁵ along with double
566 split basis set quality and core potentials for heavy Pb and I atoms. Dispersion D3 scheme was
567 included to account for van-der Waals interactions,⁴⁶ as these are expected to play an important
568 role in the packing of the organic component. As it is not currently implemented in CRYSTAL17,
569 Spin-Orbit-Coupling (SOC) has been neglected in the present calculations. Nevertheless, SOC is
570 not expected to heavily affect the ion dynamics, with current computational set-up providing
571 vibrational frequencies in nice agreement with experimental data, for the reference orthorhombic
572 phase of the 3D methylammonium lead iodide perovskite.⁴⁷

573 Calculations have been performed on the reference crystalline structure of the DJ n=2 system from
574 Ref.²⁵, adopting 2x4x4 sampling of the first Brillouin zone, in the Monkhorst-Pack scheme⁴⁸ (with
575 the less dense sampling associated to the longer plane-stacking direction). Crystalline structure
576 was fully relaxed with only constraint related to the native space group symmetry (Cc n°9). The
577 hessian was estimated at the Γ point of the Brillouin zone, via finite displacements,⁴⁹ resulting in
578 zero negative frequencies. Resulting normal modes were used as special coordinates along which
579 to distort the crystal structure and to evaluate the change in the electron diffraction pattern, as
580 exemplified in Fig. S6. These calculations reveal that antiferro-distortive phonon modes associated
581 with the octahedra rotations are indeed predicted for the crystal structure at rest, thus further
582 confirmed our hypothesis on lattice ordering via reduction of antiferro-distortion (Fig. 2).

583

584 *Electron diffraction simulation:* Snapshots of the crystalline structure as distorted along all the
585 computed normal modes were then provided as crystallographic information files (.cif) and used
586 to simulate electron diffraction intensities using SingleCrystal software. The simulated 2D patterns

587 and 1D azimuthally integrated plots were reconstructed by convolving the localized Bragg peaks
588 with gaussian shape with FWHM of 0.17Å.

589

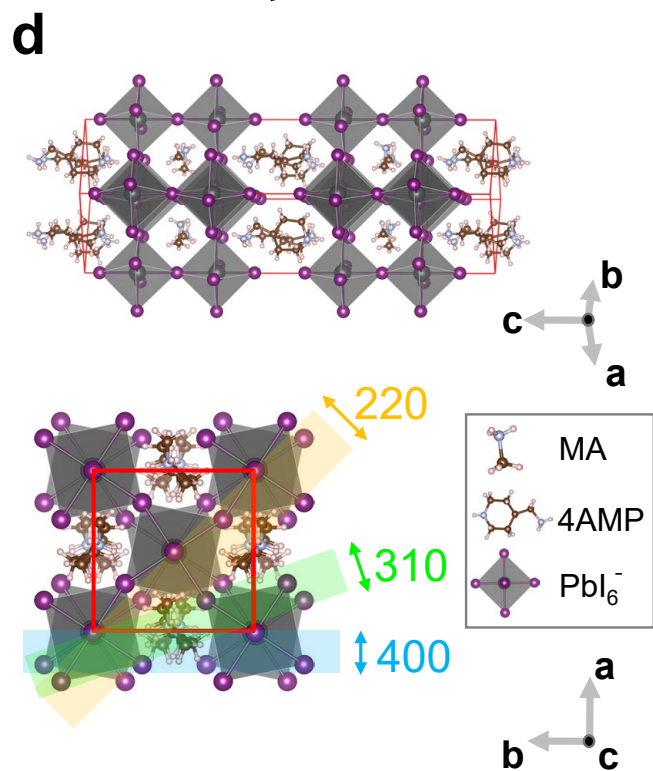
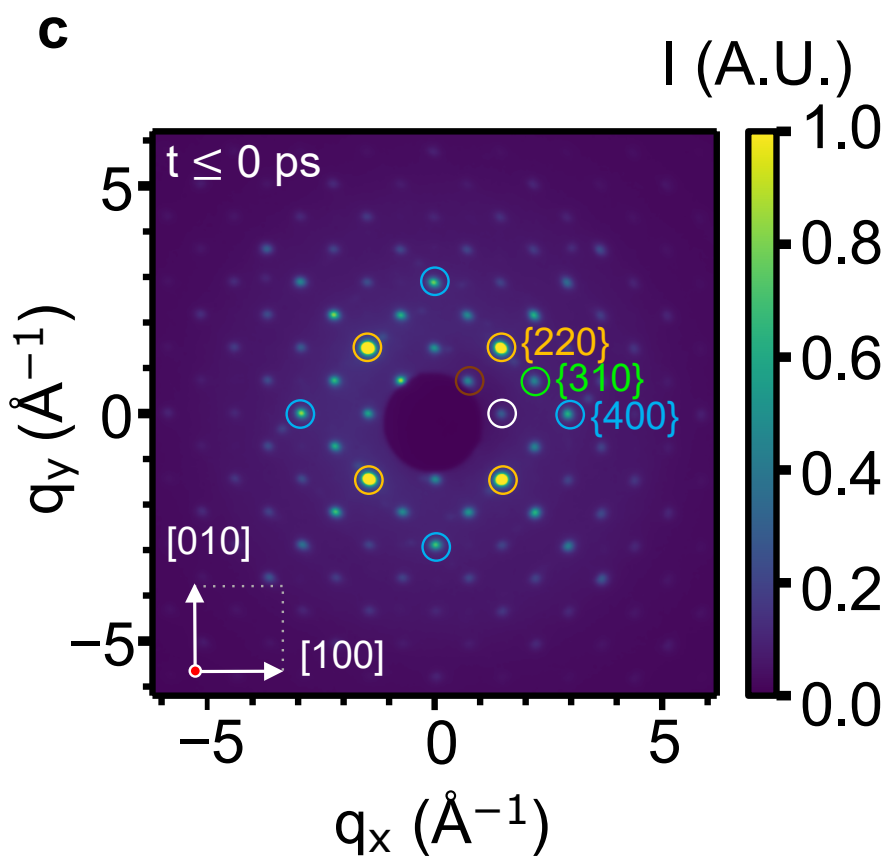
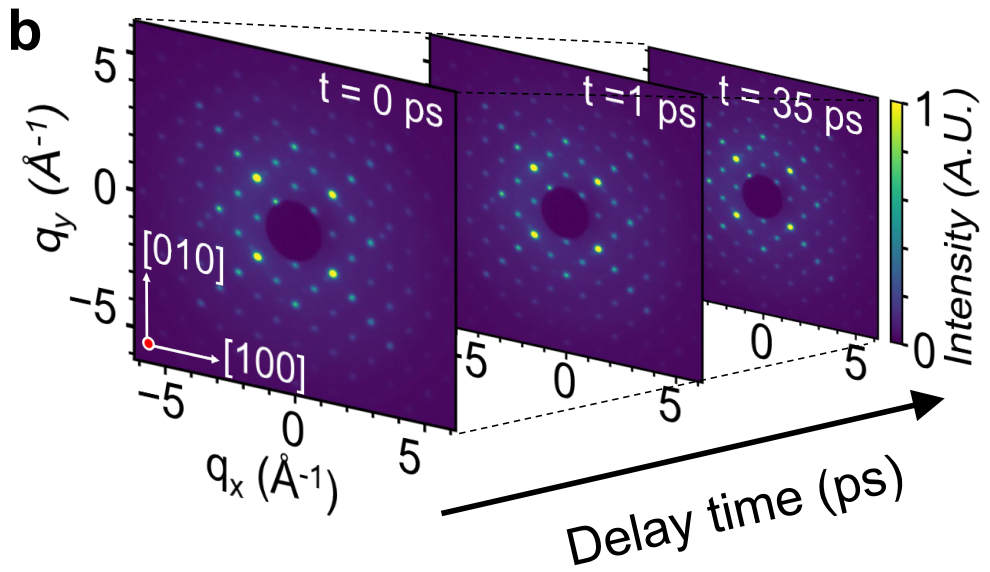
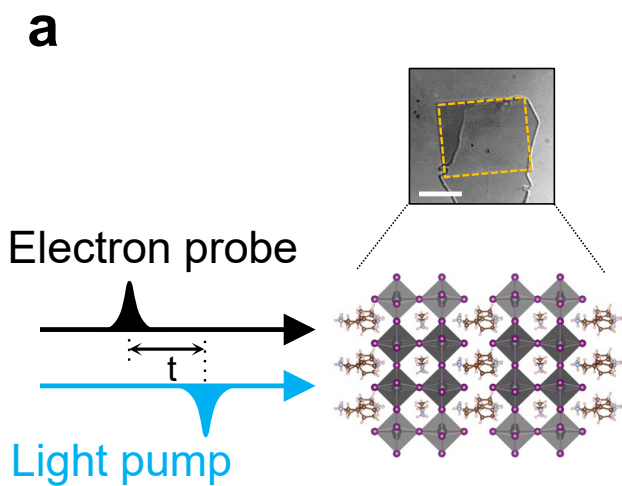
590 **Data availability**

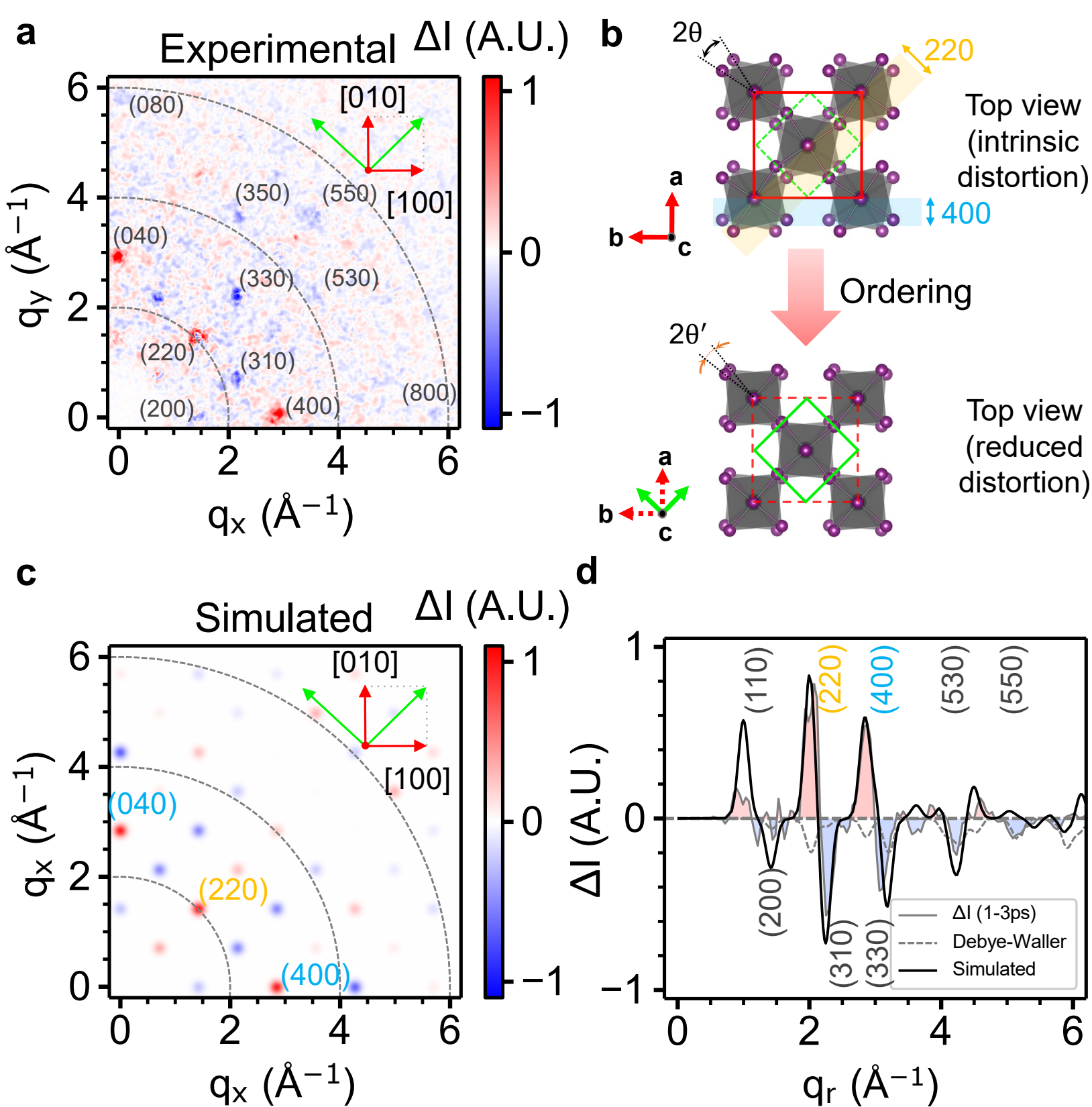
591 All the data supporting the findings of this study are available and are attached. Any additional
592 data are available from the authors upon reasonable request.

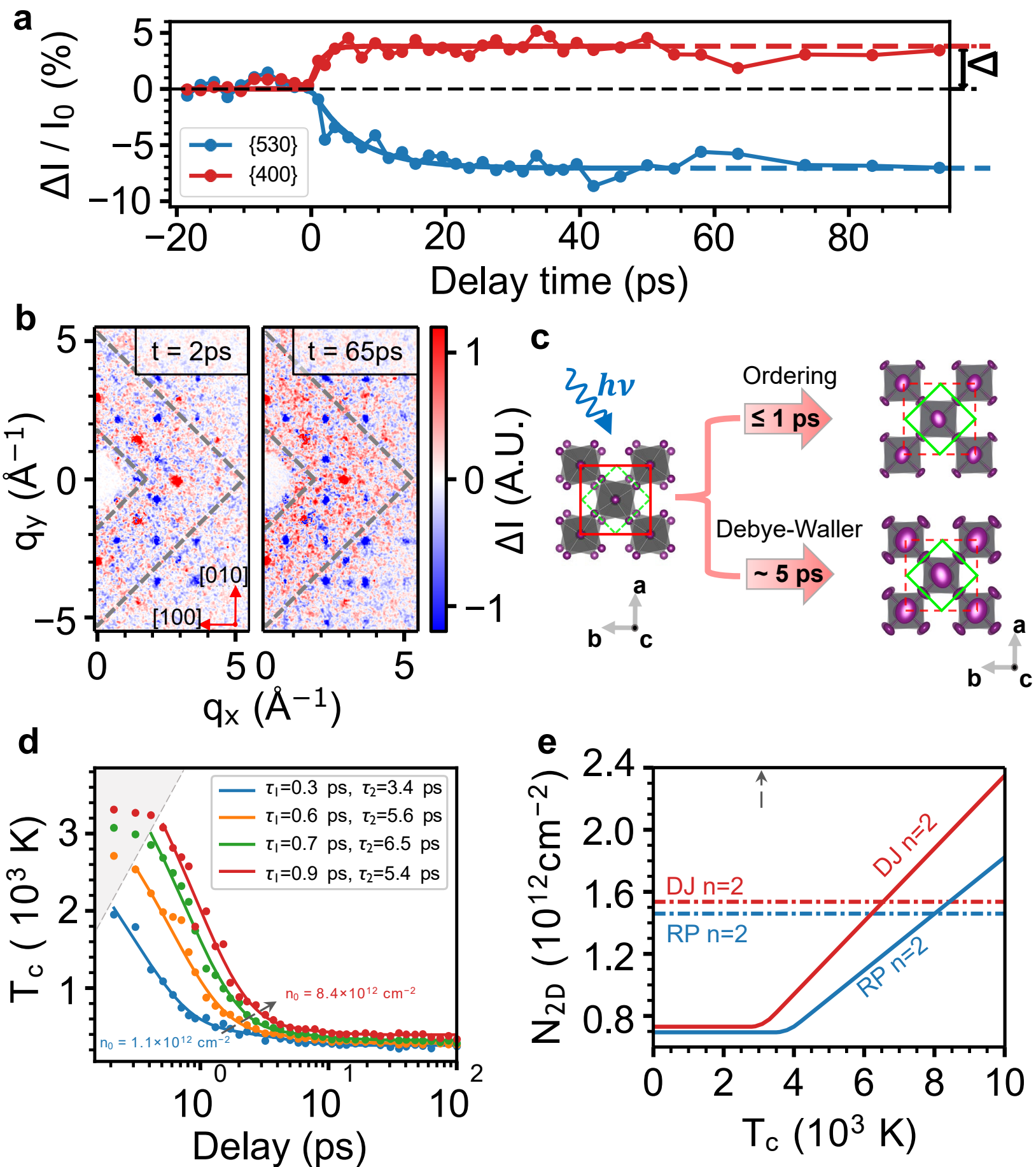
593 **Code availability**

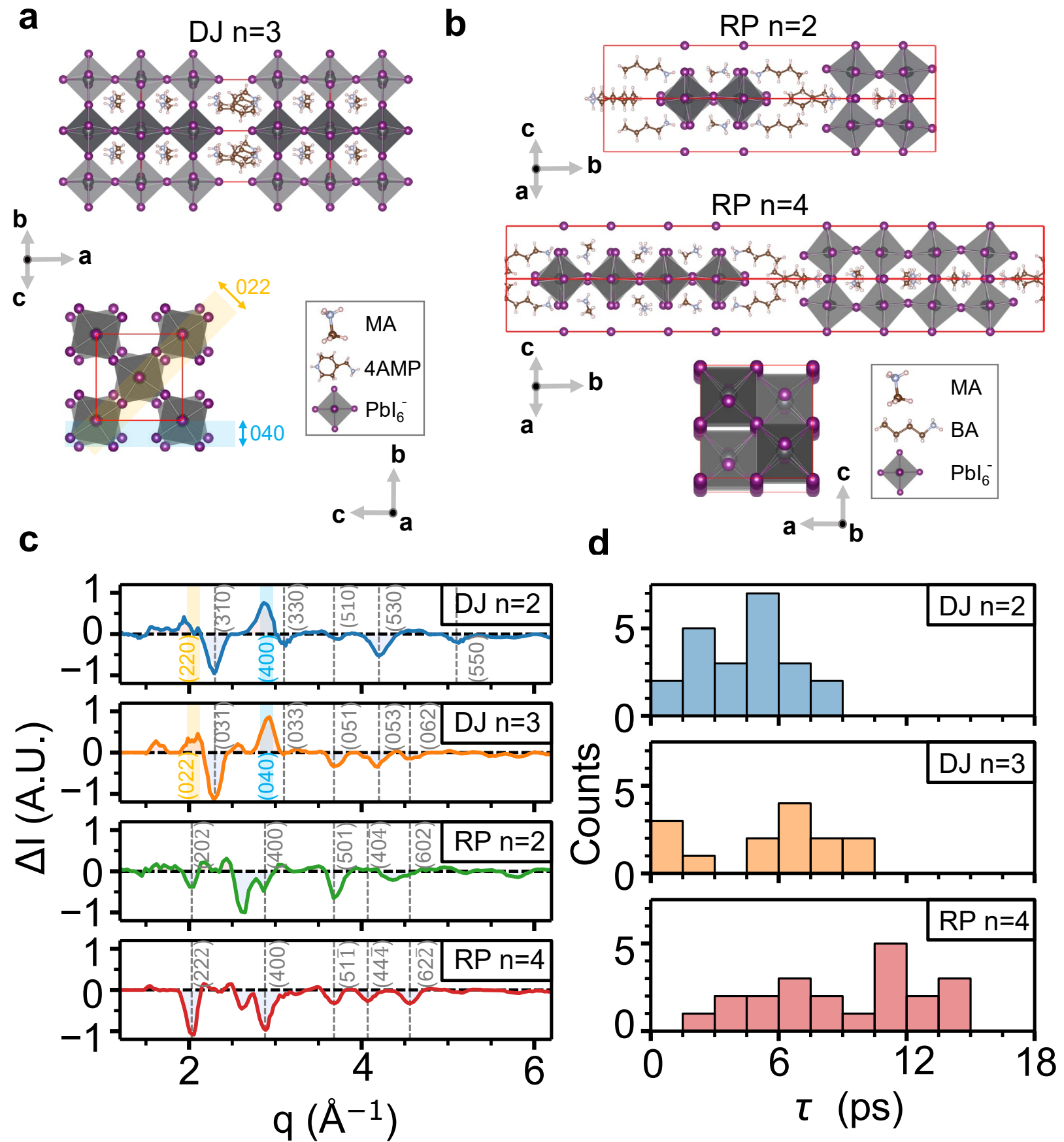
594 The analysis code for this study is available from the authors upon reasonable request.

