

Geometric Frustration in Morphologically Chiral Nanoribbons of Layered Perovskites

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Comments for the Author)

This is great work. I have seen these crystals. The phenomenology is real, striking, and thought-provoking. As the authors concede: "Understanding the mechanism of spontaneous deformation and the subsequent controlled crystallization are both demanding subjects". Indeed. The characterization of the perovskite ribbons is very complete, the considerations of elasticity are sophisticated.

That said, there are several puzzles I cannot quite reckon. The authors take the great seed pod paper (ref. 10) and try to extend this bi-layer model to the perovskites. Maybe this analog can apply but I am not certain. That doesn't mean that choosing a model and trying to fit it to the data is not a worthy challenge, with results worth reporting. However, there are so many helicoidal crystals that can not be modeled similarly, I will keep an open mind until the work further develops.

A number of my comments refer to the accuracy of the citations. Apologies. I have spent a lot of time with this literature. Ref. 1 is mainly about crystals that have become distorted in response to external mechanical or chemical forces. There is just a short section about crystals that grow as helicoids. A better review about growth-induced bending and twisting is this one: Shtukenberg AG, Punin YO, Gujral A, Kahr B. Growth actuated bending and twisting of single crystals. *Angewandte Chemie International Edition*. 2014 Jan 13;53(3):672-99. It is wholly about growth phenomena.

The authors cite ref. 13 in the following context: "in contrast to morphological chirality observed in particle aggregates¹³." I am not sure why this work is cited in the context of "particle attachment." However, it is a very good reference for the mechanism that the authors are wishing to promote. If you look in ref. 13, Figure 4, you can see pairs of benzamide crystals growing near parallel to one another. As the top crystal advances, the pair twists. As the top crystal retreats, the pair straightens. It is a crystalline analogy to the seed pod mechanism. Indeed, seed pod author Efi Efrati is one of the authors of ref. 13. This is strong evidence for crystallography-induced twisting on lengths/widths scales that are relevant to the perovskites.

On page 8, the authors describe the handedness correlations from small angle branching and secondary nucleation. "Handedness analysis of every crystallite within each cluster revealed remarkable chirality coherence, which was predetermined by the nucleating core." We have previously described the twist sense in a variety of materials being determined over mm² areas that are determined by the sense of the faces on the proto-nucleus of the core. The first example is in this paper: Cui X, Rohl AL, Shtukenberg A, Kahr B. Twisted aspirin crystals. *Journal of the American Chemical Society*. 2013 Mar 6;135(9):3395-8. Feel free to put your observations in context if you wish. I am not trying to raise my citation counts. Merely, I have a long experience studying the surprising generality of helicoidal crystallization.

On page 7, the authors write: "Due to the centrosymmetric crystal structure and the absence of chiral reagents during crystal growth, our ribbons exhibited negligible handedness preference." I don't understand what the author mean. Both space groups, P21/n and P-1 for BrCA3, are centrosymmetric. Despite the symmetry reduction, all the crystals are centric. Thus, there are no stereochemical puzzles that can be solved by differentiating the symmetries, 2/m vs -1. That said, the bilayer model is itself a mystery. Whatever happens in one bilayer, it will be undone crystallographically by the adjacent layer. The undeniable puzzle is the fact that whatever happens in a proto-bilayer, this handedness is somehow propagated. How this is propagated is not answered by the model. I would argue that the authors ought to be clearer about how the seed pod model collides with crystallography. On page 6, the authors, over several paragraphs, summarize their argument here: "At this

moment, the requirements have been satisfied for geometric frustration...It is thus expected that the mechanic and geometric frustration can be preserved within a much larger range of dimensions...and subsequently amplified by kinetic control." I am unable to join the authors on this journey. That doesn't mean that the model can't apply to the perovskites, but there is part of the mechanism, after the selection "at this moment", that continues to be vague, to the extent that I fully understand the modeling.

The transformation of the helicoids to spiraling ribbons is instructive. It suggests a relaxation mechanism by changing the angle between the monolayers that are straining against one another. This is quite different from untwisting as in ref. 22. It speaks to what may be truly unique about the perovskite system.

Small corrections

P2, L45. The authors give the IUPAC name and then say "which was derivatized with a fluorine". Without reference to Figure 2 here, the only place where the chemical structure appears, one is stymied by trying to decode the name and then deciding where the extra fluorine goes after derivatization. But there is no extra fluorine. The authors are referring to the fluorine already present in the structure named. This all could be clearer.

P4, L17. A cross-reference to the seed pod paper should appear here.

Reviewer #3

(Comments for the Author)

This manuscript reports a striking example of spontaneous morphological chirality in an achiral layered 2D perovskite, where twisted/helical nanoribbons emerge from incompatible elasticity arising from misaligned organic lattices that feature hydrogen-bonding frameworks. The authors draw inspiration from the chiral opening of seed pods in biological systems and translate the underlying mechanical/mathematical concepts into a compelling framework for 2D perovskite crystal engineering, enabling potential ensemble-level handedness control and measurable chiroptical activity. The breadth of work, spanning synthesis, structural characterization, molecular dynamics simulations, and modeling, is impressive. Overall, the story is very exciting and should be of broad interest to both the chiral materials community and researchers focused on fundamental crystal growth and morphology engineering in layered and nano- materials. It also offers an appealing alternative strategy for introducing chirality into 2D perovskites, a rapidly growing and hot research area.

I am generally positive and believe the manuscript could be suitable for publication. Nevertheless, I think the manuscript would be strengthened by addressing the following points.

1. From the optical and SEM images in the main text and SI, some ribbons appear to be flat or only weakly deformed. It would be helpful if the authors could clarify why twisting does not occur in these cases. Is there a criterion (e.g., thickness/width window, growth rate) that determines whether a ribbon twists? In addition, based on the mechanical frustration model (Eqs. 1–3), are thinner or wider ribbons expected to twist more readily (or how does the predicted twist depend on thickness and width from the view of the thermodynamic driving force, i.e., competing elastic strain and torsional deformation)?
2. Related to point 1, do the authors observe that twisting is more prevalent for a particular dimensional regime (e.g., nanoribbons vs microplates), or for a particular aspect ratio? A short summary would strengthen the discussion.
3. FCA3 and BrCA3 appear structurally similar. Could the authors provide a possible explanation for why FCA3 exhibits a 21 screw axis, whereas this feature is absent for BrCA3? A discussion in terms of factors affecting the packing preferences would be useful.
4. In the authors' previous work (Science 2024, 384, 1000), (BrCA3)2PbI4 occasionally also formed twisted nanowires, yet its crystal structure appears isostructural to (BrCA3)2PbBr4. Did the authors observe similar behavior in (BrCA3)2PbBr4? And how to rationalize such a behavior.
5. As far as we know, 2D perovskites exhibiting 21 screw axes is not unique to FCA3 and these structures would plausibly exhibit misaligned strains between the two organic layers, similar to the FCA3 case. Since this feature appears important for generating twist, it would be valuable to add a broader discussion (or a short design rule) on how to extend the concept to other spacers. In particular, is FCA3 exceptional, or is it simply one demonstrator within a larger design space?
6. The observation of CD from twisted ribbons whose pitch is far larger than the optical wavelength is intriguing. Can the authors have some possible explanations. In Extended Data Fig. 4, a higher-magnification zoom showing the highlighted CCW and CW structures would be helpful. Also, for the regions used to acquire the spectra in panels (c) and (d), what is the local pitch? A CD measurement on a flat microplate (or an untwisted ribbon ensemble) as a control would be useful.
7. Trend of w/t vs cooling rate in Fig. 3b is not clearly explained.
8. On page 7, it is unclear how the BrCA3 doping level was quantified from single-crystal XRD, since partial occupancy/disorder of organic spacers can be difficult to refine unambiguously. In addition, in Extended Data Fig. 2, it would be helpful to include representative morphology images of the doped samples for direct comparison with the other two systems.
9. The Methods section would benefit from more details, for example, the conditions used for the growth videos (cooling control method, imaging configuration) and the excitation spot size used in the chiroptical measurements.
10. Several typos are present. For example, on page 7, the sentence fragment "eliminating the spontaneous deformation observed in FCA3-based systems." and in Extended Data Fig. 2 the label "PbBr64– lattices."

Reviewer #4

(Comments for the Author)

This manuscript reports the observation of spontaneous morphological chirality in achiral layered metal-halide perovskites. The authors attribute this behavior to a form of geometric frustration, arising from an approximately 50° misalignment between two hydrogen-bonded organic frameworks (HOFs) across an inorganic slab. This misalignment is proposed to generate competing uniaxial strains, which are relieved through the formation of twisted and helical ribbon morphologies. By combining microscopy, molecular dynamics simulations, and mechanical modeling, the study presents a coherent picture of how structural frustration at the molecular scale may translate into mesoscale chiral morphologies. More broadly, the emergence of chirality from nominally achiral building blocks remains an important topic across chemistry, materials science, and biology. In recent years, there has been growing interest in morphology-driven chirality, particularly in soft matter and low-dimensional systems, where mechanical and interfacial effects can play a dominant role. Within the context of metal-halide perovskites, which are already known for their structural tunability and rich optoelectronic properties, the possibility of inducing chiral responses through purely morphological means is potentially relevant for areas such as chiroptical materials, polarization-sensitive photonics, and enantioselective interactions. From this perspective, the present work offers an interesting example of how geometric frustration could serve as a design principle for generating chiral architectures without requiring intrinsically chiral components. At the same time, because morphology-induced chirality is often sensitive to growth conditions, structural heterogeneity, and measurement geometry, careful characterization is important to establish the robustness and generality of the observations. While the overall approach in this manuscript is thoughtful and the results are intriguing, making me consider this work recommendable for publishing in *Nature Synthesis*, there are several points that would benefit from clarification or further support.

1. The manuscript would also benefit from a more complete discussion of prior work on chiral perovskite interfaces. There are a number of earlier studies involving intrinsically chiral organic cations, chirality emerging at hybrid interfaces, as well as morphology- or interface-induced chiroptical effects. These different classes of structures can give rise to optical, electronic, and mechanical responses at multiple length scales. Providing a more structured overview of these prior approaches would help place the present work in context. In particular, it would be useful for the authors to clarify how the system reported here differs from previous examples in terms of the origin of chirality and its functional consequences, and whether the morphology-induced chirality observed in this study offers any distinct advantages or limitations compared to existing strategies.

2. Chiral perovskite interfaces have also recently been reported to influence mechanical properties (see, DOI: 10.1126/science.ad05172). In this context, it would be interesting to consider whether the chiral ribbons observed in this work exhibit any distinct mechanical behavior compared to non-chiral or untwisted counterparts. While a full mechanical characterization may be beyond the scope of the present study, the authors could at least comment on this aspect and, where appropriate, relate their observations to existing studies on structure–mechanics coupling in chiral perovskite systems. Establishing such a connection would help place the current results within a broader framework and highlight potential functional implications of morphology-induced chirality.

3. While the manuscript describes a transition from twisted to helical morphologies, it is not clear how commonly this transition occurs. Providing statistical information on the fraction of ribbons exhibiting each morphology, and how this may vary between samples, would help place this observation in context.

4. For chiral materials, it is common to report the anisotropy (g -) factor to quantify circular dichroism (CD) signals. It would be helpful if the authors could either estimate the g -factor for this system or briefly comment on whether such a metric is appropriate in the case of morphology-induced chirality.

5. A control measurement on non-deformed crystals of the same composition would help confirm that the observed CD signals originate from the chiral morphology rather than other possible effects.

6. Although single-crystal XRD on twisted ribbons may be challenging, powder XRD measurements on these crystals could still provide useful information. Comparing such data with the bulk crystal structure may help verify structural consistency.

7. In the section “Crystallographic Control of Morphological Chirality,” the manuscript notes that 0.92 mol% BrCA3 leads to a change in space group from $P2_1/n$ to $P1$. Given the low dopant concentration, it would be helpful to clarify whether this reflects a uniform phase transition or whether there could be undetected phase segregation or domain formation.

8. Relatedly, some discussion of why a halogen substitution (Br to F) leads to a substantial change in crystal structure would improve the chemical context, even if only at a qualitative level.

9. The reported dimensionless width of 1.34 shows a narrow distribution. It would be useful to comment on whether this value is intrinsic to the system or whether it depends on growth conditions such as temperature or solvent.

10. The molecular dynamics simulations are based on a nanoscale monolayer, whereas the experimental structures are much larger and multilayered. A brief discussion of how these simulations relate to the behavior of bulk-like ribbons, particularly regarding the propagation of geometric frustration across many layers, would be helpful.

11. In the SI, the curvature fitting method uses the 81 nearest lead atoms. It would be useful to clarify whether edge atoms were excluded from this analysis, as their local environment may differ from that of the interior.

12. The CD measurements were performed on relatively large, hyperbranched clusters. Based on the provided images, the handedness does not appear fully uniform across these structures. It would be helpful to clarify how the measurement accounts for this, for example in terms of beam spot size or possible averaging over domains of opposite handedness.

13. It would be helpful to report the degree of linear polarization in Supplementary Figure S5, as this could be relevant for evaluating possible contributions from linear optical effects.

Reviewer #5

(Comments for the Author)

This work systematically demonstrates that through molecular design (FCA3), linearly aligned HOFs that are misaligned with respect to each other are introduced into non-chiral layered perovskites, generating incompatible strain that induces morphological chiral twisting. Geometric frustration in layered perovskites to generate morphological chirality are potentially novel. However, the central argument—misaligned lattice strain is the origin of geometric frustration and the formation of twist ribbon—exhibits a logical gap with the observed low twisting probability (<1%). The following concerns need to be addressed:

1. Figure 1e only shows the normalized PL spectral overlap between flat microplates and twisted ribbons. The similarity only indicates that the spectral shape does not change significantly, which is insufficient to support the conclusion that "bending and chiral deformation did not interfere with the PL." It is recommended to provide key parameters such as peak position (λ_{max}), FWHM, and emission intensity, along with statistics from multiple twisted ribbons presented as mean and standard deviation, rather than a single representative curve.

2. SEM analysis of 1,510 samples confirms a CW:CCW ratio of 674:836. The original manuscript only reports the ratio without specifying the statistical source of these samples. For example, how many independent sample batches did these 1,510 samples come from? Do both CW and CCW samples coexist within the same batch? Is there any regional variation? Is there a chirality bias between different batches? The authors should clearly explain the statistical source to avoid the possibility that the near 1:1 ratio overall masks batch-to-batch or region-to-region chirality bias.

3. Undeformed bulk single crystals show that misaligned HOFs are an intrinsic structural feature of the crystals, and the authors attribute morphological chirality to misaligned linear HOFs within a monolayer. However, the establishment of this mechanism is primarily based on less than 1% of twisted ribbon events. Why did only <1% of crystals grow into twisted nanoribbons during rapid crystallization? If misaligned strain were a sufficient condition, this proportion would be far too low. The authors have never mentioned whether this proportion changes under other cooling conditions. Moreover, the misaligned linear HOFs were observed in undeformed bulk single crystals. Does this imply that an additional kinetic trigger (such as a specific supersaturation, growth rate, or stochastic nucleation event) is required to activate twisting? Does an energy barrier exist from flat to twisted morphology? The authors should provide an explicit discussion on this matter.

4. The authors have provided statistics showing the effect of cooling rate on w/t, do the pitch, or node density of helical ribbons show systematic changes? Please provide relevant analysis.

5. If 0.5% doping completely suppresses twisting, while the twisting proportion in the neat FCA3 system is <1%. How can one rule out the possibility that the doping result is explained by statistical fluctuations or sample inhomogeneity rather than necessarily being attributed to symmetry changes? The authors need to provide statistically meaningful data for support, based on 'the probability of observing at least one twisted crystal if the twisting ability remains at 1%'.

