
Geometric frustration in morphologically chiral nanoribbons of layered perovskites

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Supplementary Note 1. Propagation of Geometric Frustration Across Centrosymmetric Lattices.

The geometric and mechanical frustration originates within a monolayer, where the 2_1 screw forces the two HOFs into the misaligned $[210]$ and $[2\bar{1}0]$ orientations. Because the $P2_1/n$ lattice is centrosymmetric, adjacent monolayers are related by the inversion center in the middle of the organic layer (i.e. between two monolayer, Fig. 2d), and the frustration in each monolayer might be expected to be cancelled by its inverted neighbor.

The resolution is to separate two quantities. The incompatible strain is length-like, and its elastic energy scales with the square of the misalignment. Inversion preserves all lengths, so this positive-definite strain energy is unchanged and adds with every layer.

A deeper statement is that a monolayer imposes not a twist but a saddle. A saddle is achiral - it has a symmetric curvature tensor (principal values $+\kappa$ and $-\kappa$) that carries no pseudoscalar. We hypothesize that a twist sense, or a preferred handedness appears only when this saddle meets the ribbon's long axis. Because the ribbon grows with equal preference along the two symmetry-equivalent, perpendicular directions $[110]$ and $[1\bar{1}0]$, the identical saddle yields a clockwise or a counterclockwise helicoid depending only on which edge a ribbon elongates along. The handedness is thus free rather than lattice-dictated.

Another caveat is that the frustration is volumetric rather than surface-confined, because the misalignment is set by the bulk $P2_1/n$ symmetry and recurs in every layer, unlike CdSe nanoribbons (main text refs 21, 22), where it is limited to two surface organic ligand layers. Our mechanical data analysis confirm this directly: a single $W = 497 \text{ kJ/m}^3$ fits the linear relation $p \propto \sqrt{J/wt}$ (Fig. 3d) from $t = 30 \text{ nm}$ to $3.3 \text{ }\mu\text{m}$, or ~ 15 to $1,650$ inorganic layers. Had interlayer coupling enhanced or counteracted the per-layer frustration, W would drift with thickness and break this linearity. Assuming $J \sim wt^3/3$ for $w \gg t$, the pitch increases as $p \propto t$ and the node density falls as $1/t$, which is the mechanical description of why thicker ribbons twist more gently through a larger elastic restoring torque, not a weaker strain (Fig. 3, b to d).

Handedness is thus generated crystallographically and accumulated volumetrically, but chosen spontaneously and propagated kinetically. A free-space nucleation resulted near-racemic (CW:CCW = 674:836; Supplementary Table S1), while a space-confined crystallization resulted every crystallite in a hyperbranched cluster sharing the handedness of its nucleating core through templated secondary nucleation (Extended Data Fig. 4, a and b). The microscopic event that first breaks the symmetry in a given ribbon, with a nucleation fluctuation or an edge asymmetry, remains an open question for future theory and simulation.

Supplementary Note 2. Dataset and Quantification Method for Statistical Analysis of Ribbons.

The width (w), thickness (t), and pitch (p) were extracted from the SEM images of 177 unique twisted ribbons (Fig. 3a). p is defined as the distance along the ribbon's longitudinal axis required for a twist degree (θ) of 2π (i.e. one complete 360° rotation about the central axis). t was measured from the twist node (Supplementary Fig. S14), which was defined previously as the geometric position where the ribbon's width vector is oriented normal to the substrate plane. For quantitative analysis, we exclusively examined ribbons with a minimum of two exposed nodes (i.e. $\theta \geq \pi$). This criterion enabled measurement of the half-pitch distance ($p/2$) between consecutive nodes, from which the full pitch could be determined.

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 $\overline{w/t}$ of 7.75. However, w/t exhibited strong dependence on the absolute dimensions w and t (Fig. 3b and Supplementary Fig. S20a). Specifically, rapid nucleation (rate $\sim 16^\circ\text{C}/\text{min}$) produced twisted ribbons with $w = 100\text{-}600$ nm and $\overline{w/t} = 4.97$, whereas the slowest cooling rate of $0.01^\circ\text{C}/\text{min}$ generated ribbons with 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 subjected to identical cooling rates consistently yielded samples with similar $\overline{w/t}$ values.