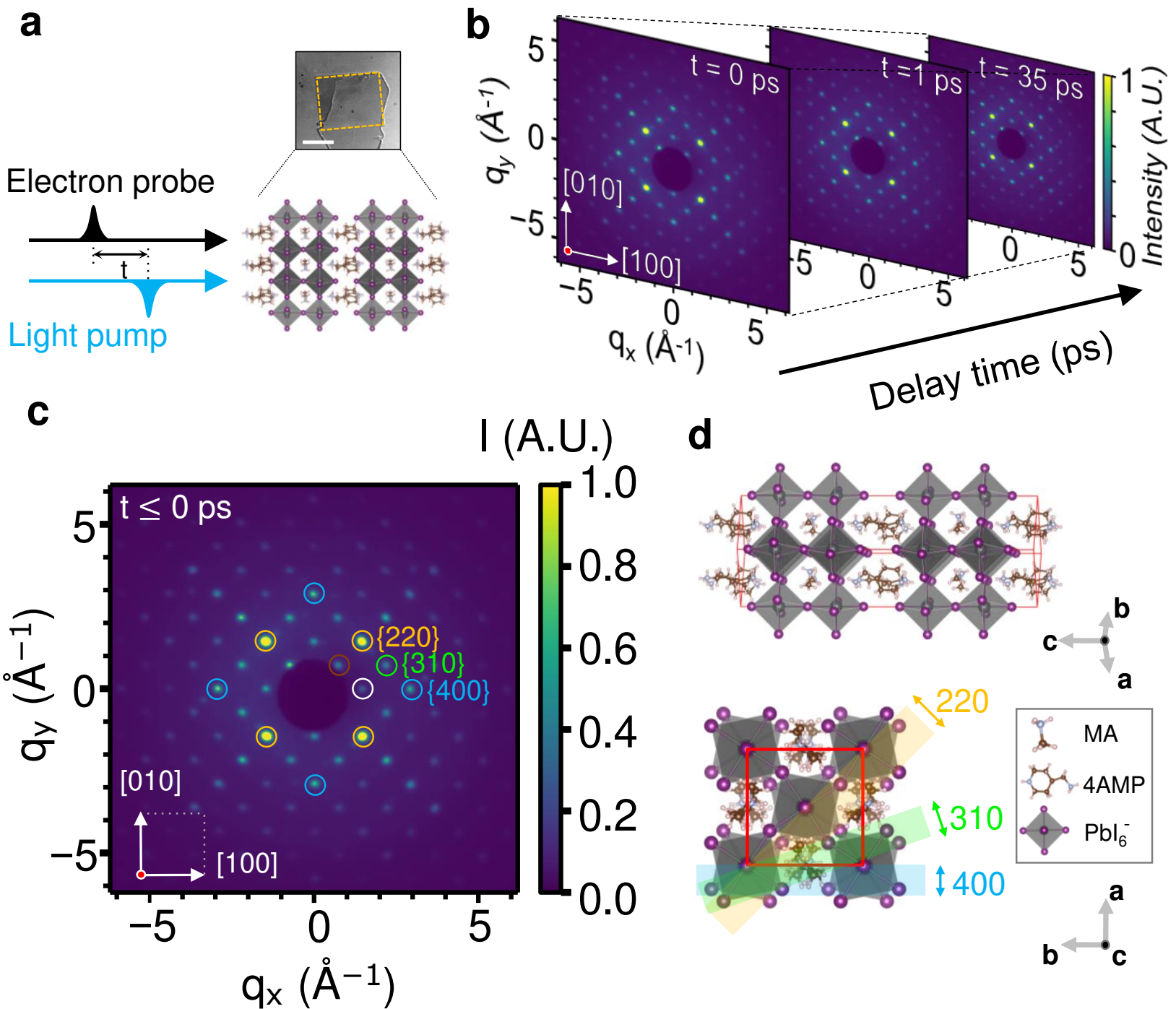
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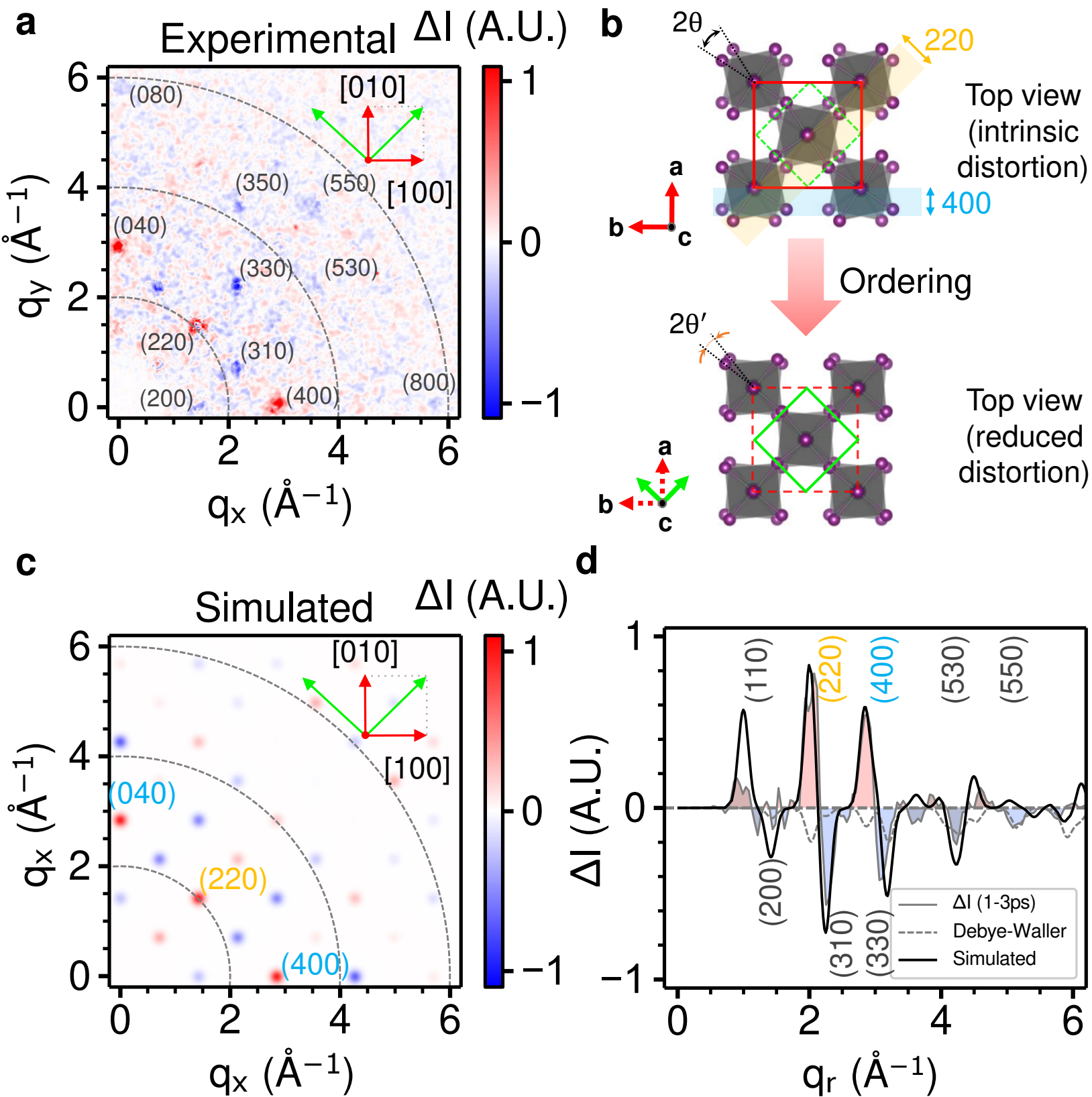


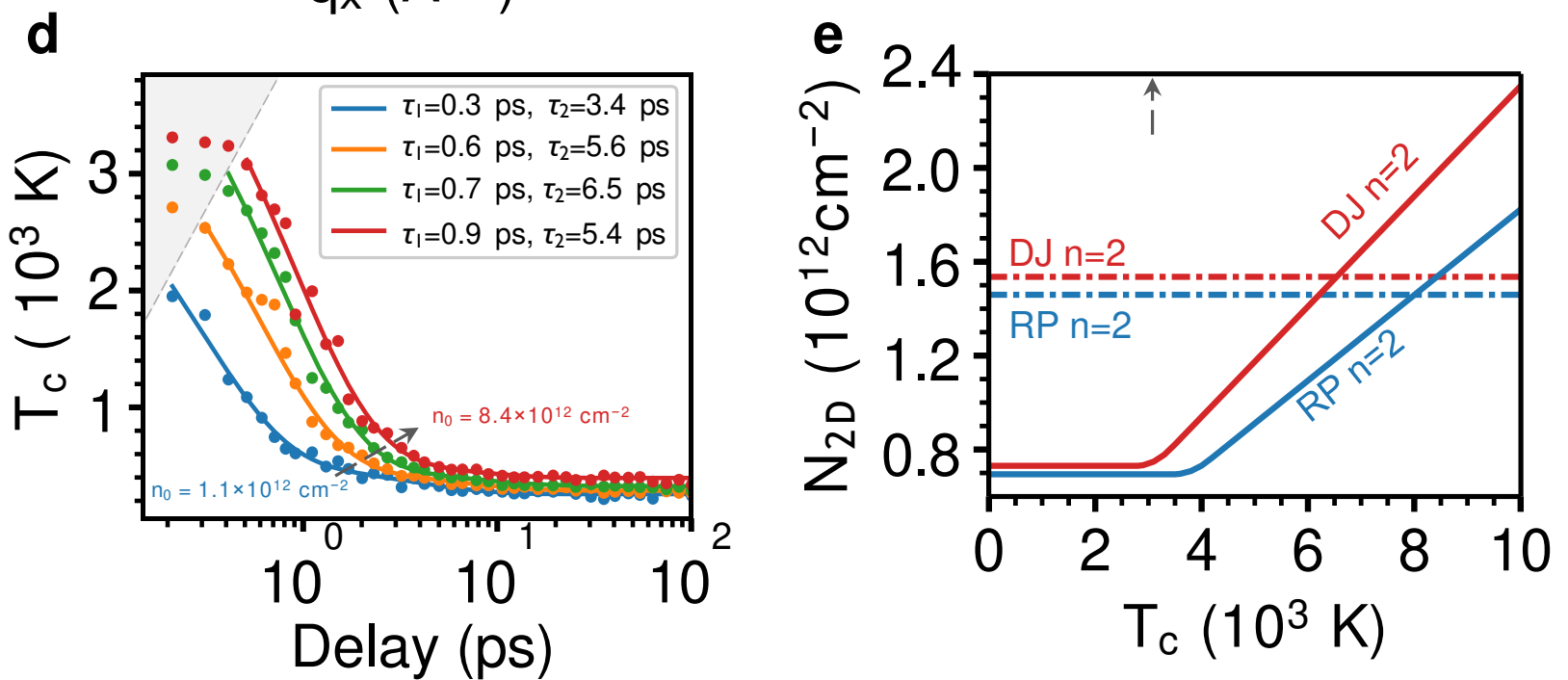
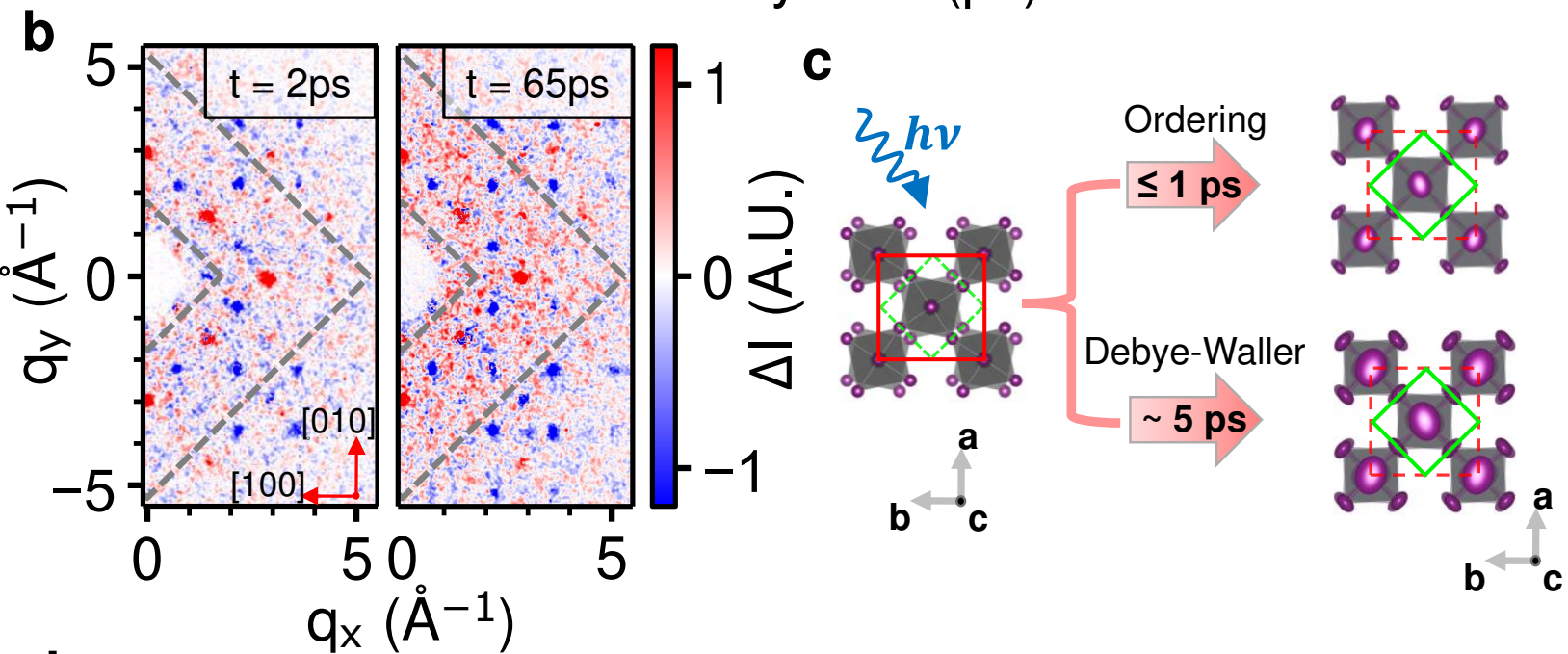
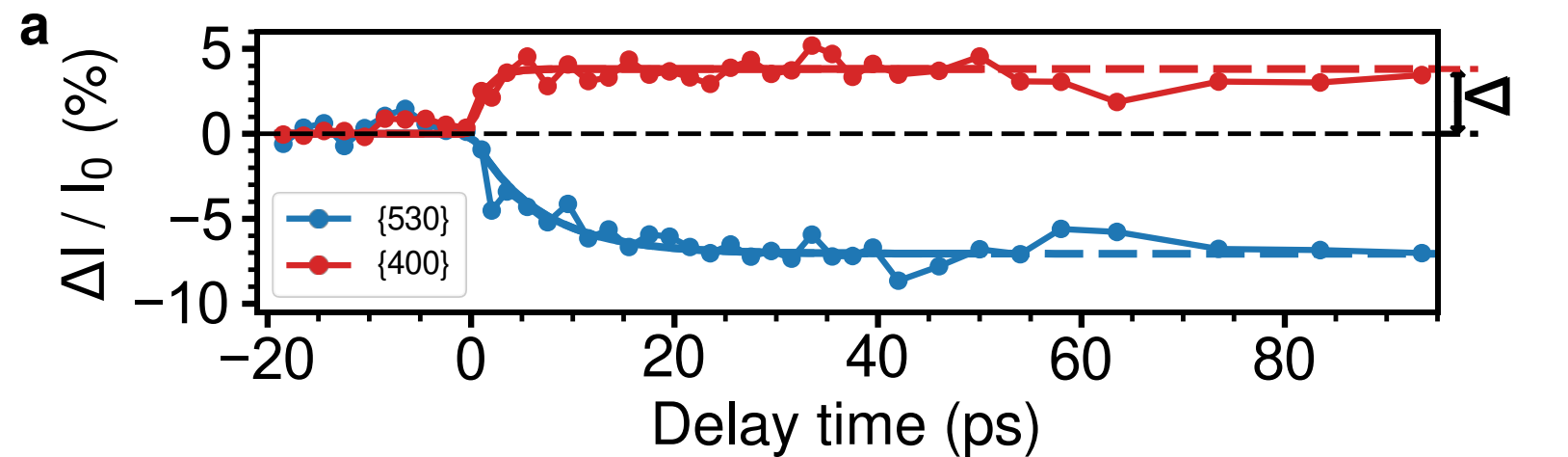


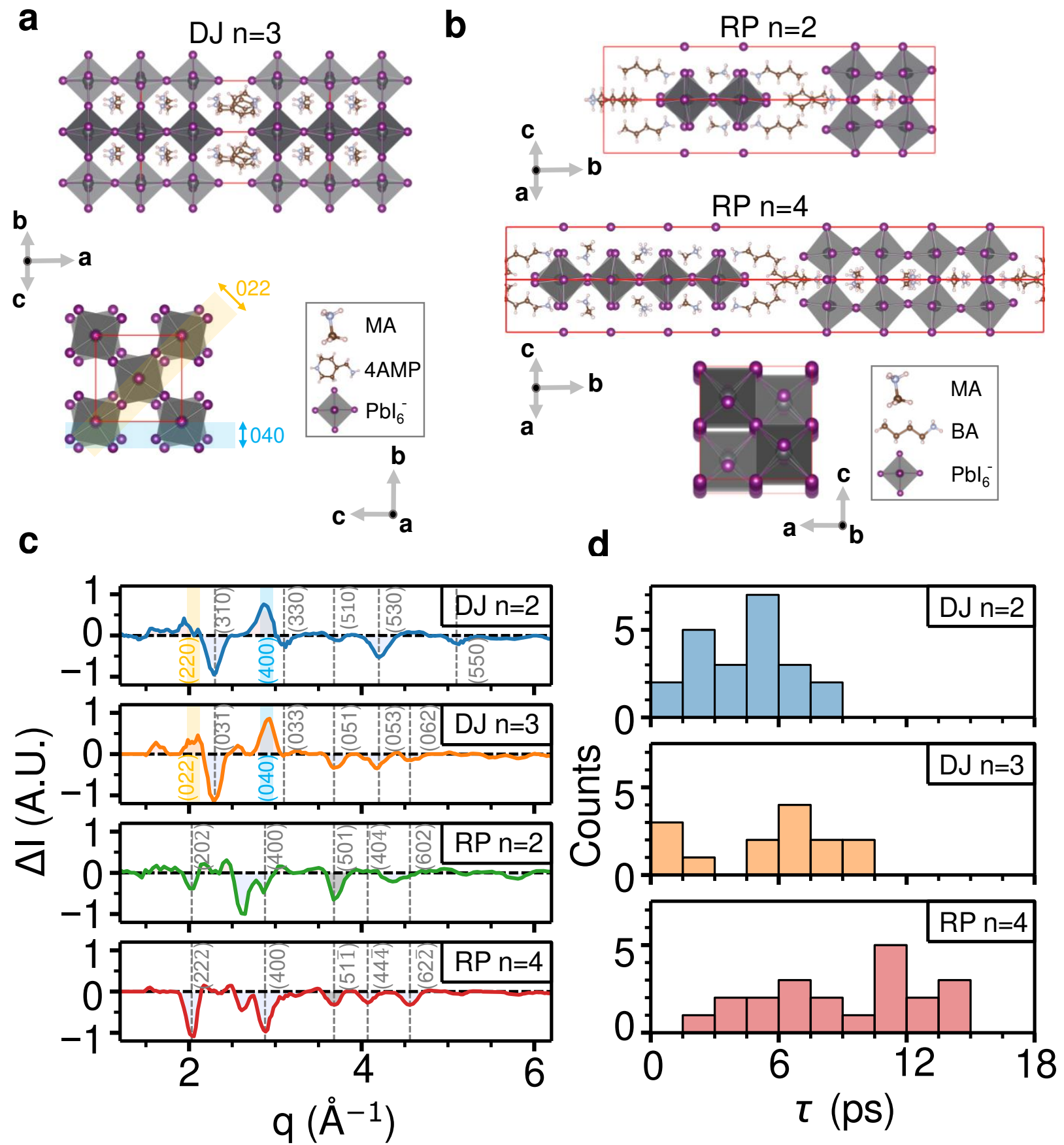












1 **This PDF file includes:**

2 Supplementary discussions 1-11

3 Figs. S1 to S26

4 Table S1 to S2

5 References

6

7 Table of Contents

8

9 **Supplementary discussions 1 - 112**

10 **Supplementary discussion 1.** Crystal orientation of DJ n=2, DJ n=3, RP n=2 and RP n=4 crystals..... 2

11 **Supplementary discussion 2.** Sample Thickness and Carrier Density Estimation..... 3

12 **Supplementary discussion 3.** Time constants of Bragg peaks of DJ and RP crystals. 4

13 **Supplementary discussion 4.** Possible reasons of Bragg peak increase in DJ perovskites. 5

14 **Supplementary discussion 5.** Estimation of antiferro-distortion in 2D perovskites..... 9

15 **Supplementary discussion 6.** Transient absorption spectroscopy of DJ n=2 crystal and carrier

16 temperature extraction. 10

17 **Supplementary discussion 7.** Estimation of saturation densities in DJ n=2 and RP n=2 crystals 11

18 **Supplementary discussion 8.** Generalizability of lattice response and order parameter on 3D

19 perovskites..... 12

20 **Supplementary discussion 9.** Comparison of electron-LO phonon coupling with RP and DJ n=3..... 13

21 **Supplementary discussion 10.** Estimation of long-time Bragg peak response and light-induced atom

22 RMS displacements u_2 14

23 **Supplementary discussion 11.** Time evolution of diffraction intensities through the UED run. 15

24 **Supplementary Figures S1 – S2616**

25 **Supplementary Tables S1 - S2.....41**

26 **References.....42**

27

28

29 **Supplementary discussions 1 - 11**

30

31 **Supplementary discussion 1. Crystal orientation of DJ n=2, DJ n=3, RP n=2 and RP n=4** 32 **crystals**

33 The crystal orientation of each sample measured in UED was acquired by comparing the
34 diffraction patterns with the simulated diffractions viewing at different directions.