6. MD simulations show that a single molecular layer (10 × 40 nm) alone can generate twisting. However, the experimental twisted ribbons have thicknesses ranging from 30 nm to 2 μm (approximately 10–700 inorganic layers). Does interlayer coupling enhance or counteract twisting? As thickness increases, do the pitch or node density of the twists show systematic changes?

7. The ribbon forests used for CD measurements were grown directly in a 10-μm-thick sealed quartz confined space and remained immersed in the mother liquor throughout subsequent measurements. This means that the quartz substrate/interface is not merely a "measurement platform" but rather an integral part of the crystal nucleation and growth environment. Therefore, whether different substrate or interface conditions affect the nucleation mode, growth pathway, branching morphology, and chirality coherence within a given cluster should be seriously discussed.

8. The structure difference between (n-butylammonium)₂PbBr₄ and (FCA3)₂PbBr₄ is substantial, especially given the authors' claim that misaligned HOFs and strain are the core drivers of twisting. Is it reasonable to use the same shear modulus value? Is there experimental or computational support for the shear modulus of the FCA3-based system being close to 40 MPa?

Version 1:

Reviewer comments:

Reviewer #3

(Comments for the Author)

The authors have addressed all of my questions, and I have no additional comments.

Reviewer #5

(Comments for the Author)

The authors have thoroughly addressed all the issues raised. I am happy to recommend acceptance.

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RESPONSE LETTER

A List of All Revisions and Responses to Referees' Comments for Nature Synthesis Manuscript: NATSYNTH-26010091.

- Revised texts in the main article or supplementary materials are highlighted in grey.
- Response to the referees' comments is marked in blue.

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Response to Reviewer #1

This is great work. I have seen these crystals. The phenomenology is real, striking, and thought-provoking. As the authors concede: "Understanding the mechanism of spontaneous deformation and the subsequent controlled crystallization are both demanding subjects". Indeed. The characterization of the perovskite ribbons is very complete, the considerations of elasticity are sophisticated.

That said, there are several puzzles I cannot quite reckon. The authors take the great seed pod paper (ref. 10) and try to extend this bi-layer model to the perovskites. Maybe this analog can apply but I am not certain. That doesn't mean that choosing a model and trying to fit it to the data is not a worthy challenge, with results worth reporting. However, there are so many helicoidal crystals that can not be modeled similarly, I will keep an open mind until the work further develops.

Answer: Thank you for the support of our work, the in-depth reading, and the important mechanistic criticism. The suggested precedents (growth-actuated bending and twisting and the benzamide and aspirin analogues) situate our system correctly. The decisive challenge (Comment 4.2) named a gap we had left open: in a centrosymmetric stack, each monolayer's twisting tendency is reversed by its inversion-related neighbor, so how can frustration, let alone handedness, survive and propagate? We now formalize this reasoning in Supplementary Note 1, turning the reviewer's paradox into the mechanistic core of the paper. Please find our detailed response below.

Comment 1. A number of my comments refer to the accuracy of the citations. Apologies. I have spent a lot of time with this literature. Ref. 1 is mainly about crystals that have become distorted in response to external mechanical or chemical forces. There is just a short section about crystals

that grow as helicoids. A better review about growth-induced bending and twisting is this one: Shtukenberg AG, Punin YO, Gujral A, Kahr B. Growth actuated bending and twisting of single crystals. *Angewandte Chemie International Edition*. 2014 Jan 13;53(3):672-99. It is wholly about growth phenomena.

Answer: Thanks for the suggestion. We have modified Ref. 1 accordingly.

1. Shtukenberg, A. G., Punin, Y. O., Gujral, A. & Kahr, B. Growth actuated bending and twisting of single crystals. *Angew. Chemie - Int. Ed.* 53, 672–699 (2014).

Comment 2. The authors cite ref. 13 in the following context: “in contrast to morphological chirality observed in particle aggregates¹³.” I am not sure why this work is cited in the context of “particle attachment.” However, it is a very good reference for the mechanism that the authors are wishing to promote. If you look in ref. 13, Figure 4, you can see pairs of benzamide crystals growing near parallel to one another. As the top crystal advances, the pair twists. As the top crystal retreats, the pair straightens. It is a crystalline analogy to the seed pod mechanism. Indeed, seed pod author Efi Efrati is one of the authors of ref. 13. This is strong evidence for crystallography-induced twisting on lengths/widths scales that are relevant to the perovskites.

Answer: We appreciate the reviewer pointing this out. We misunderstood the results from Ref. 13 (now ref. 16) by the fine internal structure of benzamide crystals upon sublimation (Fig. 1i in the reference) and thought that each single twisted benzamide ribbon was made of random particle attachments. Ref. 13 indeed is a very good reference showing crystallography-induced twisting that generates twisted ribbons of organic crystals with a spontaneous deformation behavior very similar to our perovskite system.

The original citation of Ref. 13 was removed from its original place near line 32 on page 6 of the main text.

... in contrast to morphological chirality observed in ordered attachment of twin domains¹⁷, doped crystals^{18,19}, or even self-assembled amphiphile bilayers²⁰...

Instead, we moved it to line 18 on page 4, where the in-situ growth behavior of 2D perovskite twisted ribbons was described.

... a period of ~8.5 minutes. The in-situ growth behavior is very similar to that observed in spontaneously twisted organic single-crystalline microribbons¹⁶. The longitudinal...

16. Shtukenberg, A. G., Drori, R., Sturm, E. V., Vidavsky, N., Haddad, A., Zheng, J., Estroff, L. A., Weissman, H., Wolf, S. G., Shimoni, E., Li, C., Fellah, N., Efrati, E. & Kahr, B. Crystals of Benzamide, the First Polymorphous Molecular Compound, Are Helicoidal. *Angew. Chemie - Int. Ed.* 59, 14593–14601 (2020).

17. Imai, H. & Oaki, Y. *Emergence of morphological chirality from twinned crystals. Angew. Chemie - Int. Ed.* **43**, 1363–1368 (2004).
18. Qiu, X. D., Chen, L., Hou, J. W., Lin, H. Y., Xu, T. Y., Tong, F., Tian, H. & Qu, D. H. *Regulating Reversible Untwisting and Twisting Motions in Helical Dynamic Molecular Crystals. J. Am. Chem. Soc.* **147**, 17772–17783 (2025).
19. Tong, F., Kitagawa, D., Bushnak, I., Al-Kaysi, R. O. & Bardeen, C. J. *Light-Powered Autonomous Flagella-Like Motion of Molecular Crystal Microwires. Angew. Chemie - Int. Ed.* **60**, 2414–2423 (2021).
20. Cho, Y., Choi, Y. J., Kaser, S. J., Meacham, R., Christoff-Tempesta, T., Wu, S., Zuo, X. & Ortony, J. H. *Geometric Transformations Afforded by Rotational Freedom in Aramid Amphiphile Nanostructures. J. Am. Chem. Soc.* **145**, 22954–22963 (2023).

Comment 3. On page 8, the authors describe the handedness correlations from small angle branching and secondary nucleation. “Handedness analysis of every crystallite within each cluster revealed remarkable chirality coherence, which was predetermined by the nucleating core.” We have previously described the twist sense in a variety of materials being determined over mm² areas that are determined by the sense of the faces on the proto-nucleus of the core. The first example is in this paper: Cui X, Rohl AL, Shtukenberg A, Kahr B. Twisted aspirin crystals. *Journal of the American Chemical Society*. 2013 Mar 6;135(9):3395-8. Feel free to put your observations in context if you wish. I am not trying to raise my citation counts. Merely, I have a long experience studying the surprising generality of helicoidal crystallization.

Answer: Thank you for the suggested reference. It supports our observation well and we’ve referenced it in the text.

(page 9, line ~8) Newly formed crystals thus inherit the handedness of their predecessors, creating a cascade of chirality amplification as reported in many organic twisted crystal systems²³.

23. Cui, X., Rohl, A. L., Shtukenberg, A. & Kahr, B. *Twisted aspirin crystals. J. Am. Chem. Soc.* **135**, 3395–3398 (2013).

Comment 4.1. On page 7, the authors write: “Due to the centrosymmetric crystal structure and the absence of chiral reagents during crystal growth, our ribbons exhibited negligible handedness preference.” I don’t understand what the author mean. Both space groups, P21/n and P-1 for BrCA3, are centrosymmetric. Despite the symmetry reduction, all the crystals are centric. Thus, there are no stereochemical puzzles that can be solved by differentiating the symmetries, 2/m vs -1.

Answer: Thank you for pointing out the confusion point. This sentence on page 7 is to, first, address again that the morphological chirality exhibited by our 2D perovskite crystals originated

from lattice-mediated mechanical frustration and spontaneous deformation during growth, instead of chiral crystal structure, chiral components, or chiral reagents, which are often used in the field to induce macroscopic chirality. Second, this sentence also addresses the following context that without the aforementioned molecular-level chirality contributors, which, arguably can generate a preferential macroscopic morphological handedness, our crystals exhibit minimal handedness preference.

Comment 4.2. That said, the bilayer model is itself a mystery. Whatever happens in one bilayer, it will be undone crystallographically by the adjacent layer. The undeniable puzzle is the fact that whatever happens in a proto-bilayer, this handedness is somehow propagated. How this is propagated is not answered by the model. I would argue that the authors ought to be clearer about how the seed pod model collides with crystallography.

Answer: We appreciate this critical comment. This is a genuine caveat that our original text left unresolved. The reviewer is entirely correct: adjacent monolayers are related by the inversion center in the organic interlayer gap. Yet, the implication is that they therefore carry twisting tendencies of opposite sense but additively stackable strain. We have revised the manuscript to address directly how frustration and handedness survive this crystallographic constraint.

The resolution rests on distinguishing what inversion changes from what it preserves. Inversion reverses the sense of the twist that a monolayer induces, but it leaves the stored incompatible strain unchanged, because the elastic energy scales with the square of the misaligned strain and is blind to its sign. In other words, across the two adjacent monolayers that construct a centrosymmetric stack, the magnitude of frustration accumulates coherently while the preferred twist direction averages to zero.

This accumulation is independently supported by our statistical data: the pitch follows $p \propto \sqrt{J/wt}$ across the full dataset (thickness ~ 30 nm to $3.3\ \mu\text{m}$ or ~ 15 to 1,650 monolayers, Fig. 3d), which requires the twist energy density to be constant per unit volume. Every monolayer thus contributes equally to the driving force, as expected if the frustration magnitude is set by the inversion-invariant strain and adds with each layer.

If the lattice encodes frustration without handedness, the twist sense must be selected spontaneously as each ribbon forms, with no global bias. The near-equal CW:CCW ratio we observed (674:836 among 1,510 ribbons) is a clear manifestation of this fact. Handedness is then propagated not crystallographically, through the unit cell, but kinetically, through templated secondary nucleation (Extended Data Fig. 4), which is why an entire hyperbranched cluster shares a single handedness inherited from its nucleating core while the population as a whole remains racemic. We have added this reasoning to the main text and clarified the corresponding passages.

This incompatible elasticity within a monolayer propagates as the layers are stacked together. Adjacent monolayers are related by the inversion center in organic sublattices (Fig. 2d). Yet, inversion preserves the magnitude of the stored strain in a monolayer (Supplementary Note 1). In fact, geometric frustration has been expressed...

A reinforcement of the symmetric caveat was added to the discussion of handedness preference:

Handedness in helicoids is defined by the twist direction. Right-handed ribbons twist clockwise (CW) while left-handed twist counterclockwise (CCW). Because the centrosymmetric lattice encodes the frustration but not its handedness, each ribbon's twist direction is selected spontaneously as it forms rather than predetermined. Consistent with this, SEM analysis of 1,510 ribbons gave a near-equal CW:CCW ratio of 674:836 (Supplementary Table S1).

Further, we note that the precise microscopic event that first breaks the symmetry in a given ribbon, such as a nucleation fluctuation or a surface/edge asymmetry, remains an open question.

An additional Supplementary Note. 1. Propagation of Geometric Frustration Across Centrosymmetric Lattices was added to the revised Supplementary Materials, which was not pasted here for brevity.

Comment 5. On page 6, the authors, over several paragraphs, summarize their argument here: “At this moment, the requirements have been satisfied for geometric frustration...It is thus expected that the mechanic and geometric frustration can be preserved within a much larger range of dimensions...and subsequently amplified by kinetic control.” I am unable to join the authors on this journey. That doesn’t mean that the model can’t apply to the perovskites, but there is part of the mechanism, after the selection “at this moment”, that continues to be vague, to the extent that I fully understand the modeling.

Answer: Thank you for identifying the clarity issues within these important summary paragraphs. We found two logical steps left implicit, and the revision is proposed as follows:

1) Explicitly connecting the geometric model in 2D perovskites to the seed pod case. $[110]$ and $[1\bar{1}0]$ are the exact bisectors of the two HOF strain directions $[210]$ and $[2\bar{1}0]$ just as in the seed pod model, where the pod valve propagates along the direction bisecting the two fibril strain axes.

At this moment, the requirements have been satisfied for geometric frustration in layered perovskites, with two misaligned linear HOFs exerting incompatible uniaxial strains along $[210]$ and $[2\bar{1}0]$, and one inorganic lattice sandwiched in between

directing the ribbon growth along $[110]$ or $[1\bar{1}0]$. Thus, the longitudinal ribbon axis bisects the two HOF strain directions, which is analogous to the seed pod model where pod valves propagate along the bisector of two fibril strain axes.

2) Upon connecting the deformation of CdSe nanoribbons with layered perovskites, the assertion “it is thus expected that the mechanical and geometric frustration can be preserved within a much larger range of dimensions” should be replaced with a mechanistic argument.

Such systems would be thickness limited to <10 nm since misaligned ligands occupy only the two opposing ribbon surfaces and are progressively overwhelmed by bulk elastic resistance as the crystal thickens.

In contrast, layered perovskites are over 50% organic by volume, with each inorganic layer flanked by two organic layers with a misaligned HOF pair. Intuitively, the frustration driving force scales with volume rather than surface area and is therefore expected to persist across a much larger range of thicknesses.

We believe these two additions will allow the reader to follow the arguments without ambiguity.

Comment 6. The transformation of the helicoids to spiraling ribbons is instructive. It suggests a relaxation mechanism by changing the angle between the monolayers that are straining against one another. This is quite different from untwisting as in ref. 22. It speaks to what may be truly unique about the perovskite system.

Answer: We are glad this resonates with the reviewer. The transition in our system is indeed distinct from untwisting in *CrystEngComm* **17**, 8817–8824 (2015) (now ref. 27). Rather than a reduction in degree of twist by retracting a ribbon’s tip caused by dissolution, the relaxation we observed is a redistribution of curvature from a helicoid (negative Gaussian curvature everywhere) to a helical ribbon (near-zero Gaussian curvature) as ribbon width exceeds the critical dimensionless threshold $\tilde{w} \sim 2.5$ (ref. 10, the seed pod paper). The geometric frustration is fully preserved throughout and only the geometry of its expression changes.

Small corrections

Comment 7. P2, L45. The authors give the IUPAC name and then say “which was derivatized with a fluorine”. Without reference to Figure 2 here, the only place where the chemical structure appears, one is stymied by trying to decode the name and then deciding where the extra fluorine goes after derivatization. But there is no extra fluorine. The authors are referring to the fluorine already present in the structure named. This all could be clearer.

Answer: Thank you for pointing out the clarity issue. We have added the molecular structure of 2-(5-carboxy-2-fluorophenoxy)ethan-1-aminium (FCA3) to panel f of Fig. 1. Please find the revised Fig. 1 and modified caption below.