Supplementary Note 3. Fidelity of Mechanical model.

Equation 3 relates the equilibrium twist period p of an elastic crystal ribbon to its cross-sectional dimensions and two material constants:

$$p = 2\pi \sqrt{\frac{G}{W}} \sqrt{\frac{J(w, t)}{wt}} \quad (3)$$

Here, $J(w, t)$ is the torsional constant of the rectangular cross-section (given in the main text), G is the shear modulus of the crystal (stiffness against shear deformation), and W is the intrinsic elastic driving energy density, which we defined in the main text as now defined as the energy density per unit volume required to sustain a full twist. This formula was derived by Bardeen and coworkers (main text ref 28) from St. Venant beam torsion theory, the classical framework for computing how a uniform elastic beam (a ribbon) twists when torque is applied at its ends. The theory assumes that the cross-sections of the beam are free to warp (i.e. to displace slightly along the beam axis) without axial constraint. This free-warping condition makes the problem analytically tractable and produces accurate results for thin crystal ribbons (width $w \gg$ thickness t).

Shear stress notation and which mode ribbon torsion activates

The shear stress distribution across any cross-section is obtained from the Prandtl stress function, a mathematical tool analogous to the stream function in fluid mechanics: its spatial gradients give the two shear stress components at each point. Shear stress is written τ_{ij} , where the first subscript i gives the direction of the shear force and the second subscript j gives the normal direction of the interface being sheared (i.e. which plane the force acts across). We define coordinates with x along the ribbon long axis, y along width, and z along the stacking direction of 2D perovskites ($\perp$ to principal ribbon face and $\parallel$ to inorganic layer). For a thin ribbon ($w \gg t$), the Prandtl solution yields two components:

- 1) a dominant shear stress $\tau_{xy} = G \frac{d\theta}{dx} z$, acting in the y direction, varying linearly from zero at the ribbon midplane to $\pm G \frac{d\theta}{dx} \frac{t}{2}$ at the top and bottom faces, and integrating through the thickness to give the torsional rigidity $J = wt^3/3$ (i.e. substituting $t/w \sim 0$ to Eq. 2)
- 2) a complementary component τ_{xz} that is negligible in the ribbon interior and arises only near the narrow edges at $y = \pm w/2$. Accordingly, G in Eq. 3 is the modulus governing τ_{xy} , or the resistance to in-plane shear within each structural layer and not any inter-layer quantity.

Two mechanically distinct shear regimes in 2D perovskites

As a layered 2D perovskite, $(\text{FCA3})_2\text{PbBr}_4$ consists of alternating stiff inorganic sheets and soft organic bilayers. Two shear modes arise with fundamentally different stiffnesses, separated by approximately two orders of magnitude.

- 1) The τ_{xy} mode, representing in-plane shear within each inorganic layer, is the mode that ribbon torsion activates. It distorts metal-halide bonds within a single layer, without displacing any layer relative to the next. Its stiffness is characterized by C_{66} , the element

of the elastic stiffness tensor describing shear in the crystallographic ab plane, dominated by the stiff metal-halide bond network. Three independent density functional theory (DFT) studies of $n = 1$ layered perovskites with aromatic spacers (with benzene or fluorobenzene rings that are structurally analogous to our FCA3) reported C66 and VRH-averaged shear moduli consistently in the range 5-7 GPa. The VRH (Voigt-Reuss-Hill) average is a standard estimate of effective stiffness for a crystal measured over many orientations.