35 For the DJ systems, the experimental patterns in Fig. S2b (DJ n=2) and Fig. S13b (DJ n=3) show
36 great consistency with the simulated ones (Fig. S2a & Fig. S13a) viewed at stacking axis direction
37 ([001] for DJ n=2, and [100] for DJ n=3), confirming the horizontal orientation of the DJ crystals,
38 where the perovskite crystal layers are parallel to the substrate. The azimuthally integrated plots
39 (Fig. S2c for DJ n=2, Fig. S13c for DJ n=3) also show good agreement in peak locations and
40 convoluted intensities. The measured in-plane Bragg peaks can be properly indexed accordingly,
41 including (hk0) for DJ n=2, and (0hk) for DJ n=3. The labeled peaks are shown in 2D patterns and
42 azimuthally integrated plot.

43 For RP n=2 crystal, the simulated pattern along stacking axis [010] is shown in Fig. S20a, where
44 all the peak locations agree with the experimental ones in Fig. S20b, confirming the major
45 orientation of the RP n=2 crystal is horizontal, same as DJ crystals discussed above. Additionally,
46 concentric rings are observed between $q=2 \text{ \AA}^{-1}$ and 3 \AA^{-1} , as observed in Fig. S20b, suggesting the
47 existence of poly-crystalline like crystal structure with mixed orientations. The azimuthally
48 integrated plots (Fig. S20c) show good agreement in peak locations and convoluted intensities,
49 with additional unassigned peaks at $q=2.6 \text{ \AA}^{-1}$ and 3.7 \AA^{-1} . We've excluded the possibility of PbI_2
50 diffraction by comparing with the electron diffraction of PbI_2 thin film.¹ We attribute them to the
51 possible perovskite diffraction from out-of-plane or mixed directions, or an unidentified phase of
52 2D perovskites, and have excluded them from the discussion of in-plane Bragg peaks responses of
53 RP n=2 crystals.

54 For the RP n=4 crystal, the simulated pattern along stacking axis [010] is shown in Fig. S21e, with
55 corresponding 1D azimuthally integrated plot in Fig. S21f. However, this pattern doesn't match
56 with the experimental one (Fig. S21a) based on the following observations: 1) more peaks are
57 observed in static UED patterns, such as $q=2.2 \text{ \AA}^{-1}$ and 3.8 \AA^{-1} as shown in Fig. S21f; 2) anisotropic

58 intensity distribution along q_x and q_y directions, which is different with Fig. S21e with 4th fold
59 symmetry. Therefore, we conclude the beam direction is not perfectly along the stacking axis as
60 observed in DJ and RP n=2 crystals. As shown in Fig. S21c & Fig. S21d, we find that the [011]
61 orientation gives the best match for RP n=4, with 7.8 degrees deviation from stacking axis [010],
62 as sketched in Fig. S21b. As a result, some out-of-plane Bragg peaks can be detected as well,
63 which may explain the anisotropic UED response between q_x and q_y directions, including the
64 intensity change shown in Fig. S15 and the time constants shown in Fig. S16.

65

66 **Supplementary discussion 2. Sample Thickness and Carrier Density Estimation**

67 *Crystal thickness determination:* The thickness of the crystal was determined by comparing the
68 absorbance spectrum with the estimated one calculated from absorption coefficient of 2D
69 perovskites. Here we have referenced the absorption coefficients obtained from ellipsometry by
70 Song et al.² Applying Beer-Lambert's law and neglecting light scattering, the relation of crystal
71 thickness d and crystal transmission (T) is given by:

$$T = \frac{I}{I_0} = 10^{-OD} = e^{-\alpha d} \quad (\text{S2.1})$$

72 Where OD is the absorbance in optical density determined by transmission (I/I_0), and α is
73 absorption coefficient. The comparison of experiment and simulated absorbance spectrum is
74 depicted in Fig. S1.

75 *Carrier density:* The light-injected carrier density in quantum well is estimated by:

$$n_0 = \frac{\Phi/(h\nu) A}{d/l_w} \quad (\text{S2.2})$$

76 Where Φ stands for energy fluence of each pulse (mJ/cm^2), $h\nu$ stands for excitation phonon energy
77 (3.1 eV for UED), A stands for absorbance of the sample, d is the sample thickness, and l_w is the
78 width of quantum-well in 2D perovskites.^{3,4} Here, we've neglected the sample reflection and
79 estimated the sample absorbance by transmission data in Fig. S1. As a result, the list of thickness
80 and corresponding carrier densities of each measurement is shown in Table S1.

81 **Supplementary discussion 3. Time constants of Bragg peaks of DJ and RP crystals.**

82 A. DJ perovskites

83 Time traces of the Bragg peak families of DJ n=2 are shown in Fig. S3, with rapid rise
84 ($\tau \sim 1$ ps) in {400}, as well as slower decay (scale of 5ps) of the other major group families.
85 List of fitted intensity change (Δ (%)) and time constant (τ) of each Bragg peak (hk0) is
86 listed in Fig. S7. Both the intensity changes and time constants show a significant
87 anisotropy with respect to directions in the DJ n=2 crystals, which reflects the lack of a
88 tetragonal axis in the monoclinic centered structure (space group Cc n°9) of the crystals at
89 rest because of the geometry and structure of the 4AMP cation. We also note that the
90 intensity traces of some Bragg peaks such as {330} and {550} show a long recovery time
91 ($\tau > 30$ ps, Fig. S3a), which could be related to other heat transfer mechanisms and phonon-
92 phonon interactions.⁵

93 The responses of time scales are similarly observed in DJ n=3, including a fast rise in {040}
94 (Fig. S13), and similar distribution of time constants for other Bragg peak families (Fig.
95 4d, corresponding scatter plot shown in Fig. S18).

96

97 B. RP perovskites

98 As suggested in Fig. 4d, comparison of the histograms of the time constants τ for DJ n=2,
99 DJ n=3, and RP n=4 shows a generally slower response (up to 15 ps) for RP perovskites as
100 compared to the DJ crystals. Besides, different dynamics are observed for (400) peaks in
101 RP (Fig. S13).

102 The slow response time in RP systems can arise from the differences in the lattice softness
103 between the BA and the DJ 2D perovskites. The BA molecules reduce the rigidity of the
104 2D lattice by comparison to the DJ case, leading to an enhancement of the lower-energy
105 part of the vibrational density of states.⁶ It was indeed shown experimentally to enhance
106 the deformation potential mechanism in BA compounds, leading to carrier trapping.⁷ This
107 results is also consistent with a recent study on high-resolution resonant impulsive
108 stimulated Raman spectroscopy,⁸ showing that the vibrational relaxation in monolayered
109 bromide perovskites relatively fast with flexible alkyl-amines.

110

111 **Supplementary discussion 4. Possible reasons of Bragg peak increase in DJ perovskites.**

112 In this section, we discuss several possible mechanisms that can cause an increase in the Bragg
113 peaks, such as phase transition,⁹ and multiple scattering in monocrystalline samples.¹⁰ No signature
114 of phase transition is found in DJ n=2 perovskites, and we exclude possible effect of by the
115 estimation of extinction distance under MeV electron beams, which is much larger than the sample
116 thickness.

117 A. Phase transition from thermal lattice heating. One of the possible mechanisms that induces
118 the collective lattice ordering in DJ perovskites is the thermally induced phase transition
119 from local lattice heating. To investigate the thermal response of DJ n=2 crystals, we first
120 estimate the temperature jump induced by the laser pump, then using the differential
121 scanning calorimetry (DSC) and temperature dependent XRD results to exclude the
122 possible phase transition effect.

123

124 a. Estimation of temperature jump.

125 The local lattice temperature increase is estimated by total input pump energy and
126 samples' specific heat. For DJ n=2 crystals, a carrier density of $2.5 \times 10^{13} \text{ cm}^{-2}$
127 corresponds to a bulk carrier concentration of $n = 1.4 \times 10^{20} \text{ cm}^{-3}$, which induces total
128 energy into the lattice:

$$\begin{aligned} \Delta E &= n \times (E_{pump} - E_g) = 1.4 \times 10^{20} \times (3.1 - 2.2) \text{ eV cm}^{-3} \\ &= 20.16 \text{ J/cm}^3 \end{aligned} \tag{S4.1}$$

130 The mole of the DJ n=2 crystal is calculated from crystal structure (4 molecules per
131 unit cell):

$$m = \frac{1}{V_{UC}} \times \frac{4}{N_A} = 2.53 \times 10^{-3} \text{ mol/cm}^3 \tag{S4.2}$$

132

133 The specific heat of DJ n=2 at T~300K is estimated from DSC measurement, as
134 shown in Fig. S9:

$$C_p = 0.54 \text{ J K}^{-1} \text{ g}^{-1} = 728 \text{ J K}^{-1} \text{ mol}^{-1} \tag{S4.3}$$

135 And the corresponding estimated temperature jump is:

$$\Delta T = \frac{\Delta E}{m * C_p} \sim 11K \quad (S4.4)$$

136

137 b. Differential scanning calorimetry (DSC) results.

138 To investigate possible thermal phase transition induced by lattice heating,
139 differential scanning calorimetry (DSC) was performed from room temperature to
140 150°C, as suggested in Fig. S9. From the DSC curve, no significant phase transition
141 is observed. Based on over estimation of temperature increase induced by light (SI
142 discussion 6), the local temperature increase in the crystal lattice is below the 15K
143 and no possible phase transition is observed or reported in this range.¹¹ Therefore,
144 we conclude the collective lattice ordering in light-induced in ultrafast scale,
145 instead of thermally induced caused by lattice heating.

146

147 c. Temperature dependent XRD.

148 Additionally, we performed temperature XRD from room temperature to 55°C, data
149 shown in Fig. S10. As we can see, most of the Bragg peak intensities go through a
150 slight decrease with increasing temperature due to the presence of Debye Waller
151 effect.

152 Here we focus on the in-plane Bragg peaks, primarily related to the edges and
153 diagonal of the perovskite octahedral, which is our main focus in-plane diffraction
154 patterns in DJ n=2. Fig. S10 (b)(c)(d) plot the peak profile variation with respect to
155 the sample at room temperature, zoomed at q- regions near (220) and (400)
156 respectively. As we can see, both (220) and (400) peaks exhibit slight intensity
157 decrease, which is contradictory with the UED response.

158 Besides the intensity variations from observed from temperature XRD, we also
159 observed a global peak shifting (upto 0.15%, Fig. S10 (f)). A global shifting of
160 Bragg peaks toward low-q values is generally expected from the thermal expansion.
161 However, this behavior of Bragg peaks shifting is not resolved in the UED. We
162 attribute the absence of thermal expansion signature in UED diffraction patterns to
163 the low q resolution of the UED measurements ($\approx 0.17\text{\AA}^{-1}$).

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In fact, the transient increase in the collective ordering in the DJ n=2 lattice may be viewed as an ‘incomplete transformation’ towards a completely ordered phase. Indeed, no evidence of phase transition is found from differential calorimetry and XRD. Additionally, the perfectly undistorted 2D perovskite reference phase has only been observed in the fully inorganic Cs-based Cs₂PbI₂Cl₂ 2D perovskite at room temperature,¹² which emphasize the importance of the anisotropy of the 4AMP organic cations in the structure for the lattice distortion in hybrid 2D perovskites. On the contrary, undistorted phases are common for hybrid 3D perovskite compounds at room temperature and therefore any ultrafast light-induced ordering is lacking.¹³

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B. Multiple scattering effect. Another possible mechanism would be the possible multiple scattering effect in single-crystalline samples, as reported by Vallejo et al using keV electron beams.¹⁰ In fact, as pointed out by Vallejo et al, the possibility of having multiple scattering will rely on a characteristic length known as the extinction distance (ξ_g) of the samples, which is strongly affected by the electron beam energy, crystal structure and elements of material (Williams & Carter 2008¹⁴) as described by the following formula,

$$\xi_g = \frac{\pi V \cos \theta_B}{\lambda F_g} \quad (\text{S4.5})$$

180

181

Where V is the volume of the unit cell, θ_B is Bragg angle, λ is electron wavelength, and F_g is the structure factor at diffraction vector g .

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The calculation of V , λ , and θ_B is straightforward. For high energy electrons θ_B is fairly close to 0, since the electron wavelength λ is much smaller than lattice spacing ($\theta_B=0.5$ deg for Si (220) at 100keV) and therefore $\cos \theta_B \approx 1$. The F_g is estimated by the summation of all the atomic scattering factors with different atomic locations within the unit cell (Williams & Carter 2008¹⁴, Page 223):

$$F_g = F_{hkl} = \sum_{i=1}^n f_i^{(e)} e^{-2\pi i(hx_i + ky_i + lz_i)} \quad (\text{S4.6})$$

187

188

The atomic scattering factor is a function of scattering vector s ($s = \sin \theta / \lambda$). and a common approximation is fitted with the following formula¹⁵:

$$f^{(e)}(s) = \sum_j a_j \exp(-b_j s^2) \quad (\text{S4.7})$$

189 The coefficients of a_j , b_j for each atoms are listed in Table 1 in Peng et al¹⁵. For ionized
 190 atoms (such as Pb²⁺ and I⁻), additional term is included¹⁶.
 191 Based on the information above, we have estimated the extinction distance for Si under
 192 100keV and DJ n=2 perovskites under 3.7MeV, which are given by:

$$\begin{aligned} \xi_{Si|(220)} &= \frac{\pi V \cos \theta_B}{\lambda F_g} = \frac{\pi * 163.6 \text{ \AA}^3 * 1}{3.70 e - 2 \text{ \AA} * 15.06 \text{ \AA}} = 92 \text{ nm} \\ \xi_{DJ2|(220)} &= \frac{\pi V \cos \theta_B}{\lambda F_g} = \frac{\pi * 2627 \text{ \AA}^3 * 1}{2.97 e - 3 \text{ \AA} * 261.73 \text{ \AA}} = 1062 \text{ nm} \end{aligned} \quad (\text{S4.8})$$

193 The calculation of Si is close to the value reported in the literature (75.7 nm)¹⁴, giving a
 194 fair estimation. Compared to the sample thickness of $d \approx 270 \text{ nm}$ of DJ n=2 crystal, the
 195 extinction distance is ~ 4 times larger, therefore we believe the multiple scattering effects
 196 are not likely to happen in DJ n=2 perovskites.

197 Furthermore, in order to give a clear demonstration of the absence of multiple scattering,
 198 we have simulated the diffraction pattern of DJ n=2 based on kinematic scattering theory
 199 following the assumptions of weak-phase object approximation, which is a commonly used
 200 to model the crystal diffraction from electron microscopy.^{17,18} The calculated pattern for 4
 201 by 4 supercell is shown in Fig. S22. The simulated diffraction in Fig. S22(b) gives a
 202 reasonable match to the experimental diffraction of the crystal at rest Fig. S22(a), and are
 203 also in consistency with the calculations in Fig. S2(a), which is directly evaluated from the
 204 structural factor: $I_{hkl} \propto |F_{hkl}|^2$. Furthermore, the absence of Kikuchi lines in the scattering
 205 pattern also suggests lack of multiple scattering (FIG. S22(c)).¹⁹ A quantitative comparison
 206 of the linecut of the patterns is also displayed in FIG. S22(d), which gives a reasonable
 207 agreement for the intensity distribution of the Bragg peaks, especially at (400), (310) and
 208 (220) which shows the most contrast in the differential response (Fig. 2d) and are the most
 209 relevant peaks in the discussion of lattice ordering. This consistency indicates the
 210 kinematical scattering will be sufficient to describe the diffraction patterns, and the
 211 multiple scatterings are negligible.

212

213 **Supplementary discussion 5. Estimation of antiferro-distortion in 2D perovskites**

214 *A. Simplified model involving rigid octahedral rotations.*

215 Fig. S5 shows the simulated diffractions with intrinsic (Fig. S5a) and reduced antiferro-
216 distortion (Fig. S5b), as well as the corresponding crystal structures with different
217 disordering parameter viewed along stacking axis. The top (in-plane) view of 2D
218 perovskite caused by intrinsic in-plane cell doubling is shown in the schematics in Fig. S5c.
219 The tilted angle between adjacent octahedra ($2\theta = 24^\circ$) is associated with antiferro-
220 distortion, forming an initially doubled unit cell of 8.8 Å (indicated in red squares), as
221 opposed to the undistorted structure ($\theta = 0^\circ$) where unit cell is of 6.2 Å (labeled by green
222 squares). To estimate the influence on crystal structure with reduced antiferro-distortion,
223 we've constructed a hypothetic structural phase (Fig. S5d), where interlayer octahedra are
224 more aligned and simulated an electron diffraction pattern correspondingly (Fig. S5b). For
225 a direct comparison between the symmetrized and the intrinsic antiferro-distorsive phase,
226 a subtracted diffraction pattern is displayed in Fig. 2c. As we can see, the intensity
227 variations are expected in specific Bragg planes, including {400} and {220} (bright red)
228 increasing and {310} and {530} (blue).

229 To estimate the light-induced rotation angle $\Delta\theta = \theta' - \theta_0$, we calculated the percentage of
230 Bragg peak intensity variation as a function of tilting angle (Fig. S5e), and compare them
231 with the experiment data at early time ($t = 2\text{ps}$). From the responses of {310} {400}, we
232 estimated the optimal order parameter to be $\theta = 11.75^\circ$, as shown in the shadow region in
233 Fig. S5e, corresponding to an octahedral tilt of $\Delta\theta = 0.25^\circ$.

234

235 *B. Phonon mode simulations on DJ n=2 crystals.*

236 Besides the simplified model involving pure rigid tilting of octahedra, we believe a more
237 complex model should involve a shift of crystal structure along the eigenvectors of specific
238 normal modes. Therefore, we perform DFT computations on DJ n=2 (Phonon Simulation
239 methods) and suggest several possible vibrational modes candidates, as well as the related
240 diffraction plots, which are listed in Fig. S6. These normal modes are indeed related to the
241 antiferro-distortions (Fig. S6a, c, &e), and shifting the crystal structure along these
242 eigenvectors result in a positive change along {220} and {400} directions, consistent with

243 the prediction in section A. Therefore, these calculations further confirmed our hypothesis
244 on lattice ordering (Fig. 2).