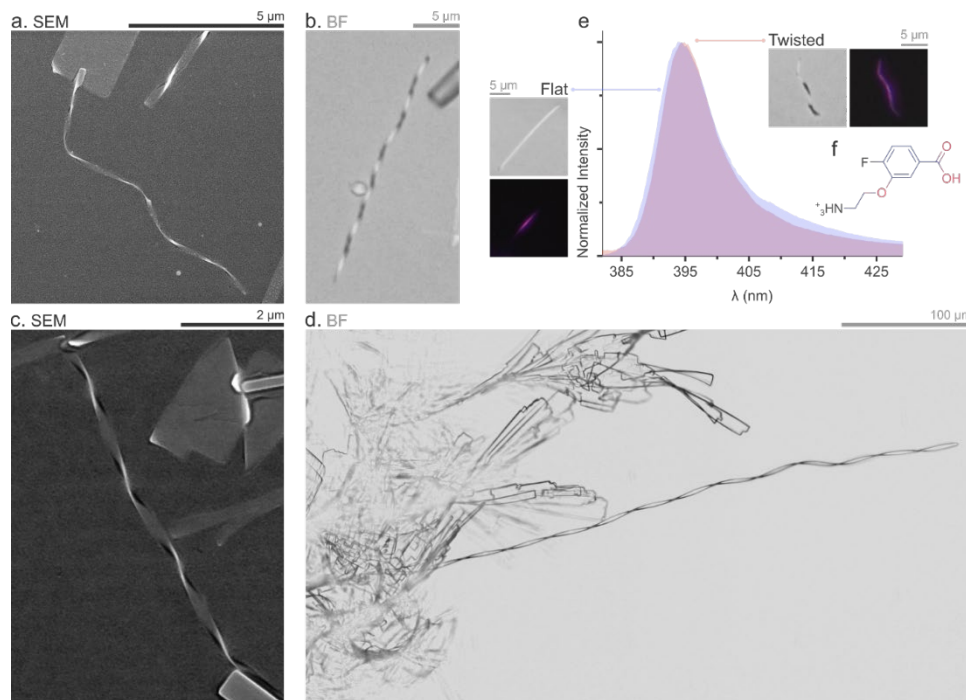


Figure 1. Twisted ribbons of layered metal-halide perovskites. ... (f). The molecular structure of 2-(5-carboxy-2-fluorophenoxy)ethan-1-aminium (FCA3), the organic spacer used.

Regarding the confusion related to the repeated derivatization statement, we've revised the sentence as follows for clarity:

The specific spacer chosen here, FCA3 (Fig. 1), is built on a benzoic acid core functionalized with a fluorine para to the COOH and an aminoethoxy side chain at the meta position for attachment to the inorganic lattice; its full name is 2-(5-carboxy-2-fluorophenoxy)ethan-1-aminium.

Comment 8. P4, L17. A cross-reference to the seed pod paper should appear here.

Answer: Thank you for the note. We have added the related reference.

...suggesting a mechanism analogous to membrane mechanics observed in seed pods¹⁰.

Response to Reviewer #3

This manuscript reports a striking example of spontaneous morphological chirality in an achiral layered 2D perovskite, where twisted/helical nanoribbons emerge from incompatible elasticity arising from misaligned organic lattices that feature hydrogen-bonding frameworks. The authors draw inspiration from the chiral opening of seed pods in biological systems and translate the underlying mechanical/mathematical concepts into a compelling framework for 2D perovskite crystal engineering, enabling potential ensemble-level handedness control and measurable chiroptical activity. The breadth of work, spanning synthesis, structural characterization, molecular dynamics simulations, and modeling, is impressive. Overall, the story is very exciting and should be of broad interest to both the chiral materials community and researchers focused on fundamental crystal growth and morphology engineering in layered and nano- materials. It also offers an appealing alternative strategy for introducing chirality into 2D perovskites, a rapidly growing and hot research area.

I am generally positive and believe the manuscript could be suitable for publication. Nevertheless, I think the manuscript would be strengthened by addressing the following points.

Answer: Thank you for an exceptionally constructive reading that sharpened the design logic of the paper. The reviewer's questions probed exactly the part of the story most useful to the materials community: which crystals twist, and which structural features are responsible. Their most consequential concern was whether FCA3 is exceptional or one instance of a broader design space (Comments 3 and 5), alongside why some ribbons remain flat (Comments 1 and 2). We make the governing rule explicit in the response: twisting requires not a special spacer but a specific symmetry: the inversion center must sit in the organic interlayer gap rather than within the inorganic slab, so that the two organic sublattices of a monolayer are related by the 2_1 screw alone and adopt misaligned HOF orientations. Together these establish a transferable design principle rather than a single demonstrator. Please find our point-by-point response to each Comment below.

Comment 1.1. From the optical and SEM images in the main text and SI, some ribbons appear to be flat or only weakly deformed. It would be helpful if the authors could clarify why twisting does not occur in these cases. Is there a criterion (e.g., thickness/width window, growth rate) that determines whether a ribbon twists?

Answer: We thank the reviewer for this important question. Two distinct mechanisms account for ribbons that appear flat or weakly deformed. First, for thin ribbons that have not yet traversed a full quarter-turn between nodes before sample preparation, the adhesion energy to the substrate can exceed the elastic energy of the helicoid configuration. Such ribbons can be deformed in solution but appear flat when dried or deposited on a surface. This is confirmed by the observation that deformed morphology is prevalent in samples that grew slowly into larger and thicker crystals (Extended Data Figure 2b, which was grown at 0.044 °/min and has mean width of 4.1 μm and mean thickness of 0.52 μm according to Supplementary Fig S20a). The larger cross-sectional

dimensions store greater torsional elastic energy in the helicoid configuration, enabling these ribbons to overcome substrate adhesion and maintain their deformed geometry during sample preparation and imaging.

As for the criterion that determines whether a ribbon twists, it's important to acknowledge that spontaneous deformation is prevalent in wide and thick ribbons that are able to overcome substrate adhesion (Extended Data Fig. 2b). Yet, they might not have grown long enough to express one twist node. In other words, wide or thick crystals have pitch values that can far exceed their length. According to Eq. 3, using our estimated $W = 497 \text{ kJ/m}^3$ (updated in the revised manuscript, see Supplementary Note 2 and answer to Reviewer 5 Comment #8), a ribbon with thickness $= 1 \text{ }\mu\text{m}$ has a predicted pitch of $\sim 300 \text{ }\mu\text{m}$ (Supplementary Fig. S21c). Ribbons that crystallize shorter than half a pitch appear flat despite retaining the same intrinsic strain misalignment. The necessary condition for a visible twist is $L \geq p/2$, or equivalently, that the crystal grows to a length comparable to half a pitch before terminating.

We have added a brief discussion of the first criteria to the end of the “Geometric Frustration in Layered Perovskites” section of the revised manuscript, as follows:

This observation is critical, as it reinforces spontaneous deformation as an intrinsic propensity encoded in the lattice structure, expressed through nucleation, and subsequently amplified by kinetic control. Twisted microribbons free of internal boundaries were also achievable with deliberate crystal handling, as shown in representative images examined under cross-polarization or PL mode (Extended Data Fig. 3). Under rapid cooling, however, crystal growth terminates before ribbons reach one full pitch period, so the helicoid geometry is not expressed at the observable scale. Thin nanoribbons with length shorter than one-quarter pitch period can additionally be flattened by substrate adhesion during sample preparation, which explained the mere occasional twist observed earlier (Supplementary Fig. S1).

Comment 1.2. In addition, based on the mechanical frustration model (Eqs. 1–3), are thinner or wider ribbons expected to twist more readily (or how does the predicted twist depend on thickness and width from the view of the thermodynamic driving force, i.e., competing elastic strain and torsional deformation)?

Answer: Thank you for this incisive question. Regarding the thermodynamic driving force and its dimensional dependence, the key insight from Eqs. 1–3 is that the elastic strain energy density W (497 kJ/m^3) is a material constant that does not depend on ribbon dimensions. The dimensional dependence appears instead in the equilibrium pitch. In the high-aspect-ratio limit applicable to our ribbons ($w/t \sim 10$, Fig. 3b), the torsional constant reduces to $J \sim t^3 w/3$ (assuming $\frac{t}{w} \rightarrow 0$ and $\tanh(\frac{\pi w}{2t}) \rightarrow 1$). Substituting into Eq. 3, the width dependence cancels and $p \propto t$ (i.e. the predicted equilibrium pitch scales linearly with thickness and is independent of width).

This has two consequences. First, thinner ribbons express visible twisting over shorter lengths (L), not because of a stronger driving force, but because their shorter pitch satisfies the $L \geq p/2$ criterion within a shorter crystal. Thick ribbons carry the same intrinsic strain but require much longer growth to manifest even a single twist node. Second, width does not determine whether a ribbon twists (at fixed thickness), but controls the type of deformation: as the dimensionless width $\tilde{w} = w\sqrt{\kappa/t}$ increases beyond ~ 2.5 , the ribbon transitions from twisted helicoid to helical morphology, as described in the "Dynamic and Versatile Morphological Chirality" section and Fig. 4.

In summary, the dimensional window in which twisted ribbons are most readily observed corresponds to thin ribbons (short pitch) with moderate width ($\tilde{w} \sim 1.34$), consistent with the nanoribbon population shown in Fig. 1, a to c.

Comment 2. Related to point 1, do the authors observe that twisting is more prevalent for a particular dimensional regime (e.g., nanoribbons vs microplates), or for a particular aspect ratio? A short summary would strengthen the discussion.

Answer: As discussed in response to Comment 1, the prevalence of visible twisting is governed by the geometric criterion $L \geq p/2$, where p scales with thickness at the high-aspect-ratio regime. Consistent with this, our dataset (177 twisted ribbons spanning t from 30 nm to 3.31 μm and w from 104 nm to 47.9 μm) demonstrated that twisting is not restricted to nanoribbons but is observed across three orders of magnitude in dimension. Equiaxed microplates without apparent long axes do not twist not because of a dimensional threshold but because they lack the elongated geometry required to satisfy $L \geq p/2$. No systematic trend in w/t was found to gate whether twisting occurs. Rather, w/t controls whether the morphology is a twisted helicoid or a helical ribbon, as summarized in the "Dynamic and versatile Morphological Chirality" section.

We added the following brief clarification to the empirical discussion of dataset at the beginning of the "Statistical and Mechanical Analyses" section:

These data points were selected from multiple crystallization batches with varied cooling rates. The dataset encompassed w ranging from 104 nm to 47.9 μm and t from 30.3 nm to 3.31 μm . Twisted ribbons were observed across this entire dimensional range with no evidence of a threshold below or above which twisting is suppressed. A preliminary analysis yielded an overall mean aspect ratio...

Comment 3. FAC3 and BrCA3 appear structurally similar. Could the authors provide a possible explanation for why FCA3 exhibits a 21 screw axis, whereas this feature is absent for BrCA3? A discussion in terms of factors affecting the packing preferences would be useful.

Answer: We sincerely appreciate this important structural question, which we have sought to address more explicitly in the revised manuscript. We agree it points toward a rich avenue for future investigation in the field of lattice-induced mechanical frustration.

The key distinction lies not in the organic spacer layer directly, but in the symmetry of the inorganic $[\text{PbBr}_4]^{2-}$ layer. Both $(\text{FCA3})_2\text{PbBr}_4$ ($P2_1/n$) and $(\text{BrCA3})_2\text{PbBr}_4$ ($P\bar{1}$) are centrosymmetric, which is consistent with the general tendency of crystals to adopt centrosymmetric packing. However, the inversion center sits at different locations. In $(\text{BrCA3})_2\text{PbBr}_4$, it resides within each individual inorganic slab, making the two faces of the slab crystallographically equivalent and yielding parallel HOF chains on both faces. In $(\text{FCA3})_2\text{PbBr}_4$, however, the inversion center instead sits in the organic interlayer gap between adjacent bilayers. Each individual inorganic slab therefore has only the 2_1 screw symmetry without local inversion, making the two faces inequivalent and forcing the organic spacers into misaligned HOF orientations. Geometric frustration, and thus spontaneous twisting, is a direct consequence of this arrangement.

Why F to Br substitution on the organic spacer shifts the preferred location of the inversion center, from the interlayer gap to within the slab, is a mechanistic question that cannot be resolved from crystal structure data alone. It likely reflects differences in how each spacer templates the Pb-Br-Pb bond angle distortions at the organic-inorganic interface. Yet, the physical intuition behind this templating effect remains to be an open and highly significant question for the broader field of lattice-induced mechanical frustration in layered materials. We have clarified this picture in the manuscript and hope this framing provides a productive starting point for future investigations.

First, we added the following structural clarification to the first paragraph of the section “Crystallographic Control of Morphological Chirality”.

...with inversion centers in $(\text{BrCA3})_2\text{PbBr}_4$ ($P\bar{1}$), reflecting a symmetry reduction (Extended Data Fig. 2, a and c). A key distinction is where the inversion center resides: in $(\text{BrCA3})_2\text{PbBr}_4$ it sits within each individual $[\text{PbBr}_4]^{2-}$ slab, making both faces of the slab crystallographically equivalent; in $(\text{FCA3})_2\text{PbBr}_4$, however, it sits in the organic interlayer gap, so each individual slab retains only the 2_1 screw axis and its two faces are inequivalent. While both structures are centrosymmetric, it is the location of the inversion center, within or between slabs, that determines whether the organic spacers on opposite faces adopt misaligned or parallel HOF orientations. As a result, the uniaxial strain...

Second, the following perspective was added to the beginning of page 8, after the conclusion of the doping experiments.

The physical origin remains an open question of why F-to-Br substitution on the organic spacer shifts the inversion center from the interlayer gap into the inorganic slab, and thereby switches off the geometric frustration. This likely reflects subtle changes at the organic-inorganic interface that modify distortions in the Pb-Br-Pb bonding network, although the governing structural and chemical factors are not yet established. Understanding how organic network structures template lattice symmetry

in layered perovskites is an important direction for future studies on tuning lattice-induced mechanical frustration in 2D materials, and may also extend to other systems where competing crystallographic symmetries give rise to emergent mechanical, optical, or electronic properties.

Comment 4. In the authors' previous work (Science 2024, 384, 1000), (BrCA3)₂PbI₄ occasionally also formed twisted nanowires, yet its crystal structure appears isostructural to (BrCA3)₂PbBr₄. Did the authors observe similar behavior in (BrCA3)₂PbBr₄? And how to rationalize such a behavior.

Answer: Thank you for raising the question. The occasional twisting of (BrCA3)₂PbI₄, described in Fig. 4B of Science 2024, 384, 1000, appeared to be a random behavior likely resulted from crystals' growth imperfections, such as stacking faults. Also described in Science 2024, 384, 1000 was the occasional bending and twisting of (BrCA3)₂PbBr₄ nanowires (Fig. 2I, Fig. 5B, and 5C), which was attributed to be caused by external mechanical forces been applied to the crystals, such as when transferring them from suspensions to substrates. Overall, the occasional twisting of (BrCA3)₂PbBr₄ and (BrCA3)₂PbI₄ cannot be attributed to lattice-induced spontaneous morphological deformation.

Comment 5. As far as we know, 2D perovskites exhibiting 2₁ screw axes is not unique to FCA3 and these structures would plausibly exhibit misaligned strains between the two organic layers, similar to the FCA3 case. Since this feature appears important for generating twist, it would be valuable to add a broader discussion (or a short design rule) on how to extend the concept to other spacers. In particular, is FCA3 exceptional, or is it simply one demonstrator within a larger design space?