- PEA_2PbI_4 $G_{\text{VRH}} = 5.4\text{-}7.0$ GPa^{1,2}.
 - $(o\text{- or } m\text{- or } p\text{-})\text{FPEA}_2\text{PbI}_4$ $G_{\text{VRH}} = 6.0\text{-}7.1$ GPa^{2,3}.
 - Note, G is labeled G_{VRH} above to represent the range of values derived from these methods.
- 2) The τ_{xz} mode representing inter-layer sliding is physically distinct, and its notation carries subtlety. τ_{xz} means a shear force in the x (lateral) direction acting on a z -normal interface. For instance, Li et al. measured this modulus for 2D perovskite⁴ using an AFM tip to apply a lateral force in x across the top (001) facet of $(n\text{-BA})_2\text{PbBr}_4$, causing inorganic layers to slide bodily in x against one another across the horizontal van der Waals (vdW) bilayer, whose normal is z . Although the applied force is lateral and within the ab plane, leading one to intuitively call this “in-plane shear”, the interface being sheared is the z -normal vdW bilayer, not an in-layer plane. In other words, the mode is therefore τ_{xz} , not τ_{xy} . This distinction is important: τ_{xz} requires the entire inorganic sheet to translate relative to one another, whereas τ_{xy} shears material within a single layer without crossing any z -normal interface at all. For τ_{xz} , the stiff inorganic layers and the soft vdW bilayer are in mechanical series along z . Because the vdW interface is more compliant than the inorganic layer, it absorbs most of the shear displacement. This is the Reuss composite lower bound, in which the softest member in a series stack controls the effective overall stiffness. The measurement in Li et al. resulted $G_{xz} \sim 30\text{-}80$ MPa⁴ depending on the layered stacking number of $(n\text{-BA})_2\text{PbBr}_4$, which is 2 orders of magnitude lower than the DFT-calculated shear modulus of common 2D perovskites¹⁻³.

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 $G \sim 2$ GPa⁵ lies between these DFT values¹⁻³ and Li et al.'s value⁴, reflecting partial inter-layer sliding during bending (i.e. a bending-mode effective compliance rather than a pure shear modulus).

For our ribbons with principal faces parallel to the inorganic layers and twist axis x , torsion activates τ_{xy} , and the modulus entering Eq. 3 should be $G_{xy} \sim 5\text{-}7$ GPa. The original application of this model by Bardeen and coworkers (main text ref 28³) 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.

¹ Rathore et al. *J. Alloys Comp.* **936**, 168328 (2023).

² Saadatmand et al. *ACS Omega*. **9**, 24928 (2024)

³ Shokouhi et al. *Sci. Rep.* **15**, 20707 (2025).

⁴ Li. et al. *J. Phys. Chem. C* **123**, 15251 (2019).

⁵ Reyes-Martinez et al. *ACS Appl. Mater. Interfaces* **12**, 17883 (2020).

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 $G_{eff} \sim 1\text{-}7$ GPa as the physically reasonable range.

Using $G = 5$ GPa in the main text (midrange, consistent with Bardeen and coworkers), W was estimated as 497 kJ/m^3 , which represents the torsional elastic energy stored required to sustain one full twist.

Computational Methods

The initial $(\text{FCA3})_2\text{PbBr}_4$ structures for simulation were derived from the experimentally resolved crystal. The unit cell was expanded to a supercell and cleaved to generate a rectangular slab with in-plane edges parallel to $[110]$ and $[\bar{1}\bar{1}0]$. The slab was then extended so that the in-plane dimensions met or exceeded the target sizes ($\sim 40 \times 10 \text{ nm}^2$ and $\sim 20 \times 100 \text{ nm}^2$). Surface terminations were adjusted with bromide and FCA3^+ . All edges were capped with FCA3 to maximize symmetry (i.e., similar terminations on opposing edges) and to favor lower surface energies. Prior work (main text ref 12) indicates that FCA3-terminated surfaces with carboxylic acid groups pointing toward the vacuum are energetically preferred and that termination was adopted here.

Molecular dynamics (MD) simulations were performed in LAMMPS⁶ using the GPU package to accelerate pairwise interactions. Interatomic potentials for all atoms in the structure followed the modified MYP model⁷, which has been shown to qualitatively reproduce experimental trends in related systems⁸. All simulations used a 1 fs time step and periodic boundary conditions (PBC)⁹. Long-range electrostatics were treated with the particle–particle–particle–mesh (PPPM) algorithm, and Lennard-Jones interactions were truncated at 15 Å.