245

246 **Supplementary discussion 6. Transient absorption spectroscopy of DJ n=2 crystal and carrier**
247 **temperature extraction.**

248 The transient absorption (TA) measurements are performed on nearly identical 2D perovskite
249 crystals (similar lateral size $L \approx 200 \mu\text{m}$, thickness $d \approx 300 \text{nm}$ and composition (DJ n=2) as used for
250 UED). We used an optical pump set at 3.1 eV (same as UED) with $0.1\text{-}0.75 \text{ mJ/cm}^2$ ($1.1 \times 10^{12} \text{ cm}^{-2}$
251 $- 8.4 \times 10^{12} \text{ cm}^{-2}$, corresponding to an excitation regime similar than in the UED measurements),
252 followed by a white-light probe monitoring the transmission variations of the sample (see Method
253 Section on transient absorption spectroscopy). Therefore, for similar optical pump conditions, we
254 had access to an optical probe in TA, yielding complementary information with respect to the
255 structural ones provided by the UED experiment. The results are displayed below in Fig. S11.

256 From our TA data, several major observations are summarized:

257 A. Strong bleaching of exciton states. Fig. S11 (c) shows absorbance spectra at different
258 fluences. We observed a significant bleaching of the exciton peak at 2.18 eV monotonically
259 increasing with excitation densities upto 0.75 mJ/cm^2 . From our TA studies extrapolated
260 to a fluence of $1\text{-}2 \text{ mJ/cm}^2$, we will expect an almost complete bleaching of the exciton
261 resonance leading essentially to a hot electron-hole pair plasma just after the pump in the
262 UED experiment. Furthermore, Fig. S11(f) shows a long lifetime ($\tau \sim 10^2 \text{ps}$) of exciton
263 dynamics, indicating a high density of carriers is still bleaching the exciton resonance over
264 long time, consistent with the observed long lifetime of lattice response in UED.

265 B. Hot-carrier cooling dynamics. As indicated in Fig. S11 (b), at 0.75 mJ/cm^2 , we have
266 observed the cooling phenomenon starting at $t \sim 0.4 \text{ ps}$, which is consistent with the typical
267 values reported in halide perovskites.^{20,21} We estimated the evolution of the effective
268 carrier temperature after $t \sim 0.5 \text{ps}$ by fitting the high-energy tail near the band edge with a
269 Maxwell-Boltzmann distribution (Fig. S11 (b)), which is a commonly used method to
270 approximate the carrier temperature in semiconductors.²² As estimated in Fig. 3(c), the first
271 cooling process of hot-carriers ranges from sub-ps to 1 ps. The initial carrier temperature

272 is fitted to be $T_c \approx 3700\text{K}$ for 0.75 mJ/cm^2 . We extrapolate this value to be 3300K for a
273 fluence of 1 mJ/cm^2 in the UED experiment.

274 C. Long-lived coherent acoustic waves. As shown in Fig. S12, we observed a low-frequency
275 oscillations from TA data, which is related to coherent acoustic waves. Through Fourier
276 transform in frequency domain, (Fig. S12(b)), we identify one phonon mode at 0.022 THz
277 (0.09meV), related to temporal period of 45 ps , and are consistently observed for all the
278 measured fluences ($0.1\text{-}0.75\text{mJ/cm}^2$). The activation of coherent acoustic modes with >100
279 ps lifetime suggest a long equilibration time of the phonon bath, on a time scale consistent
280 with the long lifetime of the lattice response in UED.

281 These TA results suggest that hot electron-hole plasma may be more dominant at this high
282 excitation densities, where many-body interactions and other non-linear processes could play a
283 crucial role, contradictory to the work of Thouin et al. where the excitonic regime is mainly
284 discussed.²³ This conclusion is also confirmed by the quantitative analysis defining the excitation
285 regime and carrier saturation densities vs temperature which are shown below in discussion 7.

286 In addition to

287

288 **Supplementary discussion 7. Estimation of saturation densities in DJ n=2 and RP n=2 crystals**

289 We've estimated the carrier temperature in 2D perovskites to be $T_c \sim 3300\text{K}$ for 1mJ/cm^2 .
290 (Discussion 6). The next step consists in computing the saturation densities for the excitonic
291 resonances in the DJ n=2 compound. For that purpose, the binding energy and the Bohr radius of
292 the 1S exciton resonance are considered.²⁴ It is usually considered that the binding energy is
293 reduced in DJ compounds by comparison to RP ones for the same n, but precise experimental data
294 are not available for DJ n=2. We started from the known values available for RP n=2:²⁵
295 $E_{b,RP}=245\text{meV}$ for the binding energy and $a_{B,RP}=1.60 \text{ nm}$ for the effective Bohr radius related to
296 the diamagnetic shift. Next, the effect of the smaller interlayer spacing is estimated using the
297 effective dielectric model of Ishihara et al²⁶ $\epsilon_{\text{eff},RP}=4.9$ vs $\epsilon_{\text{eff},DJ}=5.5$, leading in turn to a reduction
298 of the binding energy $E_{b,DJ}=204\text{meV}$. The BSE model²⁵ was then used to compute the diamagnetic
299 shift and finally a $a_{B,RP}=1.56 \text{ nm}$. A summary of saturation densities at different carrier temperature
300 is plotted in Fig. 3e.

301

302 **Supplementary discussion 8. Generalizability of lattice response and order parameter on 3D**
303 **perovskites.**

304 In this section, we compare the distinct ultrafast lattice dynamics of different perovskite systems,
305 and discuss the generalizability of other parameter in 3D perovskites. We believe the initial
306 antiferrodistorsive states are indeed important, not only for 2D perovskites but also for the 3D
307 perovskites. The antiferro-distorsive octahedral rotation angles of both 2D and 3D perovskites
308 systems are listed in table S2.

309 *A. 3D iodine perovskites (MAPbI₃)*

310 Wu et al have performed the same UED measurements on the polycrystalline thin film of
311 MAPbI₃.¹ The behavior of the Bragg peaks is Debye-Waller like, and no similar response
312 involving reduction of antiferro-distortion has been observed. Here, in order to examine
313 the generalizability of the order parameter in 3D perovskites, we have performed a similar
314 simulation with a hypothetic octahedral rotation model (similar as the one described in the
315 manuscript Fig.2), and compare the expected variations of diffraction intensities to the
316 experimental curve from Wu et al. The comparison is shown in Fig. S23.

317 As shown in Fig. S23, the reduction of the antiferro-distorsion present in the tetragonal
318 phase of MAPbI₃, should lead to positive intensity variations at $q=2.0$ and 2.8\AA^{-1} , similar
319 to the ones observed for DJ $n=2$ (Fig. 2d) as a result of reduced in-plane octahedral rotation
320 towards higher symmetry phase. Indeed, the characteristic positions of the Bragg peaks
321 related to the perovskite backbone are similar in iodide-based 2D and 3D perovskites,
322 because these compounds share similar lengths for the Pb-I bonds. However, by comparing
323 the simulated differential pattern with the UED results for MAPbI₃ from Wu et al, such
324 positive response is not observed in the experimental scattering intensity at different delay
325 times ($t=5, 70\text{ps}$), as indicated in Fig. S23(a). In fact, we note that MAPbI₃ exhibits a
326 similar behavior than RP phases (Fig. 4, also zoomed in at same q region in Fig. S23(b)),
327 especially in RP $n=4$ which is close to 3D perovskites. We believe that the consistency of
328 negative intensity response in both 2D RP perovskites and 3D perovskites provide clear
329 evidence of the distinct lattice dynamics in 2D DJ perovskites. The initial distortion
330 generated by the presence of di-cations in DJ perovskites instead of mono-cations for RP

331 perovskites is important, leading to different space groups, interlayer shifts and in-plane
332 octahedra tilts (Mao et al³). From that perspective, the perovskite backbone in RP phases
333 is less influenced by the flexible BA cations in the barrier and exhibit tilt patterns similar
334 to bulk MAPbI₃.

335 *B. Oxide perovskites (SrTiO₃ & KTaO₃)*

336 For oxide perovskite systems, pristine SrTiO₃ presents a cubic structure at room
337 temperature and goes through an antiferro-distorsive phase below T_c (105K). The phase
338 transition is antiferro-distorsive with an order parameter related to an octahedral rotation
339 ($\phi \sim 2^\circ$ for T = 5K²⁷) and a Bragg superlattice reflection. Indeed, Porer et al observed an
340 ultrafast relaxation of antiferro-distorsive phase in Ca: SrTiO₃, where alloying with Ca was
341 used to increase T_c (280K) and initial rotation angle. As observed by Porer et al, this
342 ultrafast lattice dynamics, characterized by superlattice diffraction, is consistently observed
343 in the tetragonal phase below the critical temperature, where a non-zero rotation angle is
344 present at equilibrium. This suggests that similar to our work, an initial octahedral tilt is
345 necessary to give rise to the ultrafast dynamics involving relaxation of antiferro-distortion
346 phase.

347 In general, in oxide perovskites, distortions can be grouped into two categories:^{28,29} either
348 antiferro-distortions (e.g. CaTiO₃, SrTiO₃) related to the octahedral tilt, or ferroelectric
349 distortions (e.g. BaTiO₃), where the B-site atom is displaced within surrounding
350 octahedron. The observation of two types of distortions can be explained by the
351 Goldschmidt tolerance factor.²⁸ In the case of KTaO₃, the ferroelectric order parameter, is
352 connected to the off centering of B-site cation.³⁰ Therefore, we believe that our results on
353 DJ 2D perovskites rather share some similarities with the reduction of antiferro-octahedral
354 rotation in SrTiO₃ with photodoping as reported by Porer et al.

355

356 **Supplementary discussion 9. Comparison of electron-LO phonon coupling with RP and DJ**
357 **n=3.**

358 To elucidate the strength and coefficients of the electron-LO phonon interactions, we performed
359 temperature-dependent PL on DJ n=3 perovskites, where we monitor the linewidth of PL
360 broadening as a function of temperature. The result is shown in Fig. S24.

361 The PL of DJ perovskite shows an asymmetric shape with two profiles. Here we focus at the
362 dominant exciton emission at higher energy and plot the FWHM as function of temperature (Fig.
363 S24(b), blue). Such behavior is also compared with RP n=3 (displayed in orange).

364 Here, the linewidth of DJ perovskites shows an anomalous broadening below 80K, which is
365 similarly resolved in MAPbI₃ system³¹, and is most likely also related to the influence of a phase
366 transition in this temperature range. However, far above 80K in a temperature range relevant for
367 the discussion of the present work, the broadening in DJ perovskites is consistent with the one in
368 RP perovskites. It suggests that the strengths of the electron-phonon coupling in DJ n=3 and RP
369 n=3 perovskites are not significantly different at high temperatures, and that the observed lattice
370 ordering in DJ perovskites is not due to a specific electron-LO phonon coupling, which would
371 otherwise cause similar lattice response between RP and DJ perovskites.

372

373 **Supplementary discussion 10. Estimation of long-time Bragg peak response and light-induced**
374 **atom RMS displacements $\langle u^2 \rangle$**

375 Due to the deviation of Debye-Waller response (Fig. S25) of DJ n=2 crystal, the Bragg peaks
376 intensity responses show competing effects between the conventional Debye-Waller effect and
377 incipient anisotropic lattice ordering:

$$I_{\text{total}}(\vec{q}) = [I_0(\vec{q}) + \Delta I(\vec{q}, \Delta\theta)] e^{-\frac{1}{3}\Delta\langle u^2 \rangle q^2} \quad (\text{S7.1})$$

378 Here $I_0(\vec{q})$ stands for the diffraction intensities at rest. The total Bragg peak intensity response
379 have two contributions: i) an initial ordering process represented in $\Delta I(\vec{q}, \Delta\theta)$, where $\Delta\theta$ is the
380 change of distortion angle (shown in Fig. 2b), which is estimated in Supplementary discussion 5.
381 $\Delta I(\vec{q}, \Delta\theta)$ is simulated based on reduction of antiferro-distortion and also shown in Fig. 2c. ii)
382 classical thermal energy transfer involving all the Bragg peaks, represented in Debye-Waller effect
383 as exponential term $e^{-\frac{1}{3}\Delta\langle u^2 \rangle q^2}$, where $\langle u^2 \rangle$ stands for atomic mean squared (RMS) displacement.

384 The competing effect of the two mechanisms is also indicated in Fig. S8, where considering only
385 the first contribution (gray dashed line, Fig. S8(b)) will not give a good prediction at long delay
386 time (40-80 ps) especially at higher q , while the combining effect of the two (black solid line)
387 matches better with the experimental response. By comparing the simulated intensity change with

388 the Bragg peak response at long time, the Debye-Waller factor is estimated to be $1.6 \times 10^{-3} \text{ \AA}^{-2}$,
389 corresponding to light-induced atom RMS displacement of $\sqrt{\Delta\langle u^2 \rangle} \sim 0.07 \text{ \AA}$ at carrier density of
390 $2.5 \times 10^{13} \text{ cm}^{-2}$.

391

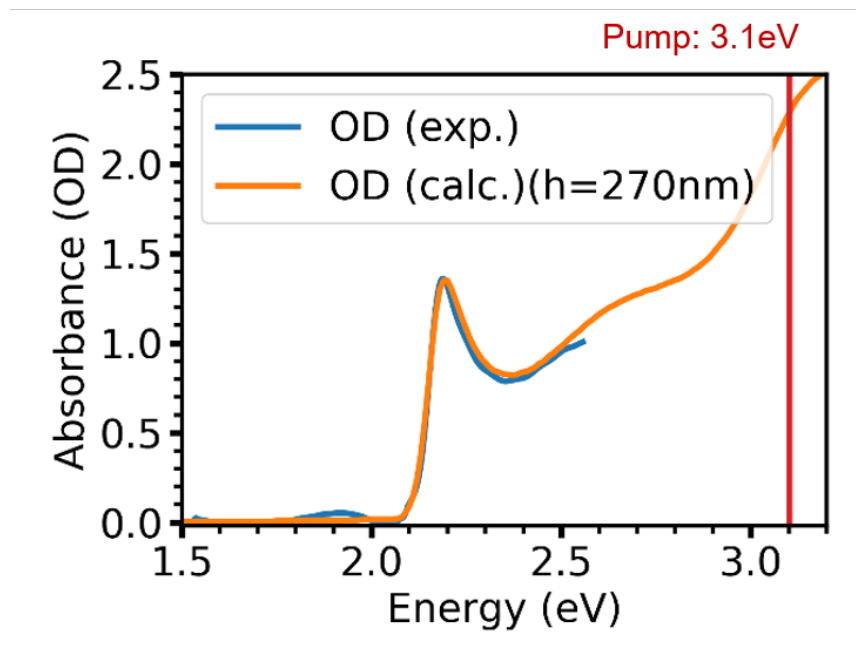
392 **Supplementary discussion 11. Time evolution of diffraction intensities through the UED run.**

393 Fig. S19 shows the time evolution over ~ 2 hours during the UED run of DJ n=2 crystal. As shown
394 in Fig. S19a, the total diffraction intensity doesn't show a significant drop over ~ 2 hours,
395 suggesting the crystal structure remains stable throughout the experiment. Fig. S19b shows the
396 comparison of the electron diffractions between 0min and 120mins, where all the Bragg peaks
397 remain existing, with a slight decrease of overall intensities. Additionally, no rings or new peaks
398 were formed through the experiments (Fig. S19c and Fig. S19d), confirming that no evidence of
399 possible sample degradation or damage is found.