Answer: We thank the reviewer for this crucial observation. 2₁ screw axes are common in 2D perovskites and are not unique to (FCA3)₂PbBr₄. However, two conditions must be simultaneously satisfied for ribbon twisting to occur. (1) Uniaxial in-plane strain. The organic spacer must generate directional, anisotropic strain along a preferred in-plane axis. In (FCA3)₂PbBr₄, this arises from the COOH dimer motif. (2) Rotational misalignment of the two organic layers sandwiching the inorganic slab. The 2₁ screw axis relates the top and bottom organic sublattices by rotation plus translation, instead of reflection. (FCA3)₂PbBr₄ ($P2_1/n$) is distinguished by the location of its inversion center at the organic midplane between adjacent monolayers. The two organic sublattices in a monolayer are therefore related solely by the 2₁ screw. Thus, their strain axes are non-collinear and yield a net incompatible elasticity. This effect is cancelled when the crystal also places an inversion center through the Pb layer. Most 2D perovskites with a 2₁ screw axis have it sitting at the inorganic layer. While (FCA3)₂PbBr₄ is one example of this design principle, we expect it to generalize to other spacers satisfying both conditions.

Comment 6. The observation of CD from twisted ribbons whose pitch is far larger than the optical wavelength is intriguing. Can the authors have some possible explanations. In Extended Data Fig. 4, a higher-magnification zoom showing the highlighted CCW and CW structures would be helpful. Also, for the regions used to acquire the spectra in panels (c) and (d), what is the local pitch? A CD measurement on a flat microplate (or an untwisted ribbon ensemble) as a control would be useful.

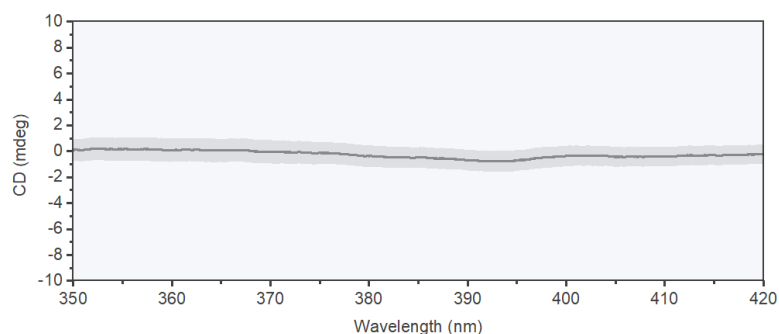
Answer: Thank you for this insightful question. We hypothesized in the main text that the CD originates from a coupled oscillator mechanism (ref. 24) in which the relevant chiral length scale is the interlayer spacing (~ 0.7 nm). In $(\text{FCA3})_2\text{PbBr}_4$ twisted ribbons, each 2D perovskite layer supports strongly in-plane-polarized excitons. Because the ribbon is twisted, successive layers are rotated by a small angle relative to their neighbors, establishing a chiral arrangement of transition dipole pairs. The rotational strength governing the CD contribution of each pair is determined purely by geometry, which means the interlayer spacing and the twist angle between adjacent layers, with no requirement that the macroscopic pitch approach the optical wavelength. All pairs along the ribbon contribute rotational strength of the same sign determined by the handedness of the twist, and their cumulative sum generates the observed signal. This mechanism was also used extensively to model the dichroism seen in helicoidal organic crystals with mesoscale pitches in the 10^1 μm regime (e.g. Cui, X. et al.; *J. Am. Chem. Soc.* **2016**, *138*, 12211-12218).

Two features of the data are consistent with this picture. First, the CD signal of twisted 2D perovskite ribbons is inherently weak: an ensemble of hundreds of crystals with uniform handedness is required for detection, which is expected when the twist angle per interlayer spacing is small (pitch $\gg \lambda$ means the rotational strength per coupled pair is small). Second, CCW clusters give positive CD and CW clusters give negative CD. This handedness-dependent sign reversal cannot arise from linear dichroism artifacts in an oriented anisotropic sample, confirming genuine chiral absorption.

Below are the responses to the additional questions:

1) CD from flat microplates. We performed CD measurements on flat microplates with the same crystal loading methods and beam size. The CD signal was minimal across the full measurement range (Supplementary Fig. S19), confirming that the observed CD in twisted ribbons is morphology-dependent and does not arise from intrinsic crystal chirality or instrument artifacts.

We have included the results in the new Supplementary Fig. S19.

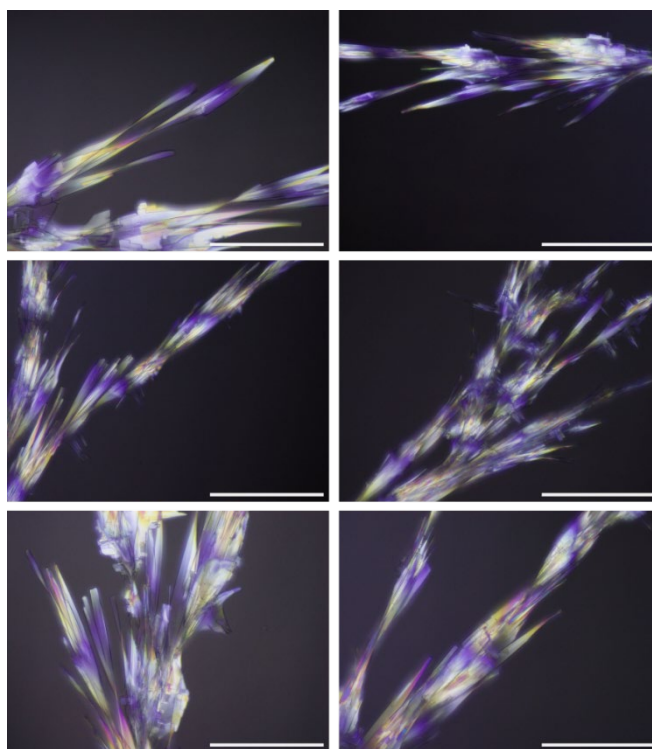


Supplementary Fig. S19. Ensemble averaged CD spectra of flat (FCA3)₂PbBr₄ crystals. Abundant flat crystals obtained by free-space rapid growth were used for this measurement.

Addition to the main text:

...CCW clusters exhibited positive CD signals while CW clusters showed negative signals. In contrast, abundant flat crystals obtained by free-space rapid nucleation displayed minimal CD signals (Supplementary Fig. S19). These results matched...

2) Higher-magnification zoom and local pitch. High-magnification cross-polarized mode images of the cluster shown in Extended Data Fig. 4a was included as the new Supplementary Fig. S18, which shows local ribbon pitches ranging from approximately 10 to 100 μm , confirming that the morphological periodicity exceeds the measurement wavelength by one to two orders of magnitude throughout.



Supplementary Fig. S18. High-magnification ribbon forest regions of Extended Data Fig. 4a, cross-polarized. Scale bars: 50 μm .

Comment 7. Trend of w/t vs cooling rate in Fig. 3b is not clearly explained.

Answer: We appreciate the Reviewer's constructive suggestion. Indeed, Fig. 3b requires further elaboration, as it reflects the characteristic growth behavior of typical 2D materials. In layered 2D perovskites, in-plane growth (lateral spreading within an existing layer) generally has a much lower energetic barrier than out-of-plane growth (nucleation of a new layer). Under slow cooling conditions, supersaturation builds gradually, favoring predominantly in-plane growth and resulting in wide, thin ribbons with high width-to-thickness (w/t) aspect ratios. In contrast, under a high temperature gradient, supersaturation rises rapidly above the threshold required for out-of-plane nucleation, leading to increased vertical growth and consequently lower w/t aspect ratios. This mechanism explains the observed trend in Fig. 3b, where w/t increases with decreasing cooling rate and eventually stabilizes at ~ 11 – 12 when the cooling rate reaches ~ 0.01 $^{\circ}\text{C}/\text{min}$.

The following sentence was added to the paragraph before Fig. 3:

...a broader width distribution (5-40 μm) and $\overline{w/t} = 12.0$. This trend reflects the lower barrier for in-plane v.s. out-of-plane growth: slow cooling favors lateral spreading (high w/t), while rapid cooling elevates supersaturation above the new layer nucleation threshold, promoting thicker growth relative to width. Parallel batches...

Comment 8.1. On page 7, it is unclear how the BrCA3 doping level was quantified from single-crystal XRD, since partial occupancy/disorder of organic spacers can be difficult to refine unambiguously.

Answer: We thank the Reviewer for raising this point. The quantification process to determine BrCA3 doping level is detailed in Table S5 and the accompanying structure refinement text. Please find a short summary below:

For the $(\text{FCA3})_{1.821}(\text{BrCA3})_{0.179}\text{PbBr}_4$ crystal structure (9.84 mol% initial BrCA3 doping), the doping level was determined directly from single-crystal XRD at 150 K using partial occupancy refinement of the organic spacer sites. The F and Br atoms occupy chemically distinct sites with well-separated scattering contrast, enabling unambiguous refinement. The refined composition, R-factors, and displacement parameters are reported in Table S4. The high-quality fit ($R_1 = 3.2\%$, $wR_2 = 6.9\%$, Table S4) confirms that the partial occupancy model is well-determined and not subject to refinement ambiguity.

For the lower-doping crystal (0.92 mol% initial BrCA3 doping), the dopant fraction is too small to be resolved at the level of partial occupancy refinement. For this sample, SCXRD was used to confirm the space group assignment ($P\bar{1}$) and the approximate parallel alignment of the HOF network, but the precise dopant stoichiometry cannot be extracted. We have clarified this distinction in the revised manuscript.

We agree that further clarification in the main text is needed. The following brief phrase was added:

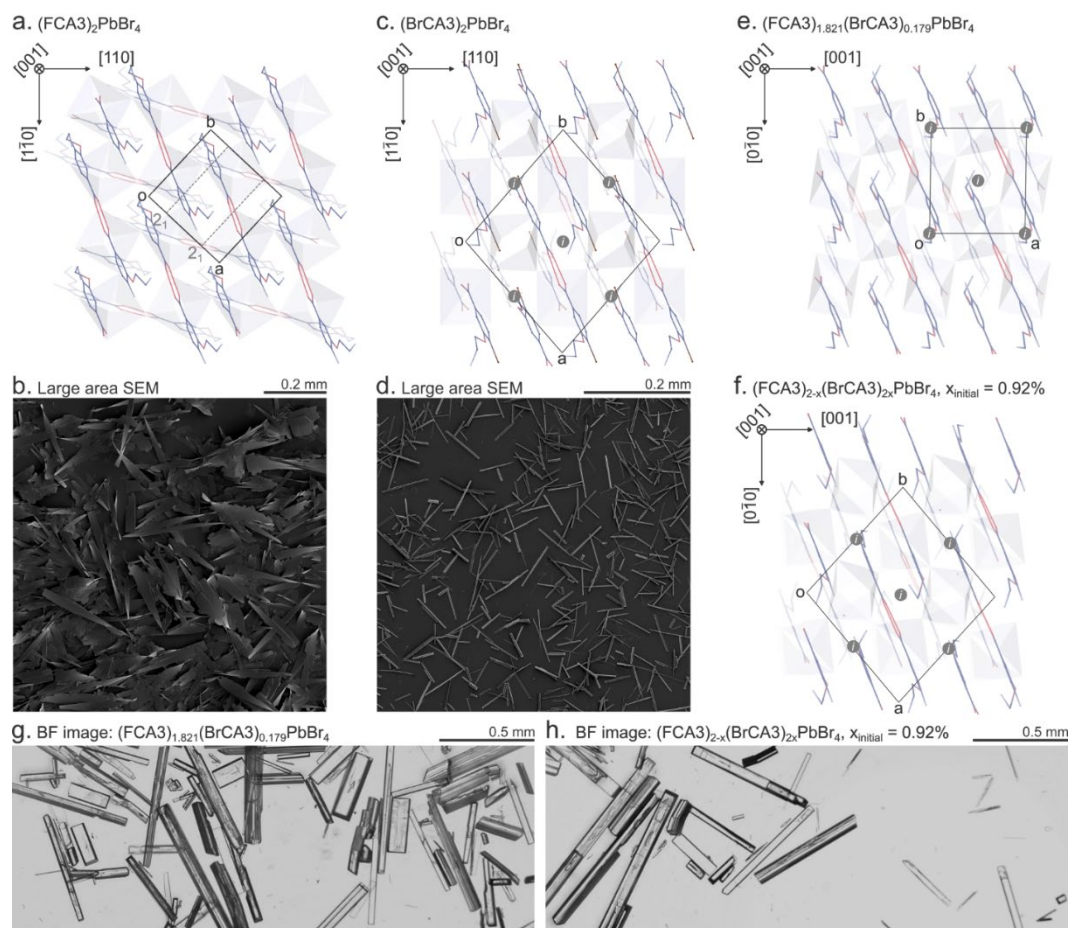
An initial BrCA3 fraction (x) of 9.84% resulted in a final doping level of $x = 8.95\%$ (Supplementary Table. S4 and related refinement details) determined by single-crystal XRD, where F and Br occupy chemically distinct sites that are resolved unambiguously by their scattering contrast.

Additionally, we've added clarification to the caption of Extended Data Fig. 2, as follows:

For (e). $(FCA3)_{1.821}(BrCA3)_{0.179}PbBr_4$, the doping level was determined by partial occupancy refinement of the organic spacer sites, where F and Br occupy chemically distinct positions resolved unambiguously by their scattering contrast (full refinement details in Table S4; CIF file provided as supplementary data). For (f), the crystal exhibited severe twinning that precluded precise quantification of the BrCA3 content; the composition shown reflects the precursor ratio. Nevertheless, space group assignment ($P\bar{1}$) and the parallel alignment of the HOF network were determined unambiguously from the integrated dataset (CIF file provided as supplementary data).

Comment 8.2. In addition, in Extended Data Fig. 2, it would be helpful to include representative morphology images of the doped samples for direct comparison with the other two systems.

Answer: Thank you for the suggestion. We have added panel g and h to the Extended Data Fig. 2 to complement the morphology images included in Supplementary Fig. S16.



Related caption:

...(g) and (h) are the bright field morphology images of (e) and (f), respectively.

Comment 9. The Methods section would benefit from more details, for example, the conditions used for the growth videos (cooling control method, imaging configuration) and the excitation spot size used in the chiroptical measurements.

Answer: Thank you for the suggested edits to the Methods section. We added the following “In-situ crystal growth” section to provide audience adequate context for the understand and reproduction of the work.

In-situ crystal growth

The in situ crystal growth experiments (Supplementary Videos 1–3) were conducted in a sealed quartz disk-shaped cuvette with a 10 μm gap under a bright-field optical microscope. The precursor solution described above was first heated to ensure complete dissolution of all precursors, followed by rapid cooling to room temperature to induce complete precipitation of the 2D perovskites. The resulting suspension was thoroughly sonicated to break up large crystals. The prepared crystal suspension was

then transferred into the growth disk, which was carefully sealed with vacuum grease to prevent solvent evaporation during subsequent in situ crystal growth.

The disk was placed on a heating stage (Instec) and initially heated to 110 °C (stage setpoint or surface temperature). For Supplementary Video 1, the stage was rapidly cooled to 95 °C, where the rectangular crystals observed at the beginning of the video emerged and stabilized, followed by rapid cooling to 85 °C during video acquisition. Supplementary Video 2 was recorded after rapidly cooling the stage to 75 °C, where twisted ribbon growth initiated, and kept cooling at rate of 2.5 °C/min till 55 °C. For Supplementary Video 3, the stage was rapidly cooled to 65 °C, where the crystals visible at the beginning of the video emerged and stabilized, followed by rapid cooling to 55 °C during video acquisition.