Simulations were initialized at 25 K and first relaxed in the NVE ensemble with atomic displacements restrained to 0.01 Å per time step for 50 ps. This was followed by a 1 ns NVT relaxation with the Nosé–Hoover thermostat, ramping the temperature from 25 to 150 K. A subsequent 1 ns NVT production was performed at 150 K with the same thermostat. To aid relaxation and prevent drift, the center-of-mass momentum of the slab was removed every time step. Simulation cell followed prior work, where surface strain governed twisting in CdSe nanoribbons (main text ref 22). Each slab was placed in a box with at least 200 Å of vacuum separating every edge from its periodic images. This setting ensured that the box in-plane dimensions were larger than the ribbon length or width and held fixed throughout the simulation, so the relaxed structure remained fully isolated and free of box-induced strain or spurious image interactions.

⁶ A. P. Thompson, et al. *Comput. Phys. Commun.* **271**, 108171 (2022).

⁷ Y. Gao, et al. *Nat. Chem.* **11**, 1151–1157 (2019).

⁸ Akriti, et al. *APL Mater.* **10**, 040903 (2022); J. Sun, et al. *J. Am. Chem. Soc.* **145**, 20694–20715 (2023); K. Wang, *Nature* **633**, 567–574 (2024); K. Wang, et al. *Nat. Commun.* **14**, 397 (2023).

⁹ S. Plimpton, *J. Comput. Phys.* **117**, 1–19 (1995)

Curvature estimation on the perovskite nanowire surface

The curvature of each simulated nanowire was estimated using the coordinates of lead ions in the inorganic layers. For a target lead atom p , the N=81 closest lead atoms centered around the p were selected to improve the stability of numerical fitting. Because the simulated sheet was not severely folded, all 81 nearest atoms were contiguous within the same plane of the ribbon, rather than being separated by folds or located on opposite sides of the structure. These 81 atoms constitute a unique curved surface for the center atom p .

We now switch from Cartesian to a surface-based coordinate system. To do this, each atom's coordinates were first centered at p to form $\mathbf{M}_{centered}$.

$$\mathbf{M}_{centered} = [\mathbf{m}_1, \mathbf{m}_2, \dots, \mathbf{m}_{81}] = [[x_1, y_1, z_1], [x_2, y_2, z_2], \dots, [x_{81}, y_{81}, z_{81}]]$$

$$\mathbf{m}_i = \mathbf{m}_{i,original} - \mathbf{p}$$

Each atom $i = 1, 2, \dots, 81$ was assigned a Gaussian weight ω_i :

$$\omega_i \propto \exp\left(-\frac{d_i^2}{2\sigma^2}\right), \quad \sigma = \text{mean}(d_i), \quad \sum \omega_i = 1$$

where d_i is the distance from p to $\mathbf{m}_i$. This normalization down-weights points farther from the center. A weighted covariance matrix was then constructed:

$$\mathbf{C} = \mathbf{M}_{centered}^T \cdot \mathbf{\Omega} \cdot \mathbf{M}_{centered}$$

where $\mathbf{\Omega}$ is the diagonal matrix of Gaussian weights that down-weights far points.

An eigen-decomposition on $\mathbf{C}$ was performed, which gave a set of three eigen vectors $\{\mathbf{t}_1, \mathbf{t}_2, \mathbf{n}\}$ that defined the new coordinate system. The two eigenvectors associated with these two largest eigenvalues defined the orthonormal tangent direction $(\mathbf{t}_1, \mathbf{t}_2)$, and the eigenvector associated with the smallest eigenvalue was the normal $(\mathbf{n})$ to the tangential plane. The coordinates $\mathbf{m}_j = [u_j, v_j, w_j]$ of each Pb atom in $\mathbf{M}_{centered}$ were projected into the surface-based coordinate system $\{\mathbf{t}_1, \mathbf{t}_2, \mathbf{n}\}$:

$$u_i = \mathbf{m}_i \cdot \mathbf{t}_1, \quad v_i = \mathbf{m}_i \cdot \mathbf{t}_2, \quad w_i = \mathbf{m}_i \cdot \mathbf{n}$$

where (u_i, v_i, w_i) were the projected new coordinates that describe the shape of the curved plane.