400

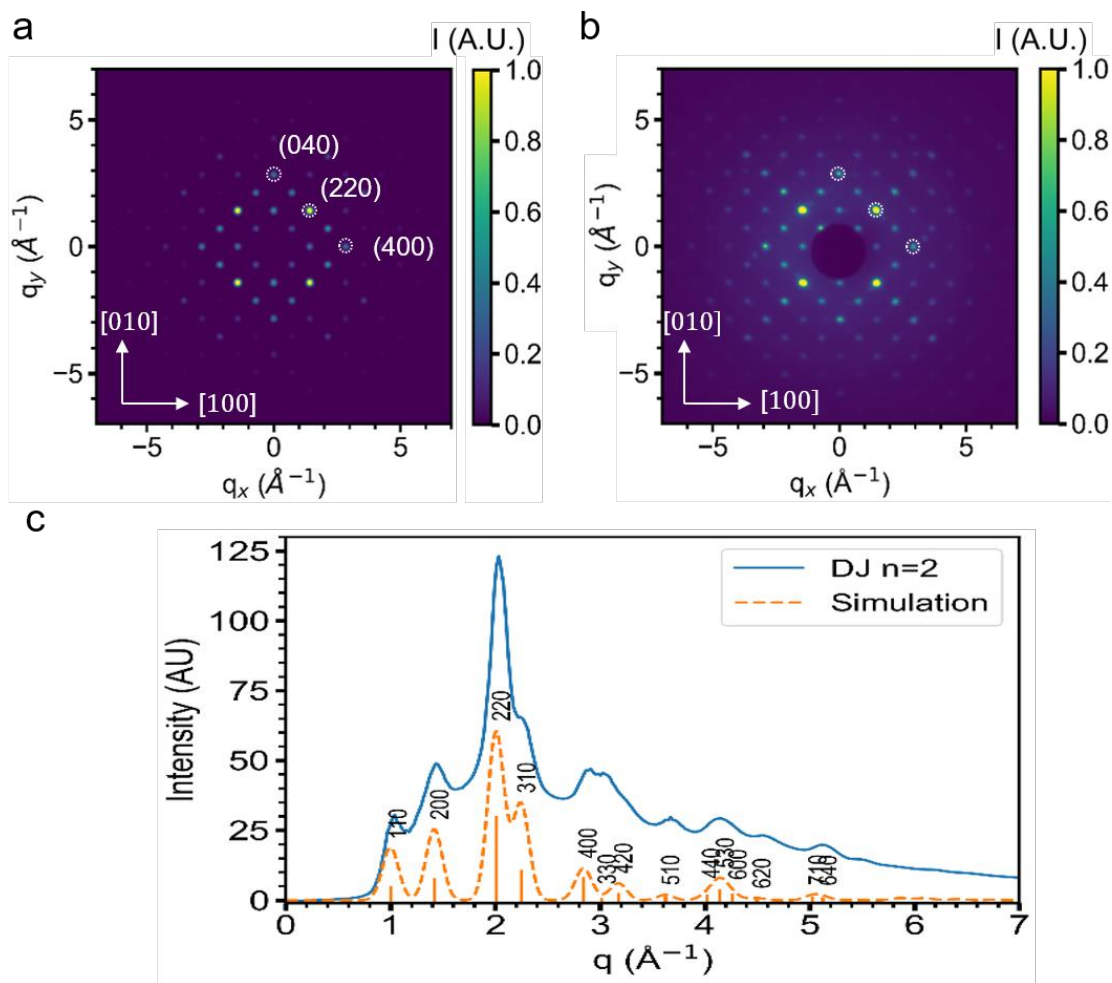
401 **Supplementary Figures S1 – S26**

402

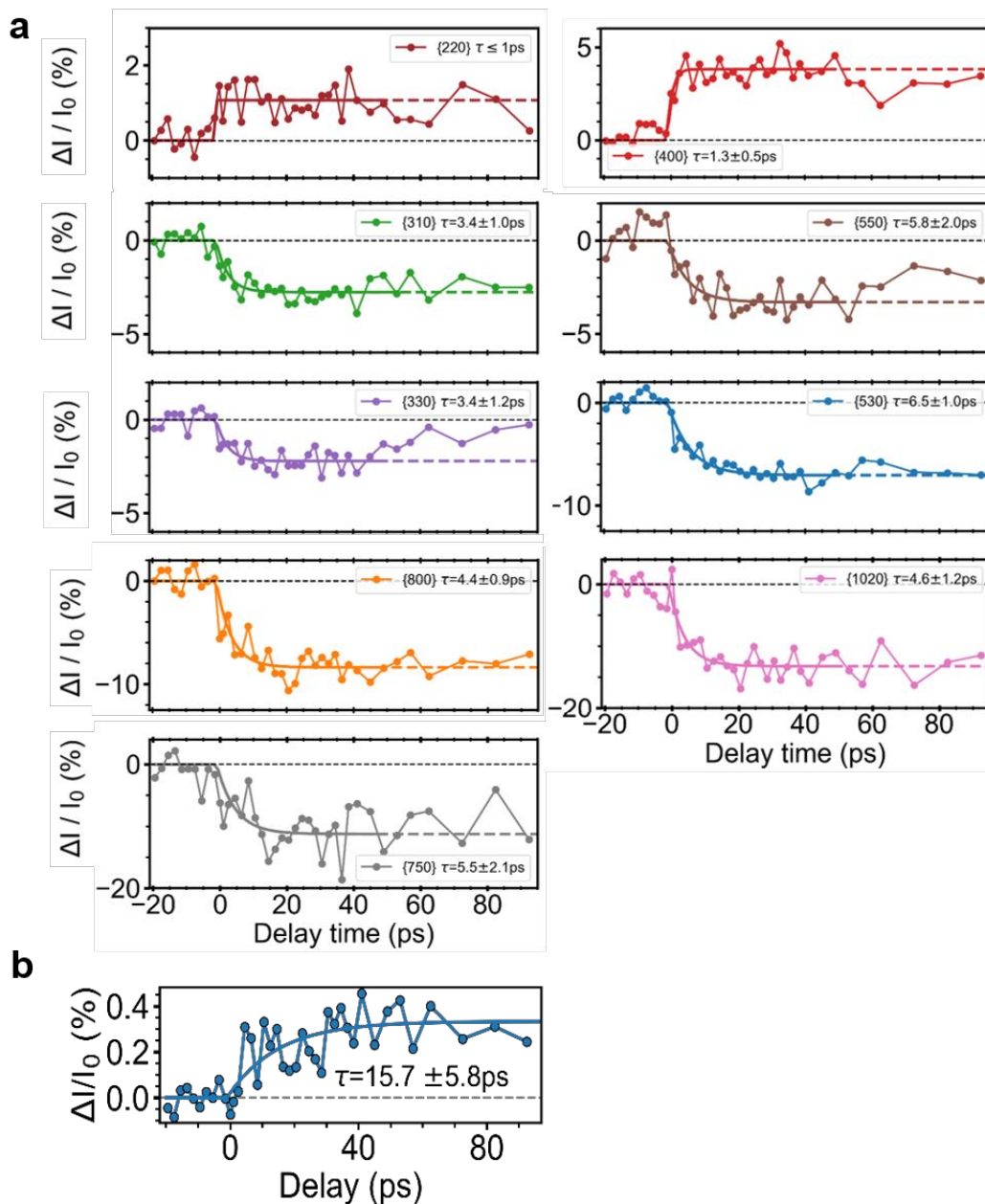


403

404 **Fig. S1 | Optical absorbance spectra of DJ n=2 crystal.** The measured absorbance is shown in
405 blue line, with calculated absorbance (orange line) with crystal thickness of 270nm, estimated
406 from the absorption coefficient as reported by Song et al.³

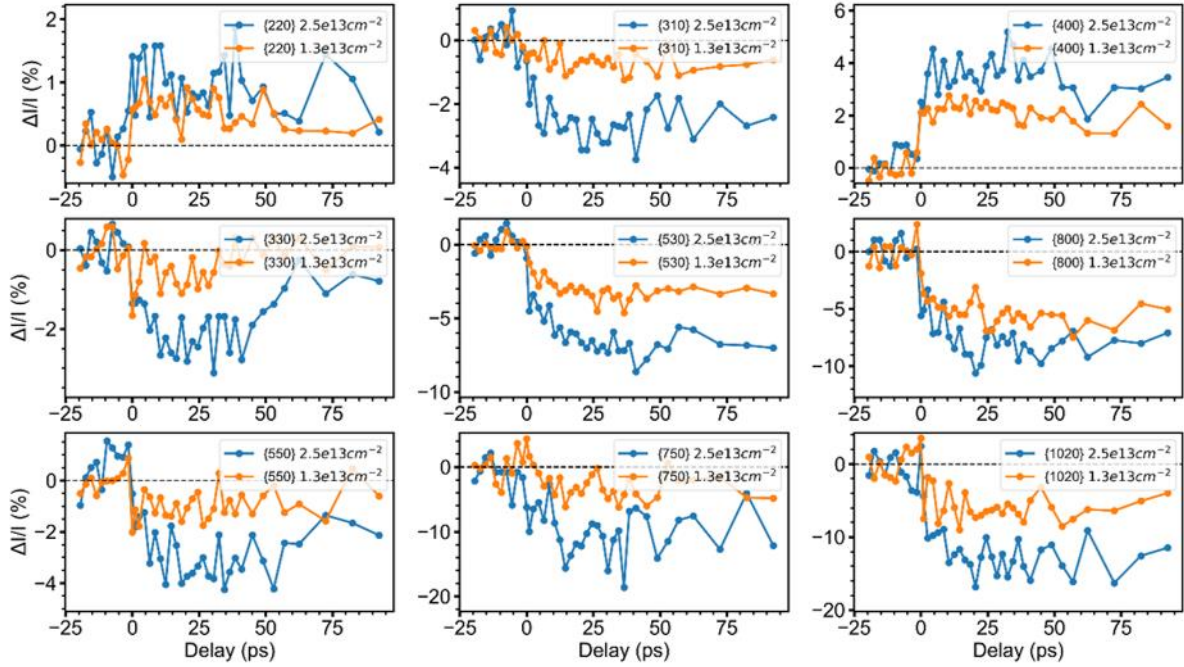


407
 408 **Fig. S2 | Simulated Diffraction Pattern & Indexing of DJ n=2 crystal.** (a) Simulated Diffraction
 409 of DJ n=2 crystal, viewing from [001] direction. (b) Static Diffraction of DJ n=2, showing same
 410 q -range as the simulated one in Fig. S2a. All the Bragg peaks are well-identified. (c) Angular-
 411 integrated diffraction of DJ n=2, showing both experimental (blue solid line) and simulated
 412 (orange dashed line) plots, as well as Indexing of Bragg peaks ($hk0$).



413

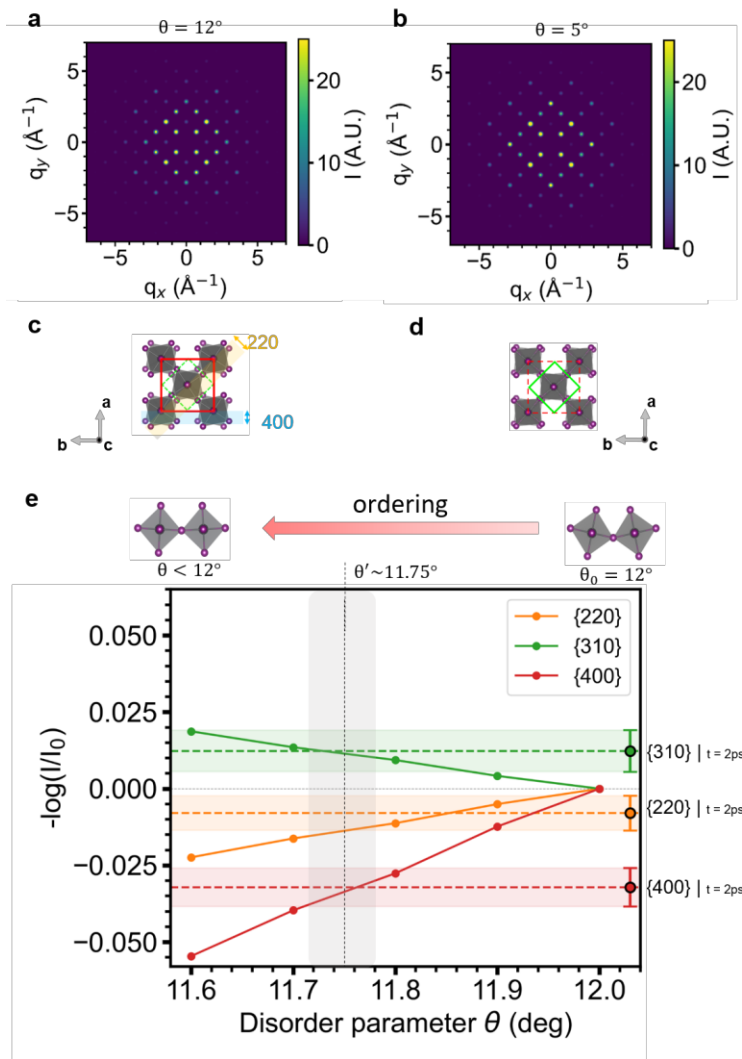
414 **Fig. S3 | Time traces of selected Bragg peak families in DJ n=2 crystal. (a)** Time traces of
 415 Bragg peaks intensities of {220} {400} {310} {330} {1020} {550} {530} {800} and {750} for DJ
 416 n=2 crystal. Errors of time constants are defined as one standard deviation errors estimated from
 417 the variance of the fitting parameters from least-squares fitting. The statistics of {220} is not good
 418 enough to be fitted with a reasonable time constant. We estimate the time scale to be ≤ 1 ps limited by
 419 temporal step size. **(b)** Dynamic plots of the total integrated diffuse scattering intensities between
 420 Bragg peaks.



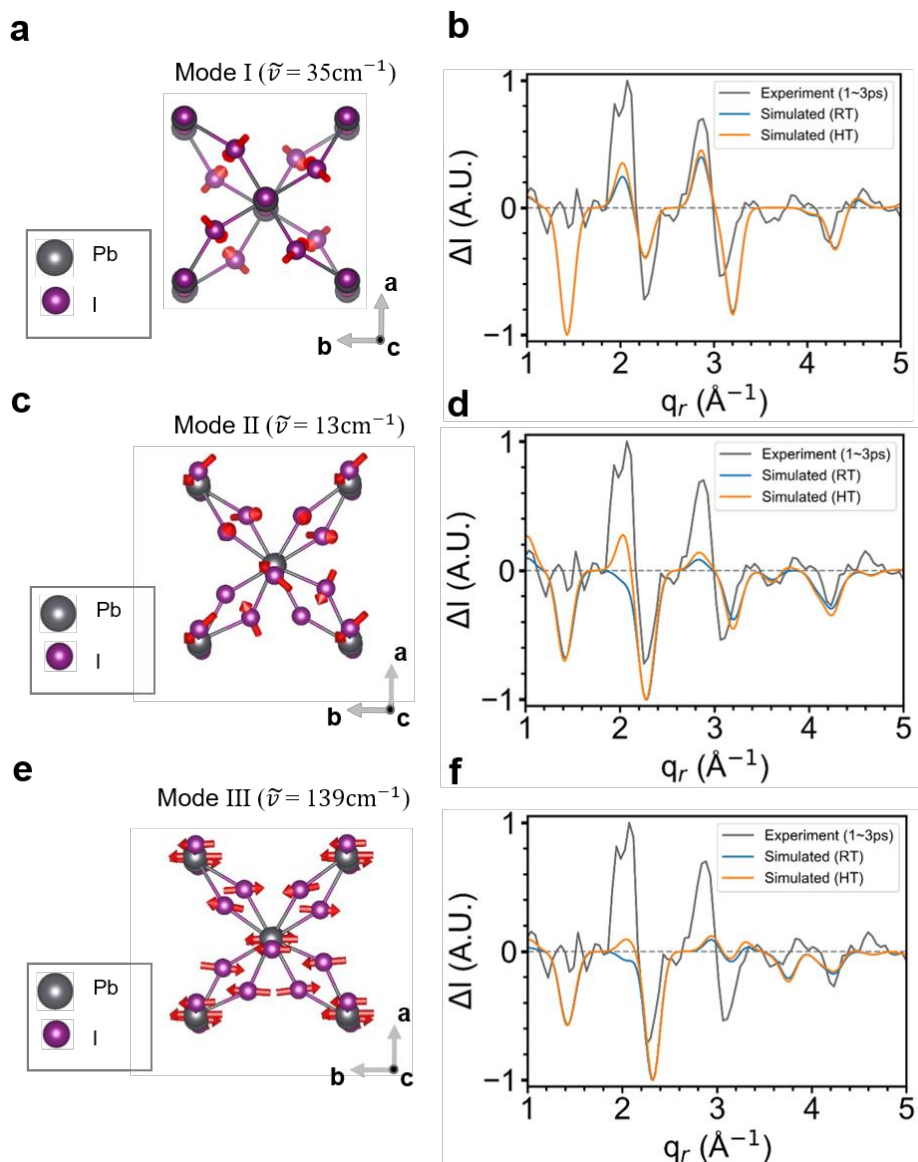
421

422 **Fig. S4 | Fluence dependence for selected Bragg peaks in DJ n=2 crystal.**

423 Time traces of Bragg peaks intensities of {220} {310} {400} {330} {530} {800} {550} {750} and
 424 {1020} for DJ n=2 crystal under 2 laser fluences: 1mJ/cm² (orange) and 2mJ/cm² (blue),
 425 corresponding to injected carrier density of 1.3×10¹³cm⁻² and 2.5×10¹³cm⁻², respectively.



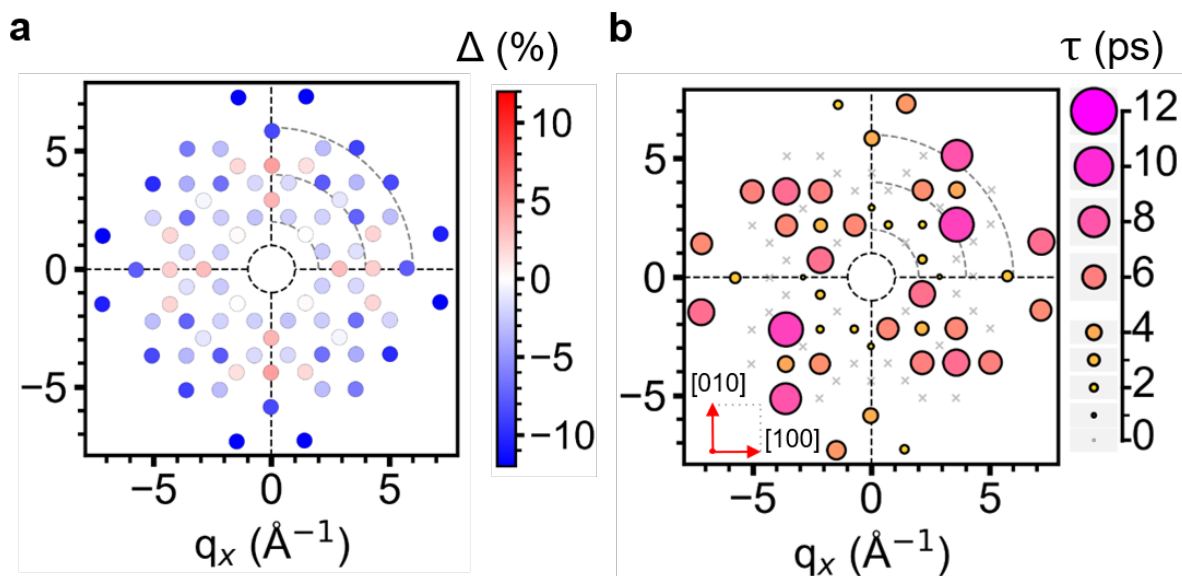
426
 427 **Fig. S5 | Simulated Diffraction Patterns with tuned antiferro-distortion.** (a) Simulated
 428 Diffraction of DJ $n=2$ at rest with intrinsic antiferro-distortion ($\theta=12^\circ$). (b) Simulated Diffraction
 429 of DJ $n=2$ with reduced antiferro-distortion ($\theta=5^\circ$). (c)(d) Corresponding schematics of distorted
 430 ($\theta=12^\circ$) and less distorted phase ($\theta<12^\circ$), respectively. (e) Simulated logarithmic intensity change
 431 ($-\log(I/I_0)$) for selected Bragg peaks as a function of disorder parameter θ , shown for {220} {310}
 432 and {400} peaks (orange, green, and red solid lines), respectively. Compared with experimental
 433 data (DJ $n=2$, $2.6 \times 10^{13} \text{ cm}^{-2}$) at $t=2\text{ps}$ (scattered points at right), the optimal change of disorder
 434 parameter is estimated to be $\Delta\theta \sim 0.25^\circ$ (regime indicated in gray shadow).



435
 436 **Fig. S6 | Examples of calculated antiferro-distortive phonon modes candidates in DJ n=2**
 437 **crystal. (a)(c)(e)** Schematic illumination of calculated normal modes (I, II and III respectively)
 438 acquired from phonon simulation (cations are neglected for visualization). The calculated
 439 wavenumbers are 35, 13, 139 cm^{-1} , respectively. The directions of the atomic displacements are
 440 indicated with red arrows, suggesting a modulation of antiferro-distortions. **(d)(e)(f)** Simulated
 441 changes of electron diffraction plots for normal mode I, II and III respectively, estimated under
 442 room temperature (RT, blue solid line) and high temperature (HT, orange solid line) regimes. These
 443 simulated plots are compared with differential diffraction plot from UED experiment (1-3 ps, gray
 444 solid line), showing consistent peak increase at (220) and (400).

445

446



447

448 **Fig. S7 | Scatter plots of fitted intensity change and time constants of DJ n=2 crystal. (a)**

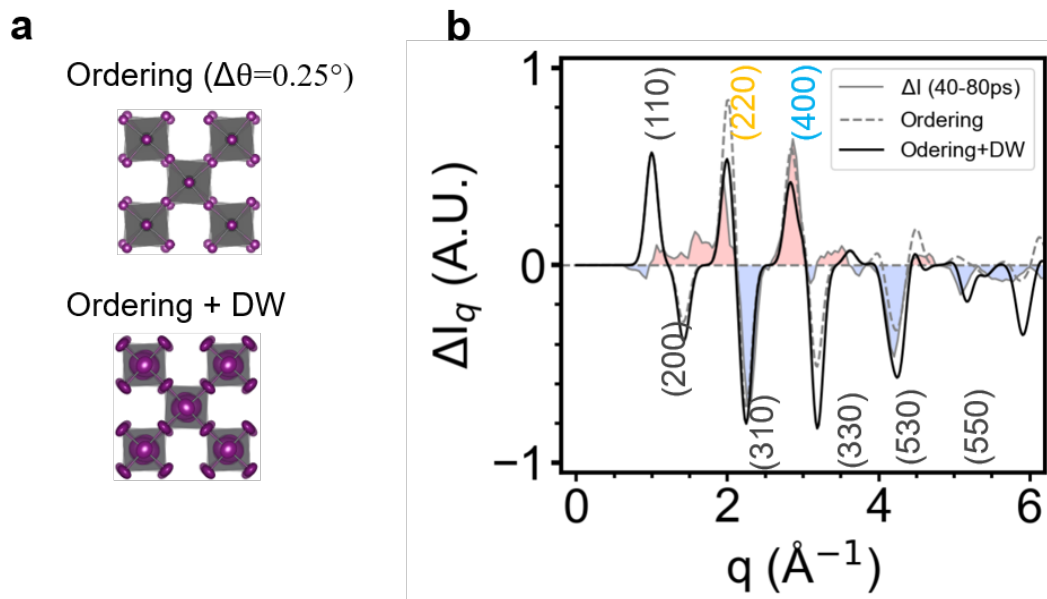
449 Scatter plots of fitted intensity change (Δ (%)) of the Bragg peaks (hk0). Each Bragg peak (hk0)

450 is averaged with (-h-k0) based on point symmetry. **(b)** Scatter plots of fitted time constant of the

451 Bragg peaks, represented in both color scale and circle size (small and orange circles for short time,

452 and large and pink circles for long time). 'x' markers stand for the Bragg peaks that cannot be well

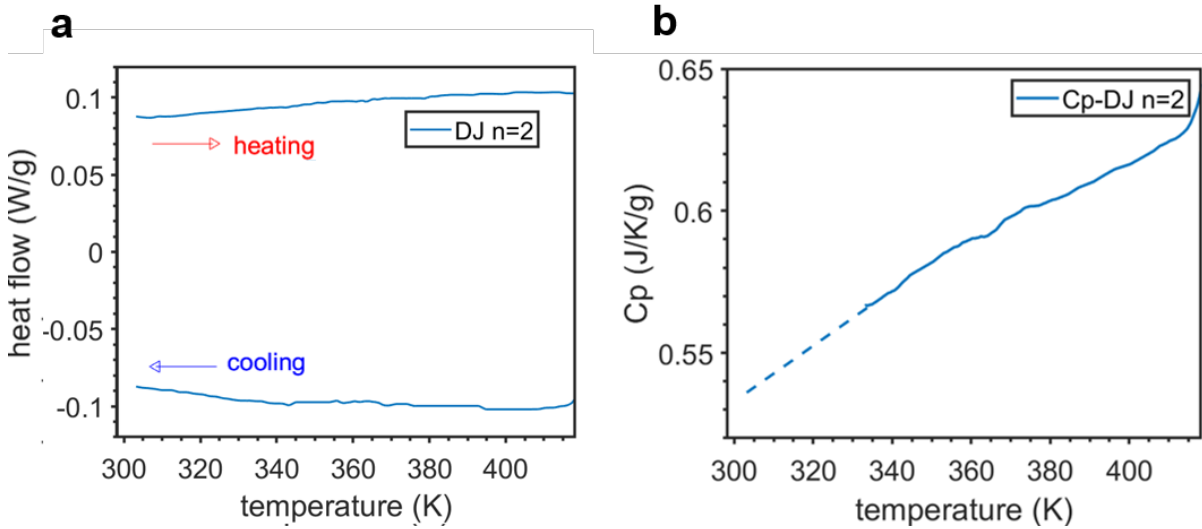
453 fit.