Regarding chiroptic measurements, we specified the spot diameter as follows:

A photomask was used to select the region under exposure. The exposed spot diameter was fixed at 5 mm. Spectra was measured...

In addition, we also detected a few clarification points in the Methods section and have replenished them accordingly, including adding the “Synthesis of organic cations” and “Computational methods” sections and reference them to relevant sections in the Supplementary Materials.

Comment 10. Several typos are present. For example, on page 7, the sentence fragment “eliminating the spontaneous deformation observed in FCA3-based systems.” and in Extended Data Fig. 2 the label “PbBr₆4– lattices.”

Answer: We thank the Reviewer for the careful reading. Regarding the sentence "...eliminating the spontaneous deformation observed in FCA3-based systems," we respectfully note that this is a complete sentence rather than a fragment: "the uniaxial strain in every organic lattice becomes compatible" is the main clause, modified by the participial phrase "eliminating the spontaneous deformation observed in FCA3-based systems."

We have corrected the typo in the figure caption of Extended Data Fig. 2 as follows:

Extended Data Fig. 2. Symmetry elements in the [PbBr₄]²⁻ lattices...

Additionally, we’ve also identified and corrected a few additional typos throughout the manuscript, including but not limited to:

1. Correct “mechanic frustration” to “mechanical frustration”, such as in abstract:
Such mechanical frustration is initiated by specific crystal symmetry controllable...
2. Correct “chiroptical” to “chiroptic”, such as on page 8 near line 20:
In such systems, chiroptic responses are often interpreted using...
3. Correct “residue” to “residual”, such as in the Chiroptic measurement Methods:
Rotation removed the residual static birefringence of the...

Response to Reviewer #4

This manuscript reports the observation of spontaneous morphological chirality in achiral layered metal-halide perovskites. The authors attribute this behavior to a form of geometric frustration, arising from an approximately 50° misalignment between two hydrogen-bonded organic frameworks (HOFs) across an inorganic slab. This misalignment is proposed to generate competing uniaxial strains, which are relieved through the formation of twisted and helical ribbon morphologies. By combining microscopy, molecular dynamics simulations, and mechanical modeling, the study presents a coherent picture of how structural frustration at the molecular scale may translate into mesoscale chiral morphologies. More broadly, the emergence of chirality from nominally achiral building blocks remains an important topic across chemistry, materials science, and biology. In recent years, there has been growing interest in morphology-driven chirality, particularly in soft matter and low-dimensional systems, where mechanical and interfacial effects can play a dominant role. Within the context of metal-halide perovskites, which are already known for their structural tunability and rich optoelectronic properties, the possibility of inducing chiral responses through purely morphological means is potentially relevant for areas such as chiroptical materials, polarization-sensitive photonics, and enantioselective interactions. From this perspective, the present work offers an interesting example of how geometric frustration could serve as a design principle for generating chiral architectures without requiring intrinsically chiral components. At the same time, because morphology-induced chirality is often sensitive to growth conditions, structural heterogeneity, and measurement geometry, careful characterization is important to establish the robustness and generality of the observations. While the overall approach in this manuscript is thoughtful and the results are intriguing, making me consider this work recommendable for publishing in Nature Synthesis, there are several points that would benefit from clarification or further support.

Answer: We are grateful to Reviewer #4 for their acknowledgement of our work and especially for pressing us to position this work rigorously within the chiral-perovskite literature, which materially improved the framing of our central claim. The reviewer's principal concern (Comment 1) was that the origin of chirality here be drawn cleanly against prior approaches, and that its functional consequences be made explicit. In the revised manuscript, we have directly stated the distinction in origin, length scale, and tunability. Please find our point-by-point response below.

Comment 1. The manuscript would also benefit from a more complete discussion of prior work on chiral perovskite interfaces. There are a number of earlier studies involving intrinsically chiral organic cations, chirality emerging at hybrid interfaces, as well as morphology- or interface-induced chiroptical effects. These different classes of structures can give rise to optical, electronic, and mechanical responses at multiple length scales. Providing a more structured overview of these prior approaches would help place the present work in context. In particular, it would be useful for the authors to clarify how the system reported here differs from previous examples in terms of the origin of chirality and its functional consequences, and whether the morphology-induced chirality observed in this study offers any distinct advantages or limitations compared to existing strategies.

Answer: We thank the reviewer for this suggestion. We have added a new opening paragraph to the Spontaneous Bending and Chiral Deformation section that provides a structured overview of prior approaches to chiroptic functionality in 2D perovskites and positions the present work in that context.

Introducing chiroptic functionality into 2D perovskites has been achieved primarily by incorporating enantiopure organic spacers, whose packing within the crystal framework generates spin-selective charge transport,¹³ circularly polarized photoluminescence,¹⁴ and, at chiral heterointerfaces, spring-like mechanical durability through closer π - π stacking of opposite enantiomers.¹⁵ In these systems, molecular chirality is the structural source, and the inorganic lattice responds passively through octahedra distortion. Here we demonstrate a different route: by designing achiral organic spacers that engineer a specific crystallographic symmetry in the inorganic lattice, we generate spontaneous morphological chirality through geometric frustration, without any chiral components.

13. Kim, Y. H., Zhai, Y., Lu, H., Pan, X., Xiao, C., Gaulding, E. A., Harvey, S. P., Berry, J. J., Vardeny, Z. V., Luther, J. M. & Beard, M. C. Chiral-induced spin selectivity enables a room-temperature spin light-emitting diode. *Science*. **371**, 1129–1133 (2021).

14. Long, G., Jiang, C., Sabatini, R., Yang, Z., Wei, M., Quan, L. N., Liang, Q., Rasmita, A., Askerka, M., Walters, G., Gong, X., Xing, J., Wen, X., Quintero-Bermudez, R., Yuan, H., Xing, G., Wang, X. R., Song, D., Voznyy, O., Zhang, M., Hoogland, S., Gao, W., Xiong, Q. & Sargent, E. H. Spin control in reduced-dimensional chiral perovskites. *Nat. Photon.* **12**, 528–533 (2018).

15. Duan, T., You, S., Chen, M., Yu, W., Li, Y., Guo, P., Berry, J. J., Luther, J. M., Zhu, K. & Zhou, Y. Chiral-structured heterointerfaces enable durable perovskite solar cells. *Science*. **384**, 878–884 (2024).

We organize prior work into two classes. In the first and most developed class, enantiopure organic spacers, such as R/S-methylbenzylammonium (MBA), generate spin-selective charge transport via chiral-induced spin selectivity (CISS) and circularly polarized photoluminescence when incorporated into 2D perovskite frameworks (ref. 13. *Science*. 2021, 371, 1129–1133 and ref. 14. *Nat. Photon.* 2018, 12, 528–533). In the second class, chiral organic spacers at the perovskite-charge-transport-layer interface create structured heterointerfaces with improved mechanical durability and carrier extraction through closer π - π stacking of opposite enantiomers (ref. 15. *Science*. 2024, 384, 878–884). In both cases, chirality originates in an enantiopure organic molecule, and the inorganic lattice responds through distortion of the metal-halide octahedra.

The present work differs fundamentally in the origin and scale of chirality. No chiral components are used; instead, two achiral organic layers are forced into incompatible orientations by the 2₁ screw axis of the inorganic lattice, generating morphological chirality through geometric

frustration. The resulting chiroptic response operates across five orders of magnitude in length scale and is tunable through growth kinetics rather than fixed by enantioselective synthesis.

Comment 2. Chiral perovskite interfaces have also recently been reported to influence mechanical properties (see, DOI: 10.1126/science.ado5172). In this context, it would be interesting to consider whether the chiral ribbons observed in this work exhibit any distinct mechanical behavior compared to non-chiral or untwisted counterparts. While a full mechanical characterization may be beyond the scope of the present study, the authors could at least comment on this aspect and, where appropriate, relate their observations to existing studies on structure–mechanics coupling in chiral perovskite systems. Establishing such a connection would help place the current results within a broader framework and highlight potential functional implications of morphology-induced chirality.

Answer: We thank the reviewer for the constructive comment and for directing us to Duan et al. (ref. 15. Science. 2024, 384, 878-884). We address the mechanical distinction between twisted and flat ribbons and relate it to structure-mechanics coupling in chiral perovskite systems.

1) Twisted ribbons are the equilibrium configuration.

The spontaneous deformation of $(\text{FCA3})_2\text{PbBr}_4$ is the mechanism by which the crystal relaxes geometric frustration. A flat ribbon retains incompatible lattice strain whereas a twisted helicoid partially relieves this strain at the cost of torsional deformation energy, reaching the equilibrium pitch described by Eq. 3. Flattening a twisted ribbon therefore requires external mechanical work, making the flat and twisted morphologies mechanically distinct despite their identical composition. We have clarified this point in the “Statistical and Mechanical Analyses” section, as follows:

...demonstrating internal consistency between the theoretical framework and experimental observations. This model also implies that the twisted geometry is the energy-minimizing configuration for ribbon-shaped $(\text{FCA3})_2\text{PbBr}_4$ crystals, while a flat plate of the same dimensions retains unrelaxed incompatible lattice strain. Consequently, flattening a twisted ribbon requires mechanical work against the frustration driving force W , making twisted and untwisted morphologies mechanically non-equivalent despite identical chemical composition.

2) Flat ribbons on substrates are not necessarily in their equilibrium state. Thin nanoribbons can appear flat because surface adhesion during transfer suppresses the equilibrium twist when adhesion and torsional energies are comparable. In contrast, ribbons observed in solution during in situ growth (Supplementary Videos S1-S3) consistently show deformation, indicating that substrate-induced flattening is an extrinsic effect. Wide and thick ribbons are less susceptible to surface effect because mechanical energy required to de-twist them (W) increases with thickness. Consistent with this picture, slow-grown ribbons show pervasive deformation (Extended Data Fig. 2b). We have added the following sentences near the end of the “Geometric Frustration in Layered Perovskites” section, as follows:

Under rapid cooling, however, crystal growth terminates before ribbons reach one full pitch period, so the helicoid geometry is not expressed at the observable scale. Thin nanoribbons with length shorter than one-quarter pitch period can additionally be flattened by substrate adhesion during sample preparation, which explained the mere occasional twist observed earlier (Supplementary Fig. S1).

In the seminal work by Duan et al. (ref. 15. Science. 2024, 384, 878-884), molecular chirality was linked to enhanced mechanical properties through tighter π - π stacking of chiral organic cations. Our system operates through a different mechanism: macroscopic helicoidal morphology arising from crystallographic frustration. Despite the different length scales, both studies demonstrate that chiral structural motifs can strongly influence mechanical behavior in perovskites and are thus complementary.

Comment 3. While the manuscript describes a transition from twisted to helical morphologies, it is not clear how commonly this transition occurs. Providing statistical information on the fraction of ribbons exhibiting each morphology, and how this may vary between samples, would help place this observation in context.

Answer: We thank the reviewer for this comment. Helical morphology is a minority population in our observations. Among all elongated ribbon crystals surveyed across 34 batches with cooling rates spanning 0.01 to 16 °C/min, fewer than 0.1% exhibited helical morphology. This scarcity reflects the growth behavior of $(\text{FCA3})_2\text{PbBr}_4$: under all conditions studied, the system preferentially produces ribbons in the narrow-width regime (mean $\tilde{w} = 1.34 \pm 0.32$), well below the helical transition threshold of $\tilde{w} \sim 2.5$. Helical ribbons require the wide-ribbon regime ($\tilde{w} > 2.5$), which demands ribbons that are simultaneously wide and thin. This is a combination our current solution-phase growth does not selectively target, as cooling rate increases both width and thickness together (Fig. 3b). The 12 helical ribbons analyzed for the p - R relationship in Fig. 4h were specifically identified from slow-cooling batches that produced the widest ribbons in our dataset and are presented to characterize the morphological transition rather than as a representative population. Achieving higher fractions of helical morphology would require independent control over ribbon width and thickness, which we identify as an opportunity for future work.

Comment 4. For chiral materials, it is common to report the anisotropy (g -) factor to quantify circular dichroism (CD) signals. It would be helpful if the authors could either estimate the g -factor for this system or briefly comment on whether such a metric is appropriate in the case of morphology-induced chirality.

Answer: We thank the reviewer for this important suggestion. While $g = \Delta A/A$ can be formally computed from our ensemble-averaged CD measurement of twisted ribbon clusters, its physical

meaning for morphological chirality fundamentally differs from molecular systems, and we have chosen not to report it for the following reason.

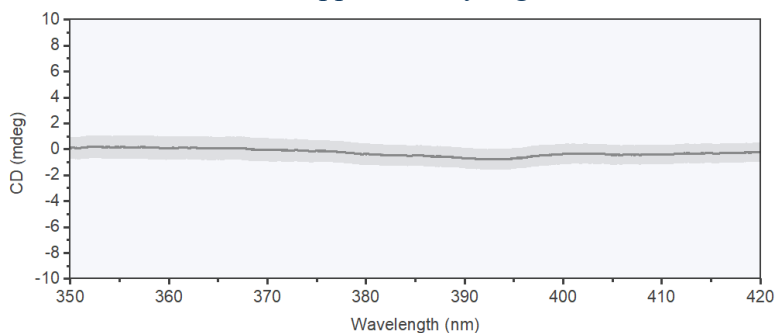
In molecular CD, the chromophore and the chiral entity are the same molecule, making g an intensive, concentration-independent material property. In our system, the two are decoupled: the chromophore is the exciton transition of $(\text{FCA3})_2\text{PbBr}_4$, which is present equally in achiral flat microplates and in twisted ribbons, while the CD signal arises solely from the macroscopic helical ribbon geometry.

Second, in an ensemble-averaged measurement, the denominator, A , includes absorption from all material in the beam path, making the formally calculated g dependent on the packing density, orientation distribution, and fraction of twisted ribbons within the measured area. Reporting such a value as a g -factor would risk misleading comparison with molecular dissymmetry factors. A physically meaningful morphological g -factor would require single-particle chiroptic measurements, where the CD and absorbance of an individual twisted ribbon can be directly correlated. This remains an important direction for quantitative characterization in our future work.

In the manuscript, we instead present the ensemble CD spectra as proof-of-concept evidence for chiroptic activity arising from morphological chirality, consistent with prior reports of morphologically induced CD in systems where the chiral length scale exceeds the optical wavelength.

Comment 5. A control measurement on non-deformed crystals of the same composition would help confirm that the observed CD signals originate from the chiral morphology rather than other possible effects.

Answer: Thank you for the suggestion. Non-deformed crystals exhibited negligible CD signals. We have included the results in the new Supplementary Fig. S19.



Supplementary Fig. S19. Ensemble averaged CD spectra of flat $(\text{FCA3})_2\text{PbBr}_4$ crystals.

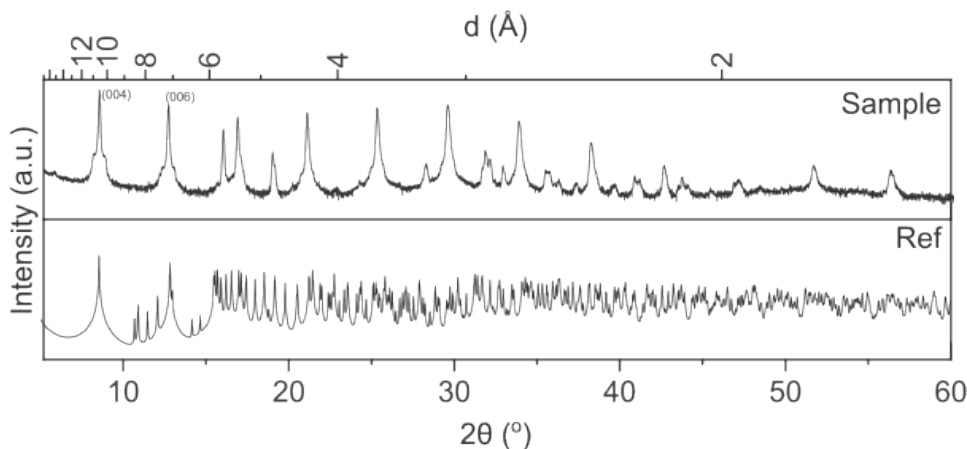
Abundant flat crystals obtained by free-space rapid growth were used for this measurement.