After change of coordinate so that the normal aligns with the w axis, locally we can solve w as a smooth function of (u, v)

$$r(u, v) = (u, v, f(u, v))$$

Because we used the tangent plane as our (u, v) -plane, the first derivatives vanish at the origin,

$$f(0,0) = 0, \quad \frac{\partial f}{\partial u}(0,0) = 0, \quad \frac{\partial f}{\partial v}(0,0) = 0$$

Using the second-order Taylor expansion and the above boundary conditions, the local surface around p was modeled as:

$$f(u, v) = f(0,0) + \nabla f(0,0) \cdot [u, v] + \frac{1}{2} [u, v] \begin{bmatrix} f_{uu}(0,0) & f_{uv}(0,0) \\ f_{vu}(0,0) & f_{vv}(0,0) \end{bmatrix} \begin{bmatrix} u \\ v \end{bmatrix}$$

$$f(u, v) \approx \frac{1}{2}au^2 + buv + \frac{1}{2}cv^2$$

where $a = f_{uu}(0,0)$, $b = f_{uv}(0,0)$, $c = f_{vv}(0,0)$.

We can fit the quadratic by minimizing the weighted residuals:

$$\min_{abc} \sum_{i=1}^{81} \omega_i \left(w_i - \left[\frac{1}{2}au^2 + buv + \frac{1}{2}cv^2 \right] \right)^2$$

The fitted coefficients a , b , and c thus defined the shape operator $\mathbf{S}$ at the target lead atom p :

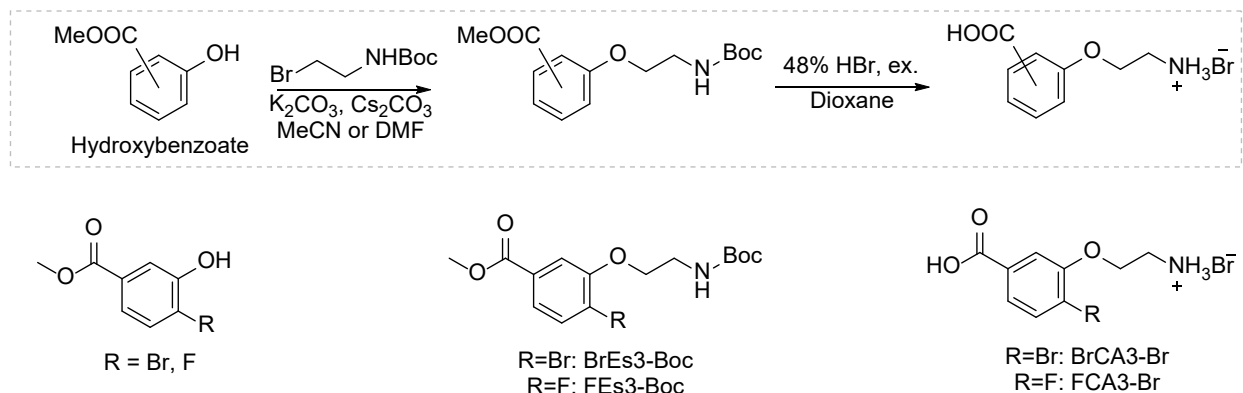
$$\mathbf{S} = \begin{bmatrix} a & b \\ b & c \end{bmatrix}$$

The principal curvatures κ_1 and κ_2 at p was obtained by eigen decomposition of the shape operator $\mathbf{S}$, and their corresponding eigenvectors are the principal curvature directions in the tangential basis $\{\mathbf{t}_1, \mathbf{t}_2, \mathbf{n}\}$. To lift the principal curvature direction back to cartesian coordinate, each eigen vector $\mathbf{e}_j = [e_{j1}, e_{j2}]$, $j = 1, 2$ was projected back using the tangential coordinates $\text{norm}(e_{j1}\mathbf{t}_1 + e_{j2}\mathbf{t}_2)$.

Synthesis of Organic Cations

- Organic cations used in this manuscript were inherited from ref 12.

BrCA3 and FCA3 were synthesized according to the following general scheme.



Scheme S1. Synthetic routes for BrCA3 and FCA3.