454

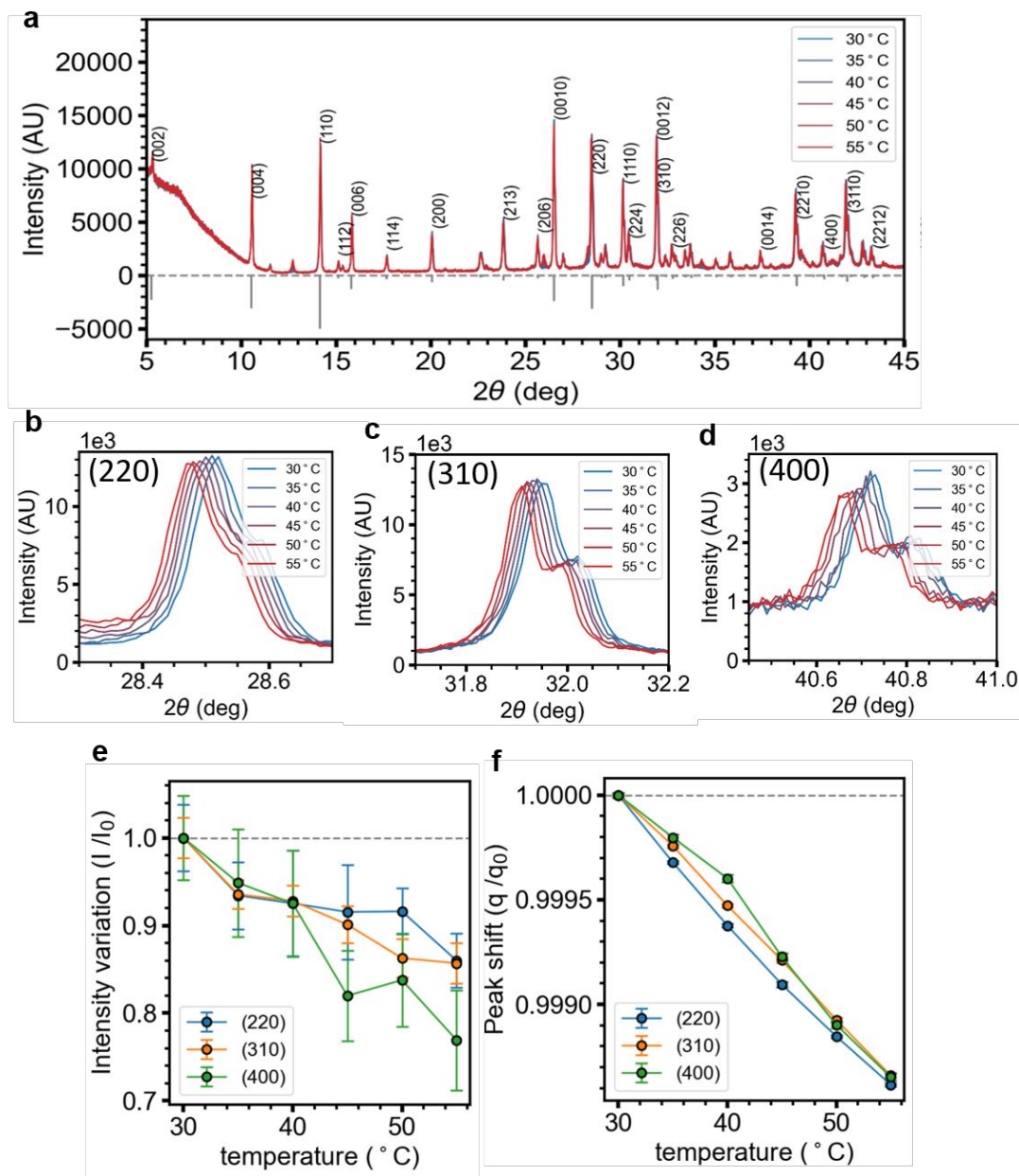
455 **Fig. S8 | Simulation of total UED response of DJ $n=2$ crystal.** (a) Simulated crystal structure
 456 (top view) for different simulation methods: lattice ordering by reducing distortion angle (top),
 457 and additional disorder involving all atoms (bottom). (b) Angular integrated differential diffraction
 458 plot, averaged between 40-80 ps (gray solid line and shadow), compared with the simulated
 459 response with only considering lattice ordering (gray dashed) and both ordering and Debye-Waller
 460 effect (black solid line). The experimental intensity around the (110) peak is partially blocked.

461



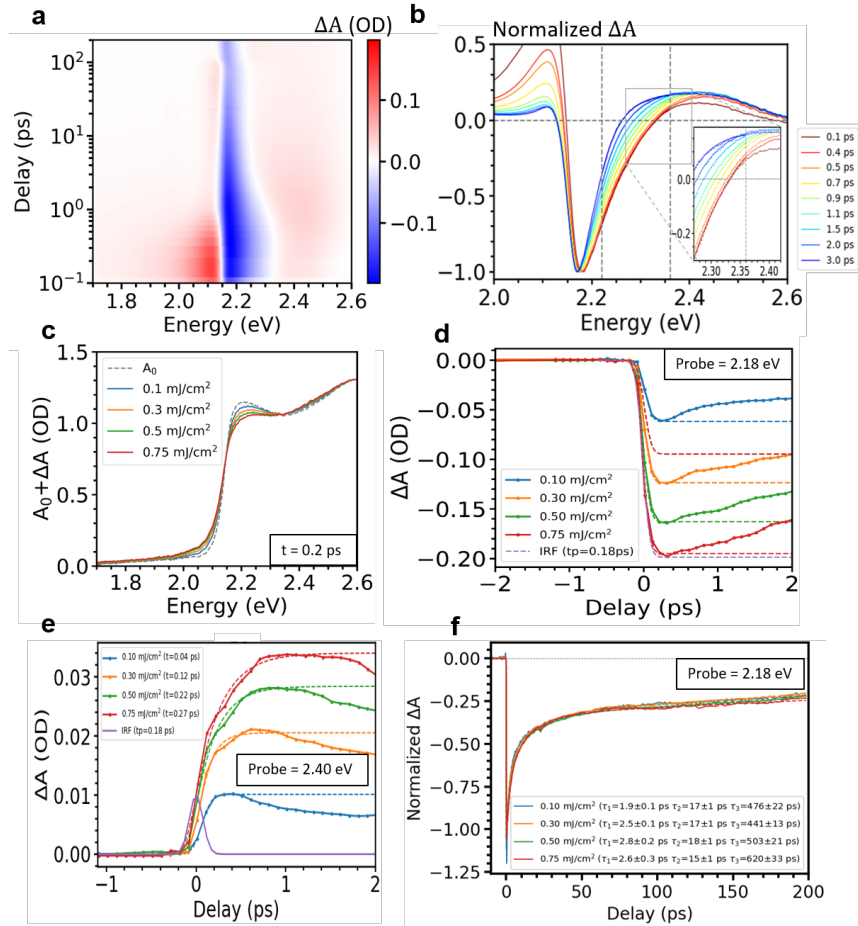
462

463 **Fig. S9 | Differential scanning calorimetry (DSC) of DJ n=2 crystal. (a)** DSC curve of DJ n=2
464 single crystals from room temperature to 150°C. **(b)** Calculated specific heat capacity (Cp) from
465 DSC.



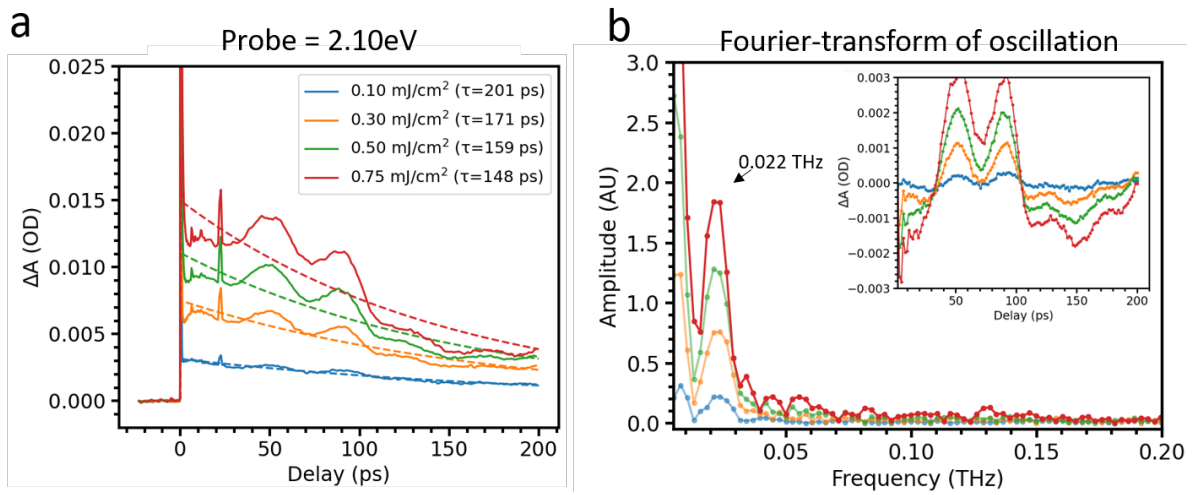
466

467 **Fig. S10 | Temperature dependent XRD of DJ n=2 crystal.** (a) Temperature dependent XRD
 468 from 30°C to 55°C. Simulated Bragg peak locations for DJ n=2 are indicated in vertical gray solid
 469 lines. (b)(c)(d) Zoomed-in XRD plots at in-plane peaks (220) (310) and (400) respectively,
 470 showing global shifting of peak locations (thermal expansion) and slight intensity decreases over
 471 temperature. (e) Analysis of relative intensity variation (I/I_0) and (f) relative peaks shift (q/q_0) for
 472 (220), (310) and (400) Bragg peaks. Error bars show the one standard deviation errors computed
 473 from the variance of the fitting parameters from least-squares fitting.



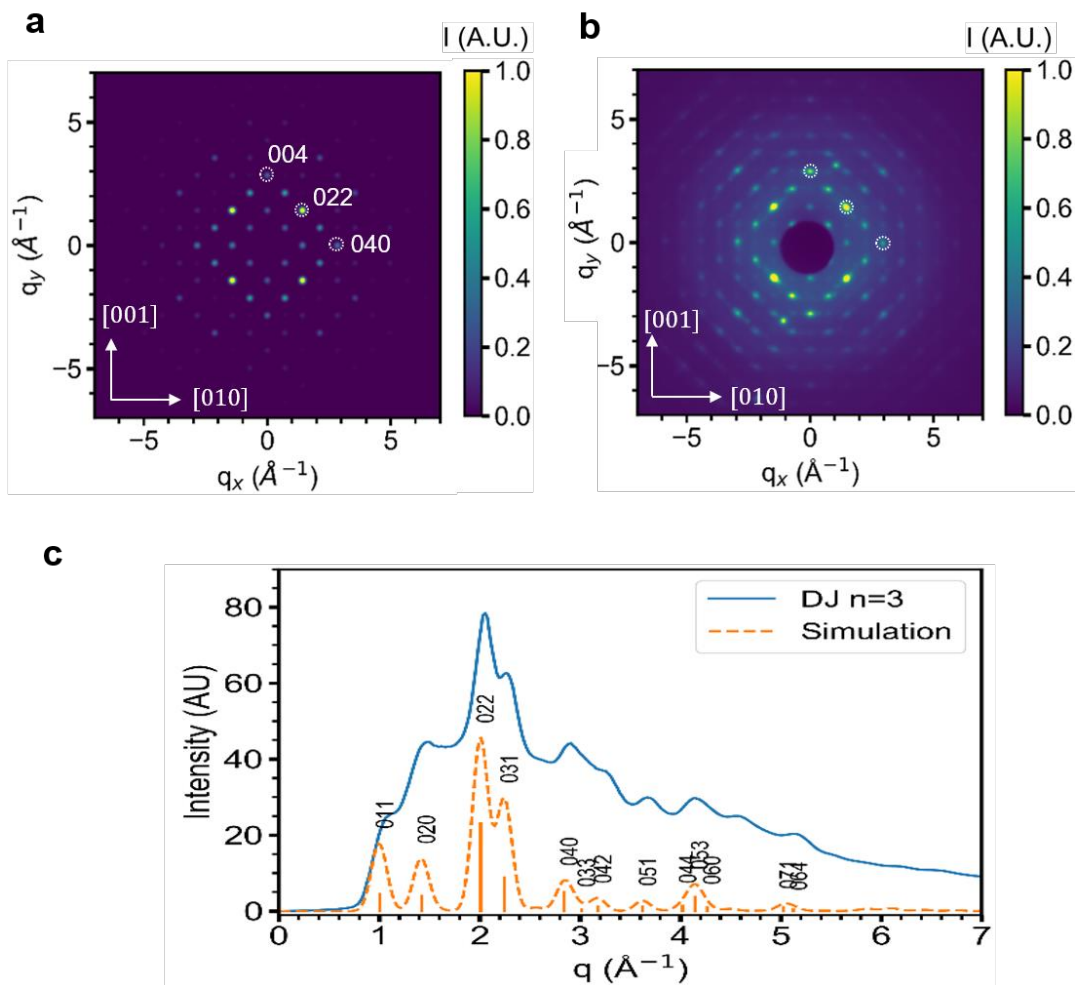
474

475 **Fig. S11 | Transient absorption spectroscopy for DJ n=2 crystal.** (a) Pseudo color
 476 representation of transient absorbance (Δ OD) as function of delay time, under 0.75mJ/cm². (b)
 477 Normalized TA spectra. The bleach amplitude at 2.18 eV is normalized to -1. High energy tails
 478 are fitted by Boltzmann distribution (black solid lines) to extract carrier temperature (shown in Fig.
 479 3d). (c) Absolute absorption at various fluences, showing almost complete bleaching of exciton
 480 resonance. (d) Ultrafast bleaching ($\tau \leq 0.18$ ps) of exciton resonance at 2.18 eV, indicating fast
 481 ground state exciton bleaching after above-band excitation. (e) Evolution of TA dynamics at
 482 2.40eV. The rise time is fitted with single exponential curve convolved with IRF (purple solid line),
 483 giving a rough estimation of carrier thermalization time. (f) Normalized exciton dynamics at
 484 2.18eV, showing a long delay time ($\tau_3 \sim 10^2$ ps), suggesting a high density of electron-hole plasma
 485 still bleaches the exciton resonance at long time over 100-200ps. Fitting errors are estimated by
 486 the one standard deviation errors computed from the variance of the fitting parameters from least-
 487 squares fitting.



488

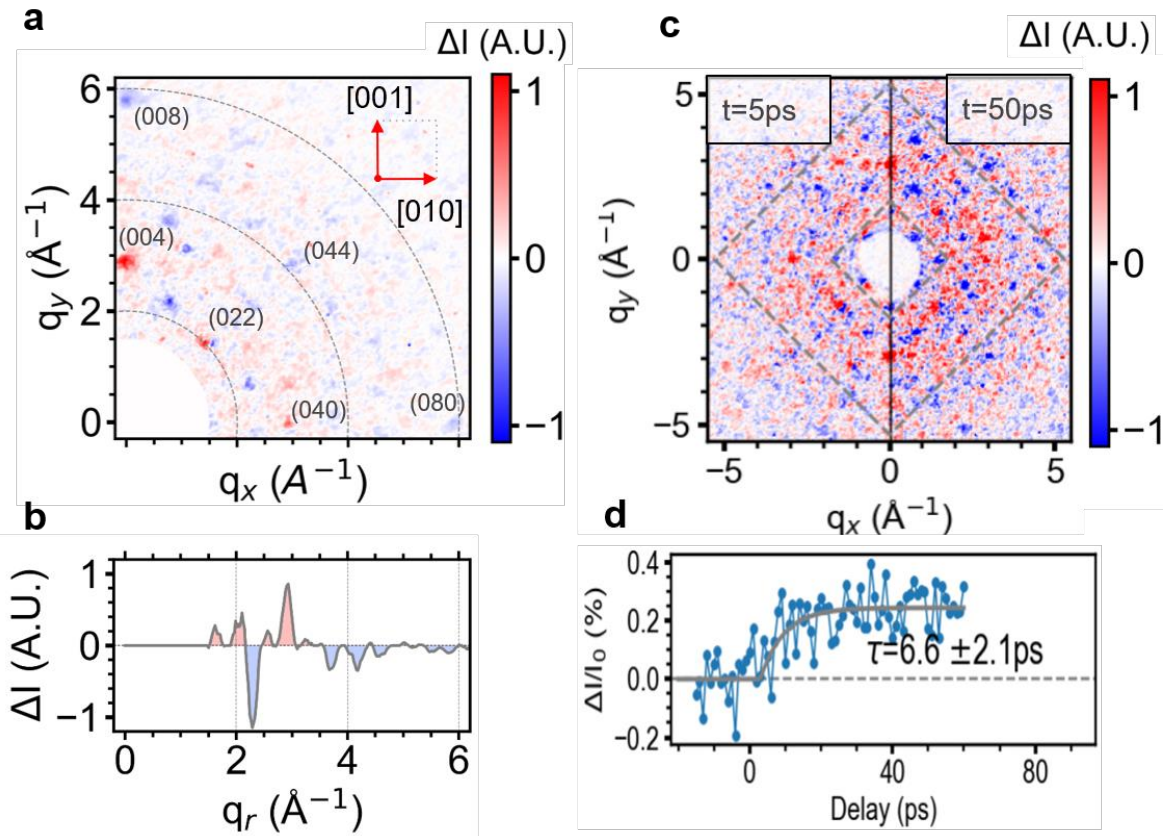
489 **Fig. S12 | Observations of coherent acoustic phonon in DJ n=2 and frequency analysis. (a)**
 490 TA decay of probed at 2.10eV, showing oscillatory components with period $T \sim 45$ ps. **(b)**
 491 Extraction of the oscillation (inset) and frequency domain analysis. Frequency below 0.0005THz
 492 is discarded due to the limited window in temporal domain (≤ 200 ps).