Addition to the main text:

...CCW clusters exhibited positive CD signals while CW clusters showed negative signals. Abundant flat crystals obtained by free-space rapid nucleation displayed minimal CD signals, on the other hand (Supplementary Fig. S19). These results matched...

Comment 6. Although single-crystal XRD on twisted ribbons may be challenging, powder XRD measurements on these crystals could still provide useful information. Comparing such data with the bulk crystal structure may help verify structural consistency.

Answer: Thank you for the suggestion. We have obtained powder X-ray diffraction spectrum directly from abundant twisted ribbons grown in Extended Data Fig. 2b. Data shows excellent match with the calculated spectrum obtained from the single-crystal structure (Response Fig. R1).



Response Figure R1. Powder X-ray diffraction spectrum of twisted $(\text{FCA3})_2\text{PbBr}_4$ ribbons (sample) compared with calculated spectrum (ref). Intensity is shown in log scale.

Comment 7. In the section “Crystallographic Control of Morphological Chirality,” the manuscript notes that 0.92 mol% BrCA3 leads to a change in space group from $P2_1/n$ to $P\bar{1}$. Given the low dopant concentration, it would be helpful to clarify whether this reflects a uniform phase transition or whether there could be undetected phase segregation or domain formation.

Answer: We thank the reviewer for raising this important point. Two lines of evidence support a uniform phase transition rather than phase segregation. First, the morphological outcome is the most sensitive indicator: phase segregation producing coexisting $P2_1/n$ and $P\bar{1}$ domains would manifest as twisted segments coexisting with straight segments within individual crystals, or a mixture of twisted and untwisted crystals within the same batch. Instead, complete suppression of

twisting was observed in every crystal across all doping levels from 0.5-10 mol% (Supplementary Fig. S16). This uniformity across batches argues strongly against macroscopic domain formation.

Second, although severe twinning in the 0.92 mol% sample precluded full structure refinement and quantification of exact BrCA3 content, the space group assignment ($P\bar{1}$) and the connectivity of the organic lattice, specifically the mutually aligned HOF configuration were all unambiguous. The well-characterized 8.95% doped structure (Table S4 and related text) further shows BrCA3 distributed statistically across both organic molecule positions in the unit cell, consistent with solid-solution mixing rather than phase-separated domains.

Mechanistically, $P2_1/n$ and $P\bar{1}$ are mutually exclusive symmetry operations. A crystal cannot simultaneously accommodate a 2_1 screw axis and an inversion center at the same site. Space group selection therefore reflects the global packing preference of the entire crystal rather than a local property of individual BrCA3 molecules. Even sub-1 mol% BrCA3 tilts this collective balance toward $P\bar{1}$, consistent with the extreme sensitivity of the crystal symmetry to dopant identity. We acknowledge that nanoscale compositional fluctuations cannot be definitively ruled out by SCXRD alone. However, the bulk structural and morphological evidence are both consistent with uniform $P\bar{1}$ throughout the crystal.

Comment 8. Relatedly, some discussion of why a halogen substitution (Br to F) leads to a substantial change in crystal structure would improve the chemical context, even if only at a qualitative level.

Answer: We thank the reviewer for this constructive comment. The question was also raised before by reviewer #3 (Comment #3). In short, $(\text{FCA3})_2\text{PbBr}_4$ exhibits a 2_1 screw axis, whereas this feature is absent for $(\text{BrCA3})_2\text{PbBr}_4$

The key distinction lies not in the organic spacer layer directly, but in the symmetry of the inorganic $[\text{PbBr}_4]^{2-}$ layer. Both $(\text{FCA3})_2\text{PbBr}_4$ ($P2_1/n$) and $(\text{BrCA3})_2\text{PbBr}_4$ ($P\bar{1}$) are centrosymmetric, which is consistent with the general tendency of crystals to adopt centrosymmetric packing. However, the inversion center sits at different locations. In $(\text{BrCA3})_2\text{PbBr}_4$, it resides within each individual inorganic slab, making the two faces of the slab crystallographically equivalent and yielding parallel HOF chains on both faces. In $(\text{FCA3})_2\text{PbBr}_4$, however, the inversion center instead sits in the organic interlayer gap between adjacent bilayers. Each individual inorganic slab therefore has only the 2_1 screw symmetry without local inversion, making the two faces inequivalent and forcing the organic spacers into misaligned HOF orientations. Geometric frustration, and thus spontaneous twisting, is a direct consequence of this arrangement.

Why F to Br substitution on the organic spacer shifts the preferred location of the inversion center, from the interlayer gap to within the slab, is a mechanistic question that cannot be resolved from

crystal structure data alone. It likely reflects differences in how each spacer templates the Pb-Br-Pb bond angle distortions at the organic-inorganic interface. Yet, the physical intuition behind this templating effect remains to be an open and highly significant question for the broader field of lattice-induced mechanical frustration in layered materials. We have clarified this picture in the manuscript and hope this framing provides a productive starting point for future investigations.

First, we added the following structural clarification to the first paragraph of the section “Crystallographic Control of Morphological Chirality”.

...with inversion centers in (BrCA3)₂PbBr₄ ($P\bar{1}$), reflecting a symmetry reduction (Extended Data Fig. 2, a and c). A key distinction is where the inversion center resides: in (BrCA3)₂PbBr₄ it sits within each individual [PbBr₄]²⁻ slab, making both faces of the slab crystallographically equivalent; in (FCA3)₂PbBr₄, however, it sits in the organic interlayer gap, so each individual slab retains only the 2₁ screw axis and its two faces are inequivalent. While both structures are centrosymmetric, it is the location of the inversion center, within or between slabs, that determines whether the organic spacers on opposite faces adopt misaligned or parallel HOF orientations. As a result, the uniaxial strain...

Second, the following perspective was added to the beginning of page 8, after the conclusion of the doping experiments.

The physical origin remains an open question of why F-to-Br substitution on the organic spacer shifts the inversion center from the interlayer gap into the inorganic slab, and thereby switches off the geometric frustration. This likely reflects subtle changes at the organic-inorganic interface that modify distortions in the Pb-Br-Pb bonding network, although the governing structural and chemical factors are not yet established. Understanding how organic network structures template lattice symmetry in layered perovskites is an important direction for future studies on tuning lattice-induced mechanical frustration in 2D materials, and may also extend to other systems where competing crystallographic symmetries give rise to emergent mechanical, optical, or electronic properties.

Comment 9. The reported dimensionless width of 1.34 shows a narrow distribution. It would be useful to comment on whether this value is intrinsic to the system or whether it depends on growth conditions such as temperature or solvent.

Answer: We thank the reviewer for this insightful question. The dimensionless width $\tilde{w}$ encodes both intrinsic material properties and growth-controlled geometry. Specifically, in the high-aspect-ratio limit, $\tilde{w} \propto \frac{w}{t} \left(\frac{W}{G}\right)^{1/4}$, where the material factor $\left(\frac{W}{G}\right)^{1/4}$ is intrinsic. W is the misalignment strain energy density and G is the in-plane shear modulus, neither of which is expected to vary with cooling rate or solvent within the conditions studied.

The aspect ratio w/t , however, does depend on growth conditions: as shown in Fig. 3b, faster cooling produces ribbons with $w/t \sim 5$ and slower cooling produces $w/t \sim 12$. This shifts the characteristic $\tilde{w}$ of each batch from 0.65-0.70 under rapid cooling to 1.55-1.60 under slow cooling. The overall mean $\tilde{w} = 1.34 \pm 0.32$ reflects the distribution of cooling rates across all 34 batches in our dataset.

The narrow, normal distribution of $\tilde{w}$ therefore reflects two things: (1) within any single batch, w/t is tightly constrained by growth kinetics at a fixed cooling rate, producing a narrow $\tilde{w}$ distribution per batch; and (2) across all batches, the mechanical model (Eq. 3) consistently maps the varying w and t values onto $\tilde{w}$ through the same material constants.

Critically, all twisted ribbons in our dataset satisfy $\tilde{w} < 2.5$ regardless of growth conditions, which is the helical transition threshold, confirming that the twisted helicoid regime is robust across the full range of conditions studied. Different solvent systems or crystallization temperatures that substantially alter w/t would shift the mean $\tilde{w}$, but the mechanistic framework relating $\tilde{w}$ to morphology would remain unchanged.

Comment 10. The molecular dynamics simulations are based on a nanoscale monolayer, whereas the experimental structures are much larger and multilayered. A brief discussion of how these simulations relate to the behavior of bulk-like ribbons, particularly regarding the propagation of geometric frustration across many layers, would be helpful.

Answer: Thank you for raising this point. The monolayer molecular dynamics simulation is intended to isolate the core mechanism that two misaligned HOFs within one monolayer generate incompatible elasticity, rather than to reproduce a bulk ribbon quantitatively. Its relevance to multilayered ribbons follows from the crystallography: the 50.2° HOF misalignment is enforced by the bulk $P2_1/n$ symmetry and is therefore present in every monolayer throughout the ribbon, in contrast to CdSe nanoribbons (ref. 21 and 22), where the frustration is confined to two surface ligand layers and is thickness-limited to below ~ 10 nm. Adjacent monolayers are related by the inversion center in the organic interlayer gap; inversion preserves the magnitude of the stored incompatible strain while reversing only the sense of the twist it induces. The geometric frustration is thus volumetrically encoded and accumulates coherently across the out-of-plane stack, whereas the handedness bias cancels, consistent with the observed near 1:1 CW:CCW ratio. This coherent propagation is confirmed experimentally by the single frustration energy density $W = 497 \text{ kJ/m}^3$ (updated in the revised manuscript, see Supplementary Note 2 and answer to Reviewer 5 Comment #8) that fits the entire dataset spanning roughly 15 to 1,650 monolayers (thickness ~ 30 nm to $3.3 \mu\text{m}$, Fig. 3d).

The discussion here connecting monolayer to multilayer 2D perovskite was elaborated further in our answer to Reviewer 1's Comment 4.2. We added a few clarification points to the main text, as follows:

This incompatible elasticity within a monolayer propagates as the layers are stacked together. Adjacent monolayers are related by the inversion center in organic sublattices (Fig. 2d) and thus carry opposite twisting tendencies. Inversion, however, preserves the magnitude of the stored strain in a monolayer while reversing only its sense. In other words, the lattice is geometrically frustrated yet achiral. In fact, geometric frustration has been expressed...

A reinforcement of the symmetric caveat was added to the discussion of handedness preference:

Handedness in helicoids is defined by the twist direction. Right-handed ribbons twist clockwise (CW) while left-handed twist counterclockwise (CCW). Because the centrosymmetric lattice encodes the frustration but not its handedness, each ribbon's twist direction is selected spontaneously as it forms rather than predetermined. Consistent with this, SEM analysis of 1,510 ribbons gave a near-equal CW:CCW ratio of 674:836 (Supplementary Table S1).

Comment 11. In the SI, the curvature fitting method uses the 81 nearest lead atoms. It would be useful to clarify whether edge atoms were excluded from this analysis, as their local environment may differ from that of the interior.

Answer: We thank the reviewer for raising the clarification. The edge atoms were excluded from the analysis. As pointed out in the current caption of Supplementary Fig. S12:

Here, only a 12×64 atom subset is shown to exclude regions with unreliable curvature extraction near the edges.

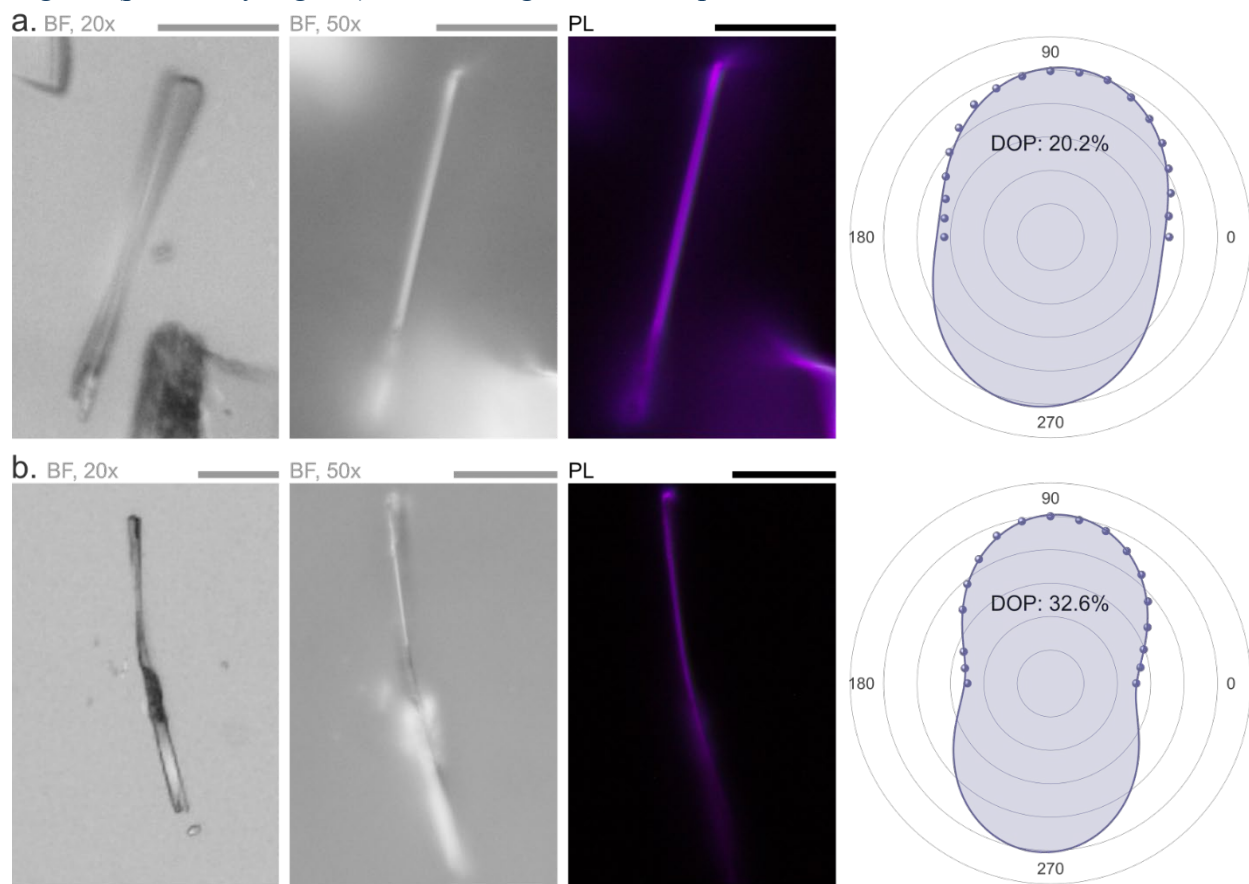
Comment 12. The CD measurements were performed on relatively large, hyperbranched clusters. Based on the provided images, the handedness does not appear fully uniform across these structures. It would be helpful to clarify how the measurement accounts for this, for example in terms of beam spot size or possible averaging over domains of opposite handedness.

Answer: We thank the reviewer for this observation. The CD measurements were performed using a beam spot diameter of 5 mm, which encompasses the majority of each centimeter-scale hyperbranched cluster. We acknowledge that, as visible in Extended Data Fig. 4, a and b, minor regions of opposite handedness can be present at the periphery of some clusters. However, these represent a small minority of the total ribbon population within the measured area, as the dominant handedness is established by the nucleating core and propagates coherently outward through the branching structure. The ensemble CD signal therefore reflects the predominant handedness of the cluster, with minor contributions from opposite-handedness regions expected to partially cancel and reduce the absolute CD magnitude. This is consistent with our interpretation of these

measurements as proof-of-concept demonstrations rather than quantitative chiroptic characterization.

Comment 13. It would be helpful to report the degree of linear polarization in Supplementary Figure S5, as this could be relevant for evaluating possible contributions from linear optical effects.

Answer: Thank you for the careful reading. We have updated the current Supplementary Fig. S6 (previously Fig. S5) with the degree of linear polarization.



Supplementary Fig. S6. (updated)

Response to Reviewer #5

This work systematically demonstrates that through molecular design (FCA3), linearly aligned HOFs that are misaligned with respect to each other are introduced into non-chiral layered perovskites, generating incompatible strain that induces morphological chiral twisting. Geometric frustration in layered perovskites to generate morphological chirality are potentially novel. However, the central argument—misaligned lattice strain is the origin of geometric frustration and the formation of twist ribbon—exhibits a logical gap with the observed low twisting probability (<1%). The following concerns need to be addressed:

Answer: We sincerely appreciate the reviewer's recognition of the novelty of our work and for identifying a source of confusion in the original manuscript regarding the statistics of ribbons exhibiting twisting. As clarified in our response below, geometric-frustration-induced bending and twisting are present in all crystals grown in the thermodynamic regime; however, rapid cooling can alter the observed statistics by prematurely terminating crystal growth.

Most importantly, we are grateful for Reviewer 5's rigorous critique of our mechanical model (Comment 8). This challenge prompted us to substantially strengthen our presentation and analysis by adding Supplementary Note 2, which provides a detailed assessment of the fidelity and validity of the mechanical model. We are indebted to the reviewer for identifying this issue and helping us improve the manuscript.

Comment 1. Figure 1e only shows the normalized PL spectral overlap between flat microplates and twisted ribbons. The similarity only indicates that the spectral shape does not change significantly, which is insufficient to support the conclusion that "bending and chiral deformation did not interfere with the PL." It is recommended to provide key parameters such as peak position (λ_{max}), FWHM, and emission intensity, along with statistics from multiple twisted ribbons presented as mean and standard deviation, rather than a single representative curve.

Answer: We appreciate the suggestion and your careful attention to detail. We agree that the original statement was imprecise. We have revised the text to specify that bending and chiral deformation has minimal effects on the PL spectral shape rather than making a broader claim about PL in general.

Bending and chiral deformation minimally interfered with the spectral shape of the purple exciton-dominated photoluminescence (PL) near 395 nm (Fig. 1e) as analyzed over a population of 5 twisted ribbons and 3 flat samples (Supplementary Fig. S4).

To support this, we overlaid normalized PL spectra from 5 independently measured twisted ribbons alongside the 3 flat references (new Supplementary Fig. S4). The spectra show consistent $\lambda_{\text{max}} = 394.9 \pm 0.8$ nm and FWHM = 10.6 ± 0.3 nm for twisted ribbons, compared with $\lambda_{\text{max}} =$

395.2 ± 1.0 nm and $\text{FWHM} = 12.2 \pm 0.9$ nm for flat samples, confirming that mechanical deformation does not perturb the excitonic emission profile. Note only apparently thin crystals were selected to reduce effects from self-absorption.

We acknowledge that deformation may affect the PL quantum yield (PLQY) of 2D perovskites. Yet, a quantitative comparison of absolute emission intensity or PLQY between flat and twisted crystals is outside the scope of this work, as it would require matched sample geometries and collection efficiencies that are not achievable for free-standing ribbons of variable morphology.

Comment 2. SEM analysis of 1,510 samples confirms a CW:CCW ratio of 674:836. The original manuscript only reports the ratio without specifying the statistical source of these samples. For example, how many independent sample batches did these 1,510 samples come from? Do both CW and CCW samples coexist within the same batch? Is there any regional variation? Is there a chirality bias between different batches? The authors should clearly explain the statistical source to avoid the possibility that the near 1:1 ratio overall masks batch-to-batch or region-to-region chirality bias.

Answer: Thank you for pointing this out. It is important indeed to clarify the source of population analysis. The 1,510 ribbons were collected from 5 independent batches. CW and CCW ribbons coexist within every batch. Batch-level CCW fractions range from 43-63%, indicating stochastic fluctuation but no persistent directional bias (Supplementary Table S1). Regional variation within a batch cannot be assessed, as ribbons are collected from free-space crystallized batches in vials suspension without spatial tracking.

Supplementary Table. S1. Handedness statistics of twisted ribbons across batches.

<i>Batch</i>	<i>Growth rate</i>	<i>CCW</i>	<i>CW</i>
<i>1</i>	<i>0.010 °/min</i>	<i>207</i>	<i>136</i>
<i>2</i>	<i>0.010 °/min</i>	<i>46</i>	<i>47</i>
<i>3</i>	<i>0.010 °/min</i>	<i>315</i>	<i>184</i>
<i>4</i>	<i>0.010 °/min</i>	<i>92</i>	<i>72</i>
<i>5</i>	<i>0.044 °/min</i>	<i>176</i>	<i>235</i>
<i>All</i>		<i>836</i>	<i>674</i>

No external symmetry-breaking field (chiral template, circularly polarized light, or directional flow) is present in free-space in-solution growth, so no mechanism exists to impose a consistent chiral preference. The twist-sense nucleation effect, where a growing ribbon can seed daughter ribbons of the same handedness [ref 23, J. Am. Chem. Soc. 135, 3395–3398 (2013)], may locally enrich one handedness within a batch, but is diluted in open solution with many independent nucleation sites. This can explain the variation of CW:CCW ratio across batches. The near 1:1

ensemble average therefore reflects genuine stochastic chirality selection; the batch-level fluctuations are consistent with finite-sample statistics.

Supplementary Table S1 was added to the revised Supplementary Materials and was cited in the revised main text when discussing the global CW:CCW ratio. The elaboration here was added to the caption to its caption.

This was confirmed by SEM analysis of 1510 samples, which displayed a CW:CCW ratio of 674:836 (Supplementary Table S1).

Comment 3. Undeformed bulk single crystals show that misaligned HOFs are an intrinsic structural feature of the crystals, and the authors attribute morphological chirality to misaligned linear HOFs within a monolayer. However, the establishment of this mechanism is primarily based on less than 1% of twisted ribbon events. Why did only <1% of crystals grow into twisted nanoribbons during rapid crystallization? If misaligned strain were a sufficient condition, this proportion would be far too low. The authors have never mentioned whether this proportion changes under other cooling conditions. Moreover, the misaligned linear HOFs were observed in undeformed bulk single crystals. Does this imply that an additional kinetic trigger (such as a specific supersaturation, growth rate, or stochastic nucleation event) is required to activate twisting? Does an energy barrier exist from flat to twisted morphology? The authors should provide an explicit discussion on this matter.

Answer: We thank the reviewer for this important challenge. We'd like to clarify first that twisting is a prevalent behavior when crystal growth enters the thermodynamic regime. At slow growth rate, every crystal was twisted or strongly deformed (Extended Data Fig. 2b). The discussion here also reflects our response to Reviewer #3's similar comment #1 and #2.

The <1% twisted ribbon fraction at rapid cooling reflects the fraction of crystals that develop elongated ribbon morphology, not the fraction where the geometric frustration mechanism is active. The misaligned HOF structure is present in every (FCA3)₂PbBr₄ crystal. However, observable morphological chirality requires two geometric conditions beyond the crystallographic one: (1) the crystal must grow as an elongated ribbon rather than an equiaxed plate, and (2) the ribbon must reach length $L \geq \text{pitch}/2$ to complete a visible half-twist.

At rapid cooling rates (~16°C/min), high supersaturation and rapid nucleation produce predominantly equiaxed microplates. The misaligned bilayer HOF in (FCA3)₂PbBr₄ renders the [110] and [1 $\bar{1}$ 0] edge energies nearly equivalent (Supplementary Fig. S8), removing the thermodynamic preference for anisotropic ribbon growth, as we discussed on page 6:

While a linearly aligned HOF promotes anisotropic distribution of dangling COOH at the [110] and [1 $\bar{1}$ 0] edges, this anisotropy disappeared in the presence of a

misaligned bilayer HOF (Supplementary Fig. S8). Thus, crystals of $(FCA3)_2PbBr_4$ were not expected to have a preferential growth direction along $[110]$ or $[1\bar{1}0]$, which is in line with the observed abundance of microplates at a rapid growth rate. The formation of elongated ribbons was a random behavior, potentially originating from local fluctuation in supersaturation.

Ribbon formation under these conditions arises stochastically from local supersaturation fluctuations. Yet, the intrinsic frustration operates in every crystal. The limiting factor is morphogenesis, not mechanism.

The proportion changes dramatically with cooling rate, as already shown in Extended Data Fig. 2b. Slow cooling ($0.044\text{ }^{\circ}\text{C/min}$) produces pervasive morphological deformation in essentially every crystal. We now make this connection explicit in the revised manuscript, near the end of the “Geometric Frustration in Layered Perovskites” section:

Under rapid cooling, however, crystal growth terminates before ribbons reach one full pitch period, so the helicoid geometry is not expressed at the observable scale. Thin nanoribbons with length shorter than one-quarter pitch period can additionally be flattened by substrate adhesion during sample preparation, which explained the mere occasional twist observed earlier (Supplementary Fig. S1).

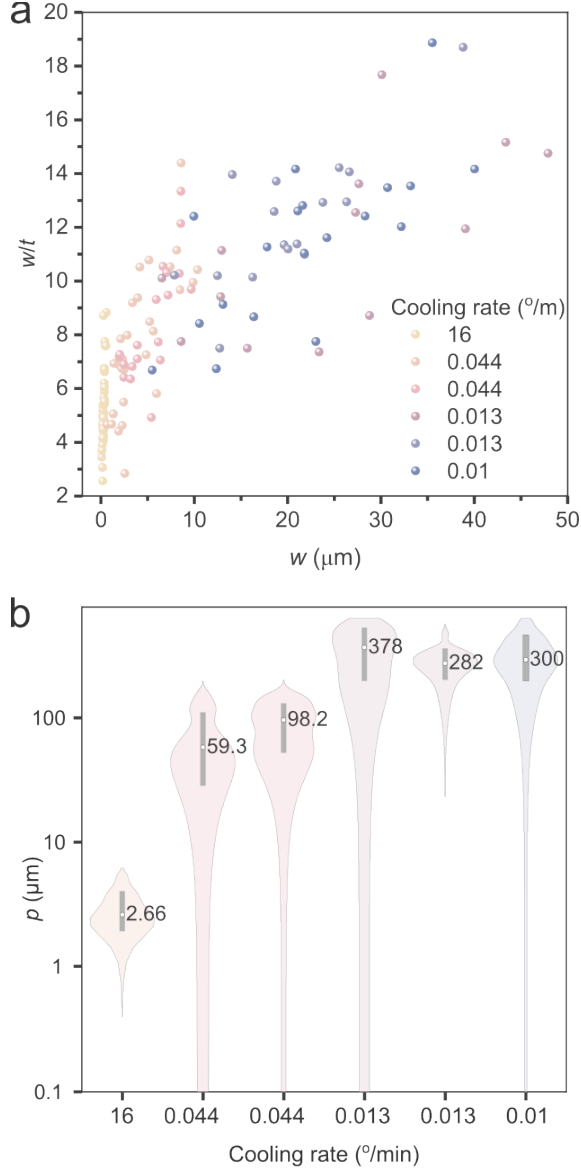
Regarding the energy barrier, no thermodynamic energy barrier separates the flat from the twisted state. A ribbon with incompatible strain is mechanically unstable against twisting. Any perturbation from flat grows spontaneously toward the helicoid configuration. Bulk single crystals appear undeformed not because the lattice frustration is absent or blocked, but because their macroscopic dimensions yield equilibrium pitch values far exceeding any practical crystal length. The misaligned HOFs are nevertheless present throughout, as confirmed by SCXRD. The kinetic trigger for ribbon formation is the stochastic onset of elongated growth, not activation of a twisting mechanism. Once $L \geq p/2$ is satisfied, twisting proceeds without incubation, as confirmed directly by in-situ growth microscopy (Supplementary Videos S1 and S2).

Comment 4. The authors have provided statistics showing the effect of cooling rate on w/t , do the pitch, or node density of helical ribbons show systematic changes? Please provide relevant analysis.

Answer: We thank the reviewer for this suggestion. We’ve added the following elaboration on the trend of w/t v.s. cooling rate (Fig. 3b), in response to Reviewer #1’s comment #7:

...a broader width distribution ($5\text{--}40\text{ }\mu\text{m}$) and $\overline{w/t} = 12.0$. This trend reflects the lower barrier for in-plane v.s. out-of-plane growth: slow cooling favors lateral spreading (high w/t), while rapid cooling elevates supersaturation above the new layer nucleation threshold, promoting thicker growth relative to width. Parallel batches...

The pitch (p) of twisted ribbons also show systematic dependence on cooling rate, consistent with the mechanical model. We plotted the pitch distribution for each cooling rate group and present this in Supplementary Fig. S20b. Pitch increases monotonically with decreasing cooling rate, directly parallel to the w/t trend in Fig. 3b. Slower cooling produces thicker ribbons and the pitch scales proportionally.



Supplementary Fig. S20. Twisted ribbon (a) w/t v.s. w distribution at various cooling rate and (b) p v.s. cooling rate distribution.

We also considered reporting node density as a function of cooling rate. However, we find this metric to be either redundant or confounded. For ribbons that satisfy $L \geq p/2$, node density along the ribbon length is simply $2/p$, which is a direct restatement of pitch rather than an independent observation.

Alternatively, counting nodes across all crystals in a batch conflates the elastic mechanics with the probability of ribbon formation and the stochastic distribution of crystal lengths, neither of which reflects the physical picture we aim to establish. We therefore only presented pitch as the additional mechanistically meaningful parameter, noting that node density follows from it trivially for any ribbon of known length.

Comment 5. If 0.5% doping completely suppresses twisting, while the twisting proportion in the neat FCA3 system is <1%,. How can one rule out the possibility that the doping result is explained by statistical fluctuations or sample inhomogeneity rather than necessarily being attributed to symmetry changes? The authors need to provide statistically meaningful data for support, based on ‘the probability of observing at least one twisted crystal if the twisting ability remains at 1%.’.

Answer: We thank the reviewer for raising this point. We’d like to clarify first that twisting is a prevalent behavior when crystal growth enters the thermodynamic regime. At slow growth rate, every crystal was twisted or strongly deformed (Extended Data Fig. 2b). The <1% twist fraction cited in the manuscript refers specifically to rapid cooling conditions (~16 °C/min), where most crystals formed equiaxed microplates and the geometric criterion $L \geq p/2$ for a full twist to become observable is rarely satisfied (please also refer to our previous response to Comment #3).