493

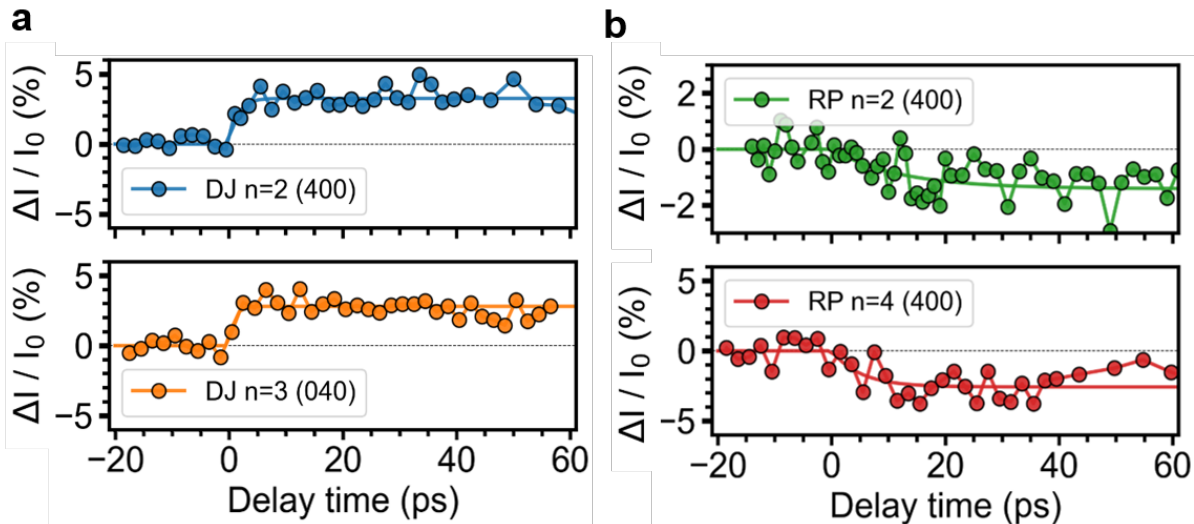
494 **Fig. S13 | Simulated Diffraction Pattern & Indexing of DJ n=3 crystal.**

495 **(a)** Simulated Diffraction of DJ n=3, viewing from $[100]$ direction. **(b)** Static Diffraction of DJ
 496 n=3, showing same q -range as the simulated one in Fig. S13a. All the Bragg peaks are well-
 497 identified. **(c)** Angular-integrated diffraction of DJ n=3, showing both experimental (blue solid
 498 line) and simulated (orange dashed line) plots, as well as Indexing of Bragg peaks (0hk).



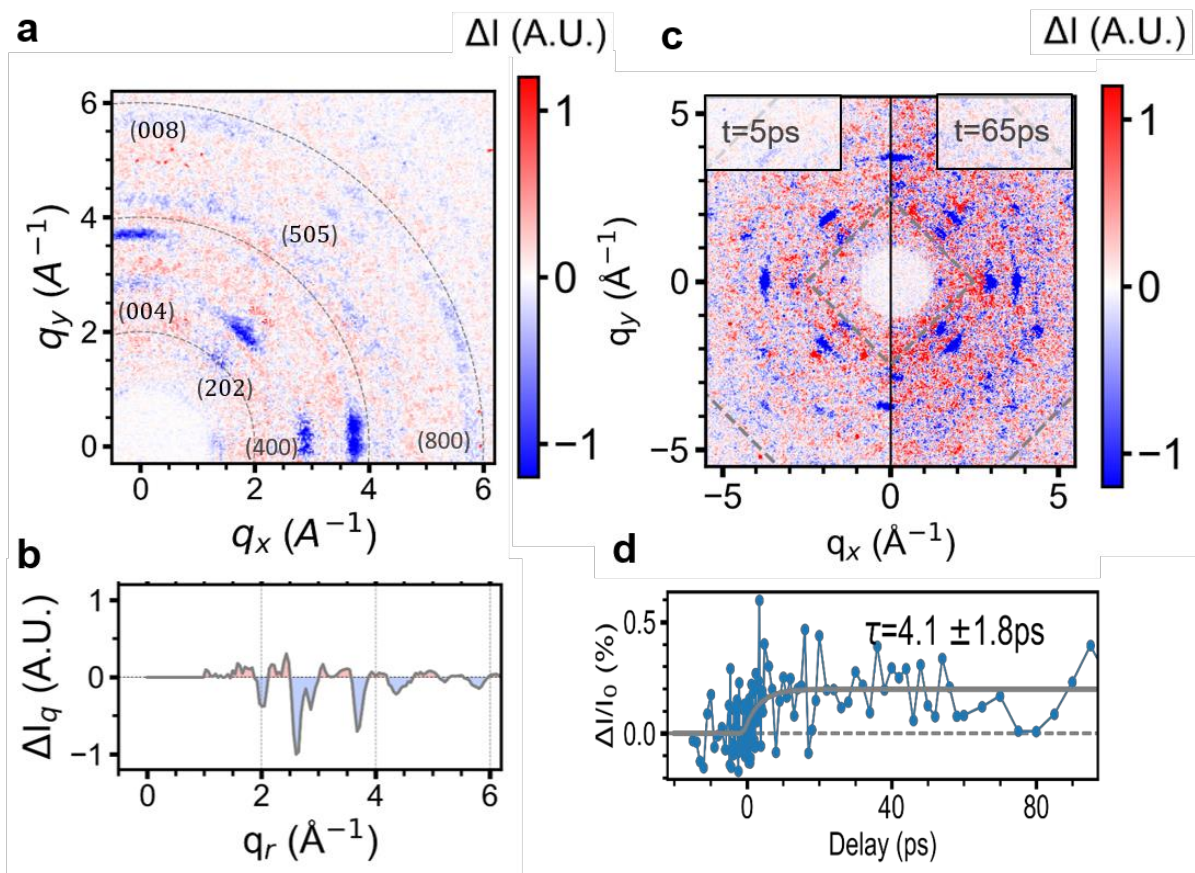
499

500 **Fig. S14 | Differential diffraction patterns of DJ n=3.** (a) Differential diffraction pattern (20-
 501 40ps) for DJ n=3, showing similar response as DJ n=2, including the positively-changing peaks
 502 (040), (022) and (004). (b) Angular-integrated differential diffraction (20-40ps) for DJ n=3. (c)
 503 Differential diffraction pattern at 5ps (left) and 50ps (right). The increasing red colors in between
 504 the peaks correlate to the diffuse scattering intensities. (d) Time traces of the integrated diffuse
 505 scattering intensities integrated with the two squares in (c). Fitting errors are estimated by the one
 506 standard deviation errors computed from the variance of the fitting parameters from least-squares
 507 fitting.



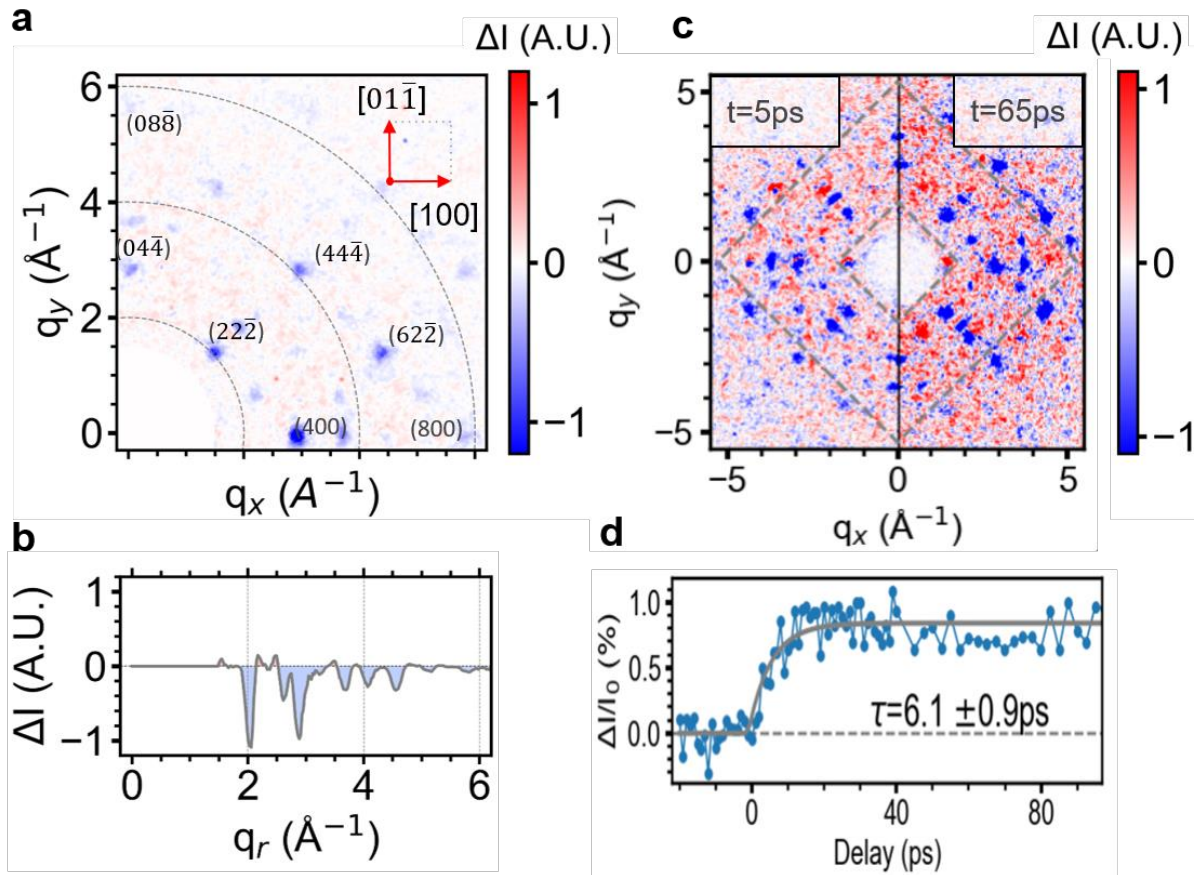
508

509 **Fig. S15 | Comparison of time traces of selected Bragg peaks in 2D perovskites. (a)** Time
 510 traces of DJ n=2 (400) (blue) and DJ n=3 (040) (orange) peak. Both peaks show a rapid increase
 511 in intensity. The rise-time constant fitted to be $\tau \sim 1.3$ ps (DJ n=2, blue solid line) and $\tau \sim 0.9$ ps (DJ
 512 n=3, orange solid line) respectively. **(b)** Time traces of RP n=2 (400) (green) and RP n=4 (400)
 513 (red) peak. Both peaks show a slower increase in intensity variations.



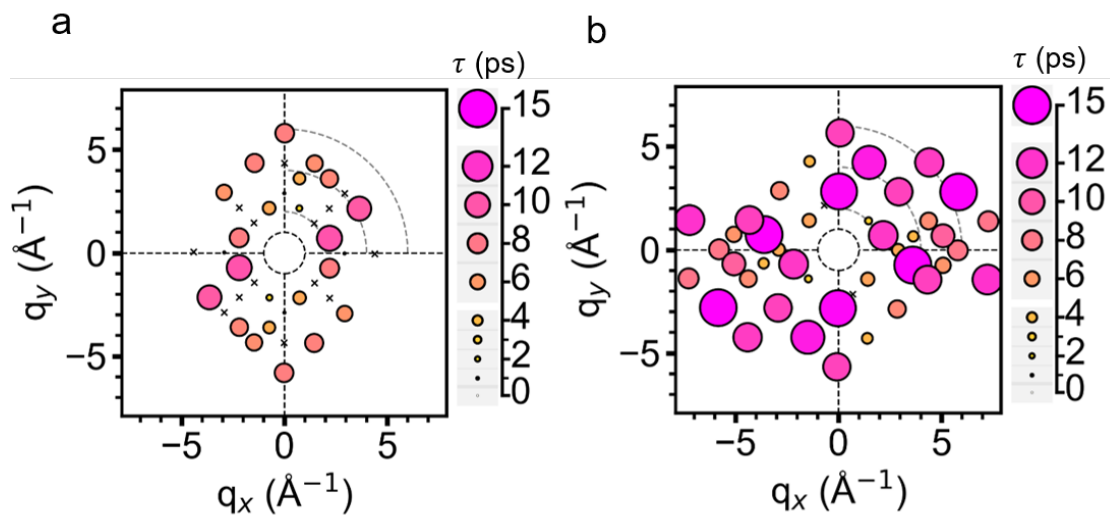
514

515 **Fig. S16 | Differential diffraction patterns of RP n=2.** (a) Differential diffraction pattern (15-
 516 40ps) for RP n=2, showing different response than DJ samples where no peaks increasing observed.
 517 (b) Angular-integrated differential diffraction (15-40ps) for RP n=2. (c) Differential diffraction
 518 pattern at 2ps (left) and 65ps (right). The increasing red colors in between the peaks correlate to
 519 the diffuse scattering intensities. (d) Time traces of the integrated diffuse scattering intensities
 520 integrated in-between the two squares in (c) (dashed line). Fitting errors are estimated by the one
 521 standard deviation errors computed from the variance of the fitting parameters from least-squares
 522 fitting.

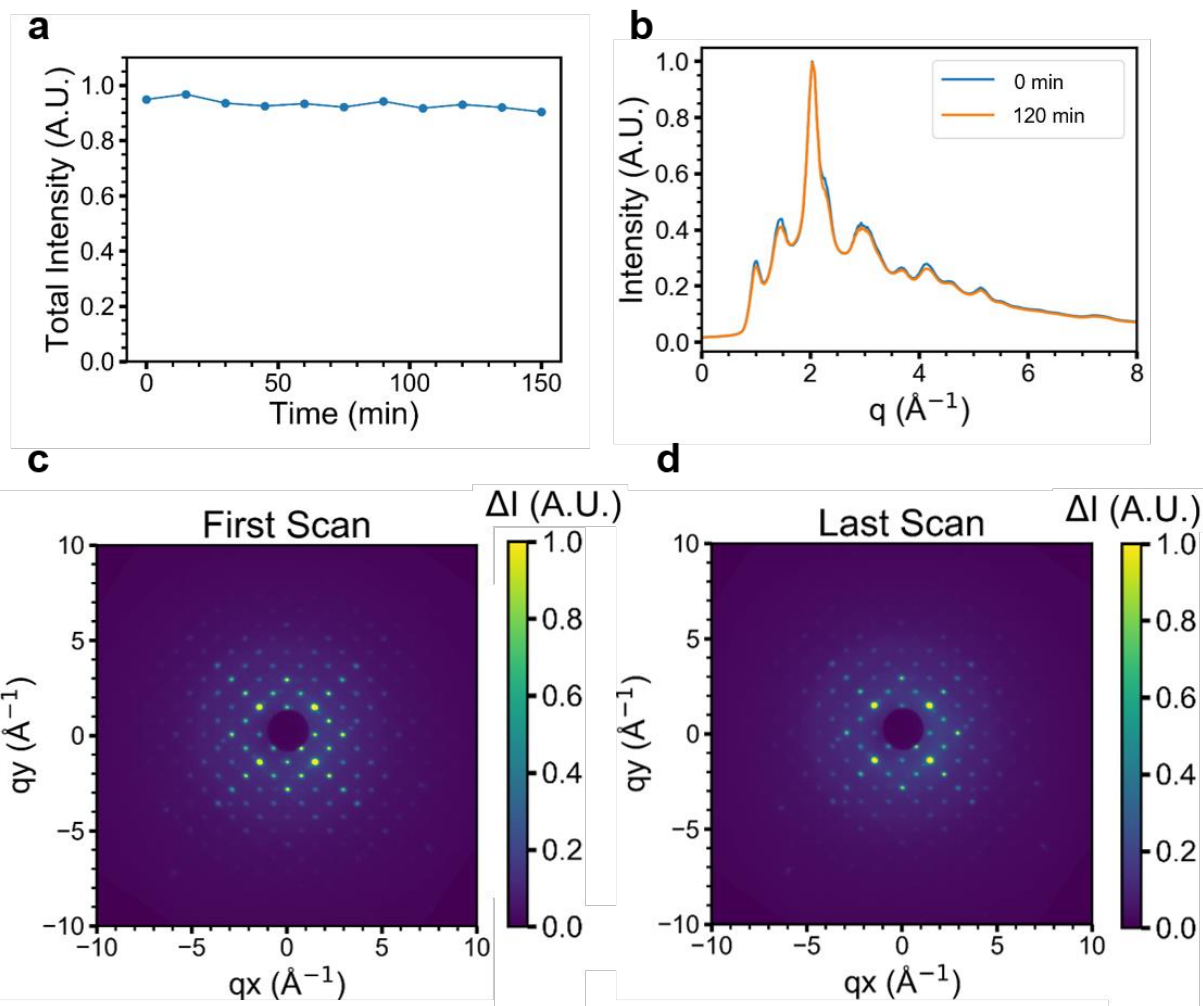


523

524 **Fig. S17 | Differential diffraction patterns of RP n=4.** (a) Differential diffraction pattern (20-
 525 40ps) for RP n=4, showing different response than DJ samples where no peaks increasing observed.
 526 (b) Angular-integrated differential diffraction (20-40ps) for RP n=4. (c) Differential diffraction
 527 pattern at 5ps (left) and 65ps (right). The increasing red colors in between the peaks correlate to
 528 the diffuse scattering intensities. (d) Time traces of the integrated diffuse scattering intensities
 529 integrated with the two squares in (c). Fitting errors are estimated by the one standard deviation
 530 errors computed from the variance of the fitting parameters from least-squares fitting.

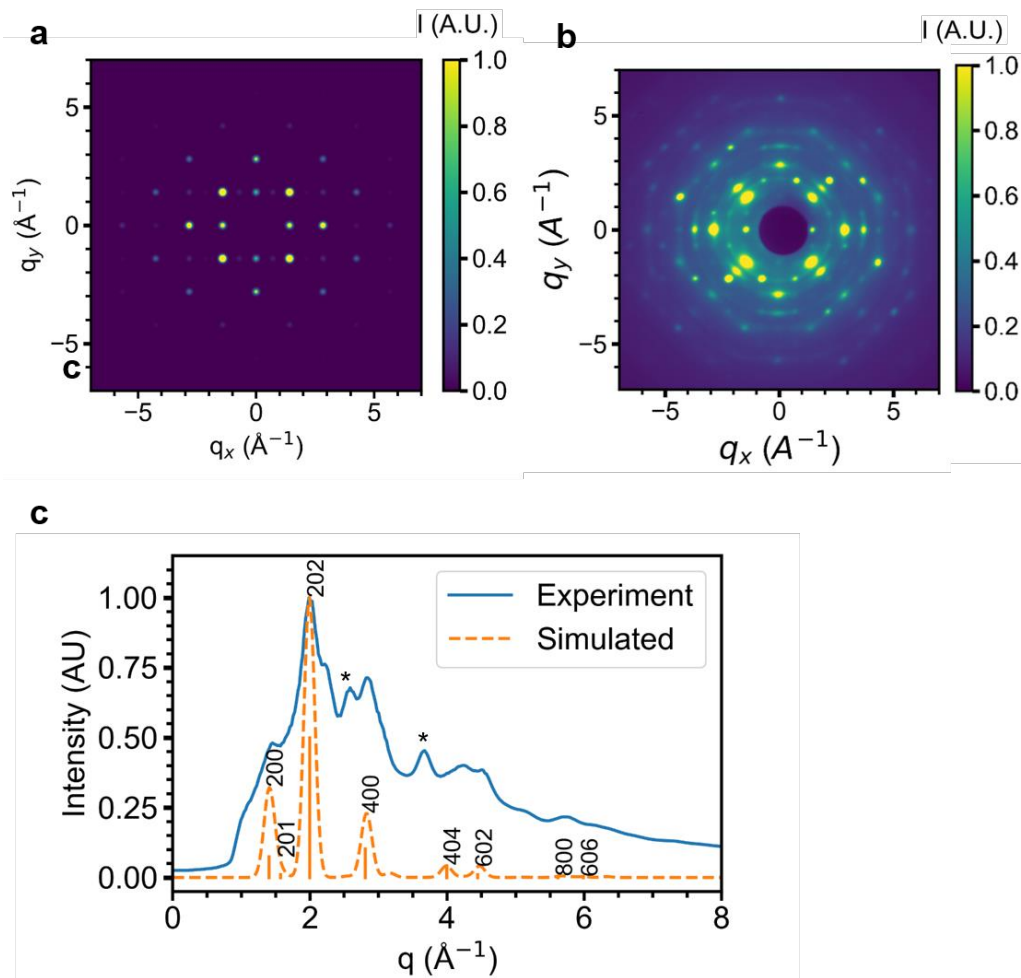


531
 532 **Fig. S18 | Time response comparison of different samples.** Scatter plots of time constants (τ)
 533 of **(a)** DJ $n=3$ and **(b)** RP $n=4$ are shown. All the time constants are extracted from single
 534 exponential time fitting of Bragg peaks (averaged within each pair $(hk0)$ and $(-h-k\ 0)$).