The doping experiments were conducted at 0.01 °C/min, which enters the thermodynamic regime in which the neat (FCA3)₂PbBr₄ system shows pervasive morphological deformation in most crystals (Extended Data Fig. 2b). The relevant baseline for the statistical comparison is therefore not <1% but the high deformation fraction observed at this slow cooling rate. The relevant discussion was added to the revised manuscript near the end of the “Geometric Frustration in Layered Perovskites” section:

Under rapid cooling, however, crystal growth terminates before ribbons reach one full pitch period, so the helicoid geometry is not expressed at the observable scale. Thin nanoribbons with length shorter than one-quarter pitch period can additionally be flattened by substrate adhesion during sample preparation, which explained the mere occasional twist observed earlier (Supplementary Fig. S1).

With the correct baseline established, the observed outcome is statistically compelling. Across all elongated crystals surveyed in the doped samples at 0.5-10 mol% BrCA3 (Supplementary Fig. S16), no twisted crystals were detected. The complete suppression of twisting under conditions where the neat system shows pervasive deformation is therefore highly unlikely to reflect statistical fluctuation alone.

This conclusion is independently supported by structural evidence. Single-crystal XRD confirms a space group change from $P2_1/n$ to $P\bar{1}$ in doped crystals, providing a direct mechanistic

explanation for the loss of deformation that is entirely independent of morphological counting. The consistent coincidence of complete morphological suppression with an unambiguous crystallographic symmetry change across all doping levels from 0.5 to 10 mol% strongly supports the interpretation that the suppression arises from the loss of strain misalignment, rather than from statistical fluctuation or sample inhomogeneity.

To clarify the confusion, we've added the following sentences to the end of page 7 where the doping results were discussed:

Surprisingly, when 0.5–10 mol% BrCA3 (relative to the total amount of organic spacers) was introduced during the crystallization of (FCA3)₂PbBr₄, spontaneous deformation was absent in all crystals at every doping concentration (Supplementary Fig. S16). It is worth noting that these doping experiments were conducted at a cooling rate of 0.01 °C/min, which is at the thermodynamic regime where (FCA3)₂PbBr₄ shows pervasive morphological deformation (Extended Data Fig. 2b). Thus, the complete absence of twisting across all doped samples represents a statistically significant suppression.

Comment 6. MD simulations show that a single molecular layer (10 × 40 nm) alone can generate twisting. However, the experimental twisted ribbons have thicknesses ranging from 30 nm to 2 μm (approximately 10–700 inorganic layers). Does interlayer coupling enhance or counteract twisting? As thickness increases, do the pitch or node density of the twists show systematic changes?

Answer: We thank the reviewer for this important question. Interlayer coupling neither cancels nor amplifies the intrinsic driving force for twisting. Each monolayer contributes the same frustration energy density, as demonstrated by the single value $W = 497 \text{ kJ/m}^3$ that fits the linear pitch $p \propto \sqrt{J/wt}$ relationship (Fig. 3d) across the full thickness range (~30 nm to 3.3 μm, or ~15 to 1,650 inorganic layers (updated in the revised manuscript, see Supplementary Note 2 and answer to Reviewer 5 Comment #8). Had coupling enhanced or counteracted the frustration, W would drift systematically with thickness and break this linearity. Mechanistically, adjacent monolayers (related by the inversion center) carry opposing twist senses, so their handedness contributions cancel, but their frustration energies add. The consequence for thickness is contained in Eq. 3: because the torsional rigidity grows with the cross-section ($J \propto t^3w$ for thin ribbons with $w \gg t$) while the torsion energy driving the twist grows with volume, the equilibrium pitch increases approximately linearly with thickness ($p \propto t$) and the node density decreases correspondingly. This trend is observed by our measurements where rapidly nucleated thin ribbons show tighter pitches while slowly grown thick ribbons show longer ones (Fig. 3, b to d, and Supplementary Fig. S20). In short, thicker ribbons twist more gently not because the frustration weakens but because the elastic restoring torque grows with cross-section.

The discussion here connecting monolayer to multilayer 2D perovskite was elaborated further in our answer to Reviewer 1's Comment 4.2. We added a few clarification points to the main text, as follows:

This incompatible elasticity within a monolayer propagates as the layers are stacked together. Adjacent monolayers are related by the inversion center in organic sublattices (Fig. 2d) and thus carry opposite twisting tendencies. Inversion, however, preserves the magnitude of the stored strain in a monolayer while reversing only its sense. In other words, the lattice is geometrically frustrated yet achiral. In fact, geometric frustration has been expressed...

A reinforcement of the symmetric caveat was added to the discussion of handedness preference:

Handedness in helicoids is defined by the twist direction. Right-handed ribbons twist clockwise (CW) while left-handed twist counterclockwise (CCW). Because the centrosymmetric lattice encodes the frustration but not its handedness, each ribbon's twist direction is selected spontaneously as it forms rather than predetermined. Consistent with this, SEM analysis of 1,510 ribbons gave a near-equal CW:CCW ratio of 674:836 (Supplementary Table S1).

Comment 7. The ribbon forests used for CD measurements were grown directly in a 10- μ m-thick sealed quartz confined space and remained immersed in the mother liquor throughout subsequent measurements. This means that the quartz substrate/interface is not merely a "measurement platform" but rather an integral part of the crystal nucleation and growth environment. Therefore, whether different substrate or interface conditions affect the nucleation mode, growth pathway, branching morphology, and chirality coherence within a given cluster should be seriously discussed.

Answer: We thank the reviewer for this thoughtful observation. The quartz confinement does serve as an integral part of the growth environment, and we agree this deserves explicit discussion.

The role of the quartz disk is primarily geometric rather than chemical. The 10 μ m confinement gap restricts out-of-plane crystal growth, promoting lateral ribbon development and thus centimeter-scale chirality-coherent clusters can be produced at a slow cooling rate. The key substrate effect is therefore the confinement geometry, not the specific surface chemistry of quartz. The fundamental mechanism of geometric frustration, twisted ribbon formation, and chirality coherence via heterogenous nucleation is substrate-independent, as demonstrated by the consistency of twisted ribbon morphology across all other experiments in the manuscript. Twisted ribbons imaged by SEM and optical microscopy throughout Figs. 1, S1 to S3, S8, S12, S13, and Extended Data Figs. 1-3 were grown in conventional glass containers under varied cooling conditions, and exhibit similar morphology and handedness statistics (Supplementary Table 1).

We acknowledge that the specific hyperbranched forest architecture, which requires both confinement and very slow cooling to develop centimeter-scale lateral extent, may depend on the

growth geometry in ways not fully explored here. Whether equivalent chirality-coherent clusters form under different substrate or confinement conditions is an interesting direction for future investigation. However, the underlying mechanism by which chirality coherence arises, that handedness inherited from the nucleating core and propagated through secondary nucleation, is a growth behavior of twisted crystals under the heterogeneous nucleation regime. This phenomenon was also previously described in the term of “twist sense” in a variety of materials being determined over mm² areas, where the clusters’ chirality coherence was determined by the sense of the faces on the proto-nucleus of the core, as Reviewer 1 pointed out. (Cui X, Rohl AL, Shtukenberg A, Kahr B. Twisted aspirin crystals. *Journal of the American Chemical Society*. 2013, 135, 3395-3398, which was included in the revised manuscript as ref. 23).

We have added a brief clarification of the quartz disk's functional role to the chiroptic measurements section of the revised manuscript.

... Newly formed crystals thus inherit the handedness of their predecessors, creating a cascade of chirality amplification as reported in many organic twisted crystal systems²³. Experimentally, this was achieved via slow recrystallization of (FCA3)₂PbBr₄ within a 10 μm-thick constrained space. The space confinement serves primarily to provide geometric confinement restricting out-of-plane growth and enabling slow, controlled lateral crystallization, rather than to chemically direct nucleation. Multiple centimeter-scale hyperbranched ...

Comment 8. The structure difference between (n-butylammonium)₂PbBr₄ and (FCA3)₂PbBr₄ is substantial, especially given the authors' claim that misaligned HOFs and strain are the core drivers of twisting. Is it reasonable to use the same shear modulus value? Is there experimental or computational support for the shear modulus of the FCA3-based system being close to 40 MPa?

Answer: Thank you for raising this insightful question, which led us to identify an error in our original choice of shear modulus G . On careful re-examination, we find that $G = 40$ MPa from Li et al. (original ref. 24: *J. Phys. Chem. C* **2019**, 123, 15251) is the incorrect tensor component for the in-plane twisting of ribbons, and we have revised the manuscript accordingly. In the course of addressing this issue, we also re-evaluated the underlying mechanical model. Below, we discuss the intuitive physical picture and its applicability to our system.

The physical origin of this error lies in the distinction between different shear modes in layered 2D perovskites. Li et al. measured the inter-layer sliding modulus of (nBA)₂PbBr₄ using contact-mode atomic force microscopy (AFM), where a lateral tip force displaces 2D perovskite layers relative to one another through the organic bilayer, directly probing the shear along the out-of-plane stacking direction (the τ_{xz} mode where z is the stacking direction and x is one of the in-plane axis, which we also assign later as the longitudinal axis of our ribbons – note, the first index in τ represents the direction of the force while the second represent the normal direction to the interface being sheared). For this mode, both a 2D perovskite monolayer and the interlayer van der Waals (vdW) interfaces are in mechanical series (Reuss composite), so the soft vdW interface

carries essentially all displacement regardless of inorganic stiffness, yielding a measured $G \sim 30$ MPa for infinite-layer structures which increases when decreasing the layer number.

(J. Phys. Chem. C 2019, 123, 15254.) The shear modulus is finally characterized at 42.4 ± 2.9 MPa for the 2D (C₄H₉NH₃)₂PbBr₄ perovskites with $2 \times 2 \mu\text{m}$ in size and 40 nm in thickness (25 layers)... (pp. 15255.) As n increases to more than 150, the shear modulus $G_m = 30$ MPa is obtained from...

However, Eq. 3 was derived by Bardeen and coworkers (Current ref. 28: *J. Am. Chem. Soc.* **2011**, 133, 12569) from St. Venant beam torsion theory, which for a thin ribbon (width $w \gg$ thickness t) predicts a dominant shear stress τ_{xy} . This stress represents the in-plane shear coupling between the ribbon longitudinal axis x to the width direction y , which varies linearly across the thickness and gives the torsional rigidity $J = wt^3/3$ (i.e. substituting $t/w \sim 0$ to Eq. 2). The complementary inter-layer component τ_{xz} is negligible in the interior of a thin ribbon. Bardeen and coworkers accordingly used $G = 5$ GPa, the bulk shear modulus of common organic crystals, and validated the result based on the fact that inferred energy density to sustain a full twist, $W = 3.4$ kJ/mol fell within the range expected for noncovalent interactions.

(J. Am. Chem. Soc. 2011, 133, 12569.) Assuming a typical value of $G = 5$ GPa, and the concentration of 9AC in the crystal as 6.3 M, we obtain $W = 3.4$ kJ/mol at the maximum photoconversion. This calculated energy density W falls within the range expected for noncovalent interactions between different molecules, indicating that this analysis leads to chemically reasonable values. Note that if the calculated value for W had fallen outside this range, we would have to consider other types of energy contributions in addition to intermolecular interactions.

The appropriate G is the in-plane shear modulus of (FCA3)₂PbBr₄ under DFT studies. Three independent DFT studies of $n = 1$ layered perovskites with aromatic spacers (with benzene or fluorobenzene rings that are structurally analogous to our FCA3) yield consistent values:

- PEA₂PbI₄ $G_{\text{VRH}} = 5.4\text{--}7.0$ GPa (Rathore et al. *J. Alloys Comp.* **2023**, 936, 168328; Saadatmand et al. *ACS Omega*. **2024**, 9, 24928.)
- (*o*- or *m*- or *p*-)FPEA₂PbI₄ $G_{\text{VRH}} = 6.0\text{--}7.1$ GPa (Saadatmand et al.; Shokouhi et al. *Sci. Rep.* 2025, 15, 20707.)
- Note, G is typically calculated using either Voigt, Reuss, or Hill approximation. Accordingly, it is labeled G_{VRH} above to represent the range of values derived from these methods.

Substituting $G = 40$ MPa (a τ_{xz} quantity from Li et al.) into a formula that calls for the τ_{xy} shear modulus is a tensor-component mismatch, independent of whether (FCA3)₂PbBr₄ is structurally similar to (*n*BA)₂PbBr₄. Although both modes involve lateral displacements directed within the 2D perovskite plane, their governing physics differ fundamentally: τ_{xz} slides one 2D perovskite layer against the next so the soft vdW bilayer loaded in series along z absorbs most strain and

yields apparently small $G_{xz} \sim 40$ MPa; however, τ_{xy} shears material within each individual 2D layer without crossing any interlayer interface, so the stiff inorganic network loaded in parallel within the layer governs and yields $G_{xy} \sim 5$ -7 GPa. The ~ 150 -fold difference between the two is a structural consequence of the layered architecture.

It is worth noting that experimentally determined values of G typically include contributions from the shearing of the soft vdW bilayer. For instance, an early study on the in-plane elastic modulus of $(\text{PEA})_2\text{PbI}_4$ using wrinkle experiments obtained $G \sim 2$ GPa (Reyes-Martinez et al. *ACS Appl. Mater. Interfaces* **2020**, *12*, 17883) lies between these DFT values and Li et al.'s value, reflecting partial inter-layer sliding during bending (i.e. a bending-mode effective compliance rather than a pure shear modulus). The authors acknowledged the discrepancy between their experimentally determined and calculated shear modulus:

(Reyes-Martinez et al. pp. 17888.) We believe that the reason behind the almost 5-fold difference in elastic moduli between the wrinkling results and DFT-derived values stems from the different nature of deformations... In contrast, for such layered (quasi)2D structures, the in-plane elastic response measured by wrinkling can be dominated by more macroscopic deformation phenomena, including sliding of entire 2D sheets and changes in their interlayer rippled structures (happening over relatively long distances).

Taken together, these data place the in-plane G of $(\text{FCA3})_2\text{PbBr}_4$ in the 5-7 GPa range, which is consistent with DFT-calculated values regardless of the choice of organic spacers, and is also consistent with Bardeen's use of 5 GPa for organic molecular crystal ribbons under the same formula.

We note a subtlety in applying the isotropic formula Bardeen and coworkers used to a layered, anisotropic crystal: the twisted ribbon develops local saddle curvature, which couples torsion to out-of-plane bending and introduces some contribution from the inter-layer bending compliance. This softens the effective G below the pure calculated value, and thus we estimate $G_{\text{eff}} \sim 1$ -7 GPa as the physically reasonable range.

Using $G = 5$ GPa (midrange, consistent with Bardeen and coworkers), W scales from the current underestimated 3.98 kJ/m^3 to 497 kJ/m^3 , which represents the torsional elastic energy stored required to sustain one full twist. We have revised the main text accordingly with the relevant references modified.

W was fitted to be 497 kJ/m^3 assuming an in-plane shear modulus of $G \sim 5$ GPa, consistent with the elastic constant of common 2D perovskites with aromatic spacers obtained from density functional theory²⁹. This in-plane G , governing shear within the metal-halide inorganic layer, is the mechanically relevant quantity for aforementioned thin ribbon torsion model Bardeen and coworkers used and is consistent with the 5 GPa applied in their original derivation of Eq. 3 for organic molecular crystal

ribbons²⁸ (see Supplementary Note 2. Fidelity of Mechanical model). Notably, the linear scaling of p with $\sqrt{J/wt}$ across ribbons of widely varying dimensions constitutes independent evidence for the geometric frustration mechanism: an intrinsic, geometry-independent elastic driving force produces precisely this dimensional scaling, whereas extrinsic sources of twist such as surface effects would not.

Additionally, we've added a Supplementary Note 2 to elaborate on the fidelity of our mechanical model. This SI note is not pasted here to keep the response letter brief.