535

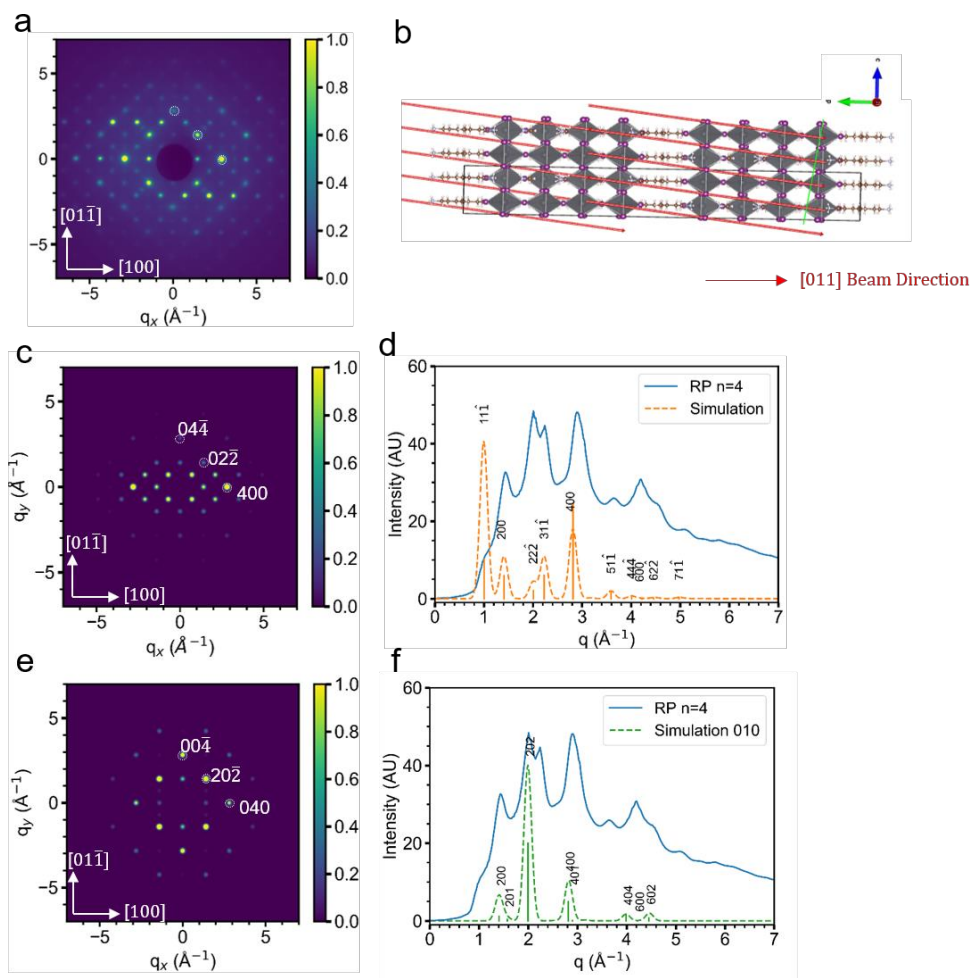
536 **Fig. S19 | Time Evolution of diffraction intensity of DJ n=2 crystal.** (a) Total electron
 537 diffraction intensity during UED measurements over 150mins. (b) Azimuth integrated plot of
 538 diffraction patterns taken at 0 min (blue) and 120mins (orange) after during the UED run. (c)(d)
 539 Diffraction images of (c) first and (d) last scan.



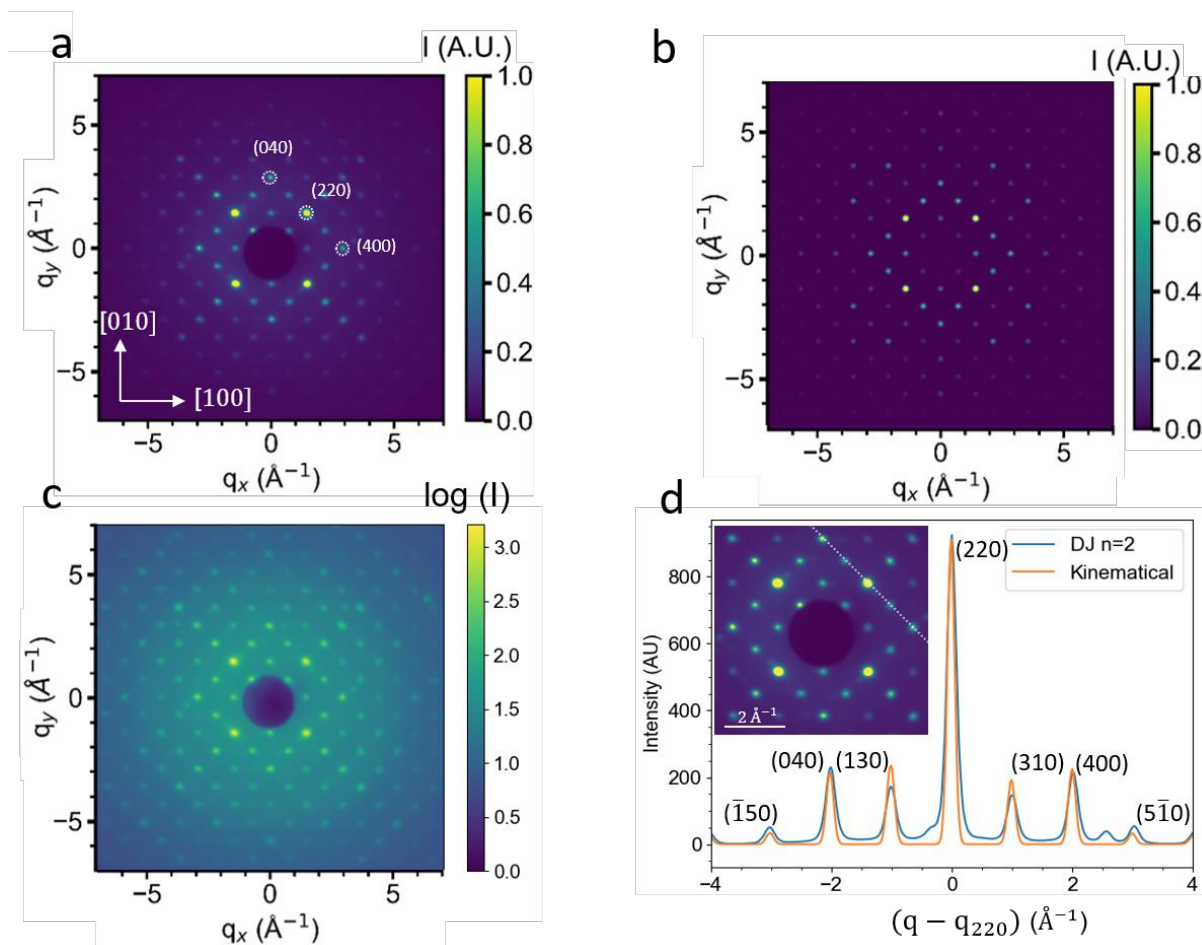
540

541 **Fig. S20 | Simulated Diffraction Pattern & Indexing of RP n=2 crystal.**

542 **(a)** Simulated Diffraction of DJ n=2, viewing from [010] direction. **(b)** Static Diffraction of RP
 543 n=2, showing same q -range as the simulated one in Fig. S20a. **(c)** Angular-integrated diffraction
 544 of RP n=2, showing both experimental (blue solid line) and simulated (orange dashed line) plots,
 545 as well as indexing of Bragg peaks (0hk).

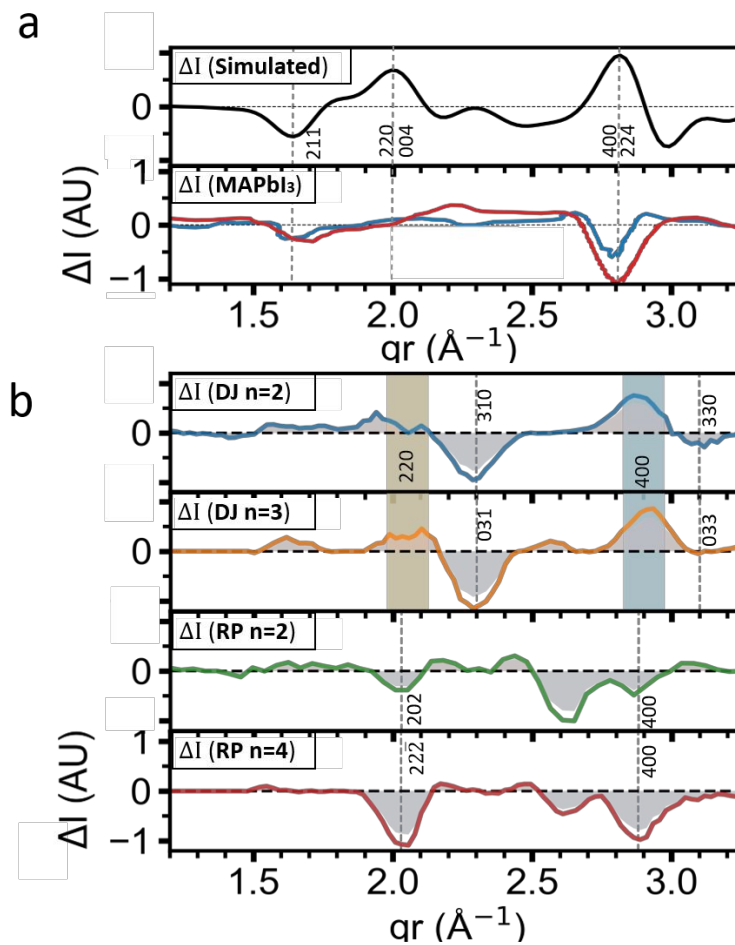


546
 547 **Fig. S21 | Simulated Diffraction Pattern & Indexing of RP n=4 crystal.** (a) Static Diffraction
 548 patterns of RP n=4. (b) Schematics of RP n=4 and indication of [011] direction (red arrows). (c)
 549 Simulated Diffraction of RP n=4 along [011] direction. (d) Angular-integrated diffraction of RP
 550 n=4 viewing at [011], showing both experimental (blue solid line) and simulated (orange dashed
 551 line) plots, as well as Indexing of Bragg peaks. (e) Simulated Diffraction of RP n=4 along [010]
 552 direction, showing a mismatch with experimental patterns. (f) Angular-integrated diffraction of
 553 RP n=4 viewing at [010], showing both experimental (blue solid line) and simulated (green dashed
 554 line) plots, as well as Indexing of Bragg peaks.



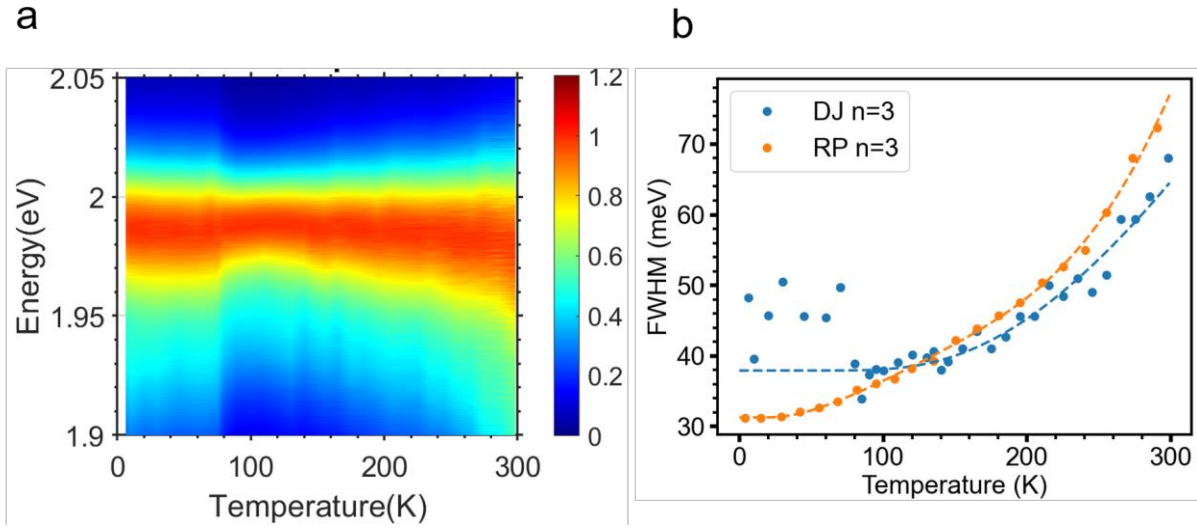
555

556 **Fig. S22 | Comparison of the diffraction pattern of DJ $n=2$ with kinematical theory.** (a) Static
 557 diffraction pattern of DJ $n=2$ crystal. (b) Simulated diffraction pattern with Kinematical scattering
 558 along c direction, computed from 4×4 supercell. (c) Logarithmic scale of the DJ $n=2$ diffraction
 559 pattern from (a), showing individual isolated Bragg peaks without Kikuchi lines. (d) Comparison
 560 of the linecuts of diffraction pattern along $(040)-(040)$ direction (indicated by white dashed line in
 561 inset), showing consistent intensity distributions between experimental diffractions (blue) and the
 562 ones from kinematic theory (orange).



563

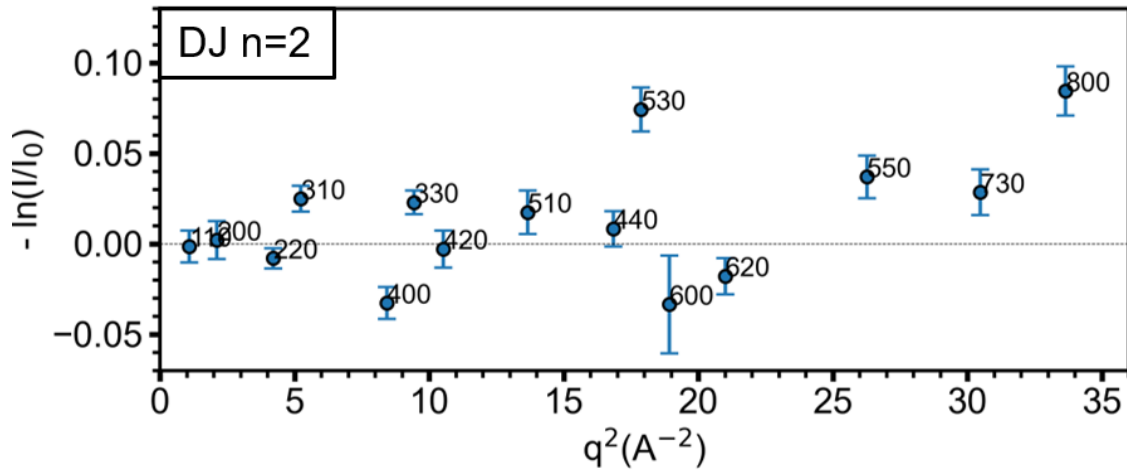
564 **Fig. S23 | Comparison of the angular-integrated diffraction of MAPbI₃, with 2D DJ and RP**
 565 **perovskites. (a)** The simulated differential diffraction pattern (black) is computed assuming a
 566 complete reduction of the antiferro-distorsion present in the tetragonal phase of MAPbI₃, leading
 567 to a cubic lattice. The Bragg indices are assigned for the initial tetragonal structure. The simulation
 568 is compared to the experimental differential diffraction curves of MAPbI₃ for delay time $t=5$ ps
 569 (blue) and $t=70$ ps (red) (Data extracted from Wu et al¹). **(b)** Differential diffraction plots of 2D
 570 perovskites reported in this work (Fig. 4c in manuscript).



571

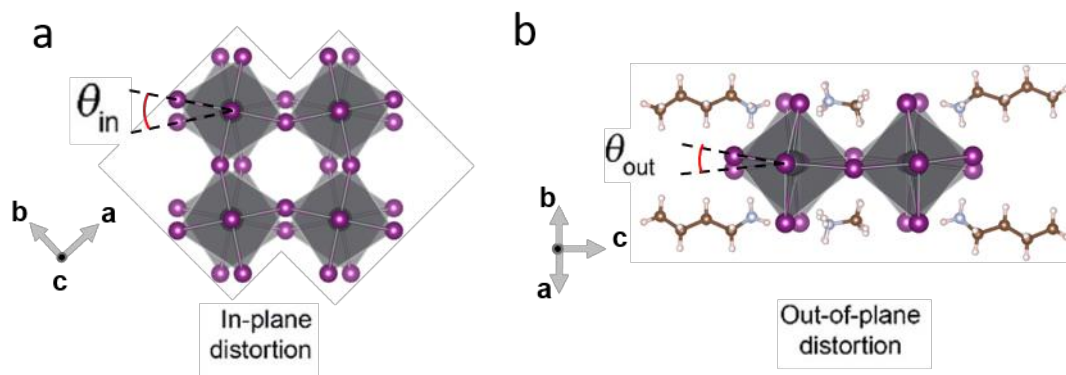
572 **Fig. S24 | Temperature dependent PL on DJ and RP n=3 crystal. (a)** Pseudo-colormap of PL
 573 as a function of temperature. **(b)** Extracted PL linewidth broadening, fitted with electron-LO
 574 phonon coupling model (dashed line).

575



576

577 **Fig. S25 | Semi-log plot of Bragg peaks intensity change as a function of q^2 for DJ n=2.**
 578 Logarithmic plot of Bragg peaks total relative intensity change ($-\log(I/I_0)$) DJ n=2 under pump
 579 fluence energy of $2\text{mJ}/\text{cm}^2$. Errors are estimated by the standard deviations of the intensity
 580 responses between 30 and 60ps (where quasi-equilibrium has been established for the Bragg peaks).



581
 582 **Fig. S26 | Illustration of in-plane and out-of-plane octahedral tilts. (a)(b)** Definitions of the in-
 583 plane and out-of-plane octahedral tilts, respectively. A list of the octahedral tilts for measured
 584 perovskites is displayed in Table S2. The stacking axis of the 2D-HaPs is represented along c axis.
 585 The organics are not displayed in (a) for simplified visualization.

586 **Supplementary Tables S1 - S2**

Sample Name	DJ n=2	DJ n=3	RP n=2	RP n=4
Excitation Energy (eV)	3.1	3.1	3.1	3.1
Fluence (mJ/cm ²):	2	2.2	0.45	2.5
Crystal thickness (nm):	270	450	200	380
Optical density (at 3.1eV):	2.2	2.5	2.5	2.5
Carrier density (cm ⁻²)	2.5×10 ¹³	2.3×10 ¹³	8.9×10 ¹²	4.2×10 ¹³

587

588 **Table. S1 | Lists of experimental conditions of the measured samples: crystal thickness,**
589 **excitation fluences and carrier densities.** Sample thickness are estimated from the optical
590 absorbance data in Fig. S1 for DJ n=2.

591

Sample Name	(4AMP)Pb ₂ I ₇ (DJ n=2)	(4AMP)Pb ₃ I ₁₀ (DJ n=3)	(BA) ₂ PbI ₂ I ₇ (RP n=2)	(BA) ₂ PbI ₄ I ₁₃ (RP n=4)	MAPbI ₃	SrTiO ₃ (< 1.5 K)	KTaO ₃
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Tetragonal	Tetragonal	Cubic
Structural phase	2D - DJ	2D - DJ	2D - RP	2D - RP	3D	3D	3D
Tilt (in-plane) (°)	11.78	11.2	0.02	0.03	/	/	/
Tilt (out-of-plane) (°)	0.72	0.46	7.66	6.42	/	/	/
Tilt (tetragonal axis) (°)	/	/	/	/	8.15	~2	0
Reference	3	3	4	4	13	27	32

592

593 **Table. S2 | List of interlayer octahedral tilts (order parameter θ) for halide and oxide**
594 **perovskites.** The values are extracted from the corresponding crystal structures at room
595 temperature (except for T<1.5K for SrTiO₃). For 2D perovskites, the octahedral tilts with in-plane
596 (along stacking axis) vs out-of-plane (perpendicular to stacking axis) directions are distinguished
597 (see Fig. S26). For 3D perovskites, similar tilt is defined along tetragonal axis.

598

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