First step: attaching Boc-protected amine side chain to hydroxybenzoates

Hydroxybenzoates (1 mmol, 1.0 eq.), potassium carbonate (K₂CO₃, from Millipore Sigma, 2.0 eq.), and *tert*-butyl (2-bromoethyl)carbamate (from Millipore Sigma, 1.5-2.0 eq.) were added to round-bottom flask charged with a stir bar. After a brief purge with Ar, anhydrous acetonitrile (MeCN, 5-10 mL, or 0.1-0.2 M) was added. After extensive purging with Ar, the suspension was stirred at 90-95°C to induce refluxing of MeCN for 12-24 h. The reaction can be further accelerated by addition of cesium carbonate (Cs₂CO₃, from Millipore Sigma, 0.5-1.0 eq.) or by replacing the solvent with anhydrous dimethylformamide (DMF) but without increasing the temperature.

Water was added, and the crude product was extracted with dichloromethane, dried over magnesium sulfate, filtered, and concentrated before being further purified with silica column chromatography (hexane/ethyl acetate). Product (boc-protected amine) and starting material (hydroxybenzoate) typically have similar R_f values and can be indistinguishable during column chromatography. Hence, considerable consumption of the starting material is crucial to obtain products with decent purity. However, a small amount of starting material in the final product can be further removed during the purification after converting the product to ammonium salts.

The recipe for each compound is specified below.

(BrEs3-Boc), methyl 4-bromo-3-(2-((*tert*-butoxycarbonyl)amino)ethoxy)benzoate

- Materials: methyl 4-bromo-3-hydroxybenzoate (4.328 mmol, 1 eq.), K_2CO_3 (8.656 mmol, 2 eq.), *tert*-butyl (2-bromoethyl)carbamate (6.492 mmol, 1.5 eq.), anhydrous MeCN (35 mL, 0.125 M).
- Hydroxybenzoate not fully consumed. Final product: pale yellow powder (ca. 6 mol% hydroxybenzoate). Yield 86.2%.
- 1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.6 Hz, 1H), 7.53 (dq, J = 3.8, 1.8 Hz, 2H), 5.05 (s, 1H), 4.14 (t, J = 5.0 Hz, 2H), 3.91 (s, 3H), 3.61 (q, J = 5.4 Hz, 2H), 1.46 (s, 9H).

(FEs3-Boc), methyl 3-(2-((*tert*-butoxycarbonyl)amino)ethoxy)-4-fluorobenzoate

- Materials: methyl 4-fluoro-3-hydroxybenzoate (5.462 mmol, 1 eq.), K_2CO_3 (10.924 mmol, 2 eq.), Cs_2CO_3 (2.731 mmol, 0.5 eq.), *tert*-butyl (2-bromoethyl)carbamate (8.194 mmol, 1.5 eq.), anhydrous MeCN (55 mL, 0.125 M).
- Hydroxybenzoate fully consumed. Final product: white powder. Yield 85%.
- 1H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.57 (m, 2H), 7.12 (dd, J = 10.6, 8.6 Hz, 1H), 5.02 (s, 1H), 4.14 (t, J = 5.1 Hz, 2H), 3.91 (s, 3H), 3.58 (q, J = 5.3 Hz, 2H), 1.45 (s, 9H).

Second step: simultaneous amine deprotection, protonation, and benzoate de-esterification

To a round-bottom flask charged with a stir bar was added the boc-protected amine from the previous reaction (1 mmol, 1 eq.), followed by anhydrous dioxane (10 mL, 0.1 M). After complete dissolution, 48% HBr (aq. 10 mmol, 10 eq.) was added. After extensive Ar purging, the solution was heated at 95°C to induce mild refluxing of solvents for 12 h. The reaction mixtures will gradually turn yellow.

Solvents were then completely removed from the solution through rotary evaporation, including water contained in HBr. Then, the crude product was reprecipitated at least thrice by dissolution in acetone followed by addition of diethyl ether. The crude products usually have decent solubility in acetone for the iodine salts, but bromides are only poorly soluble. Thus, the crude bromide salts were extensively sonicated in acetone before addition of ether.

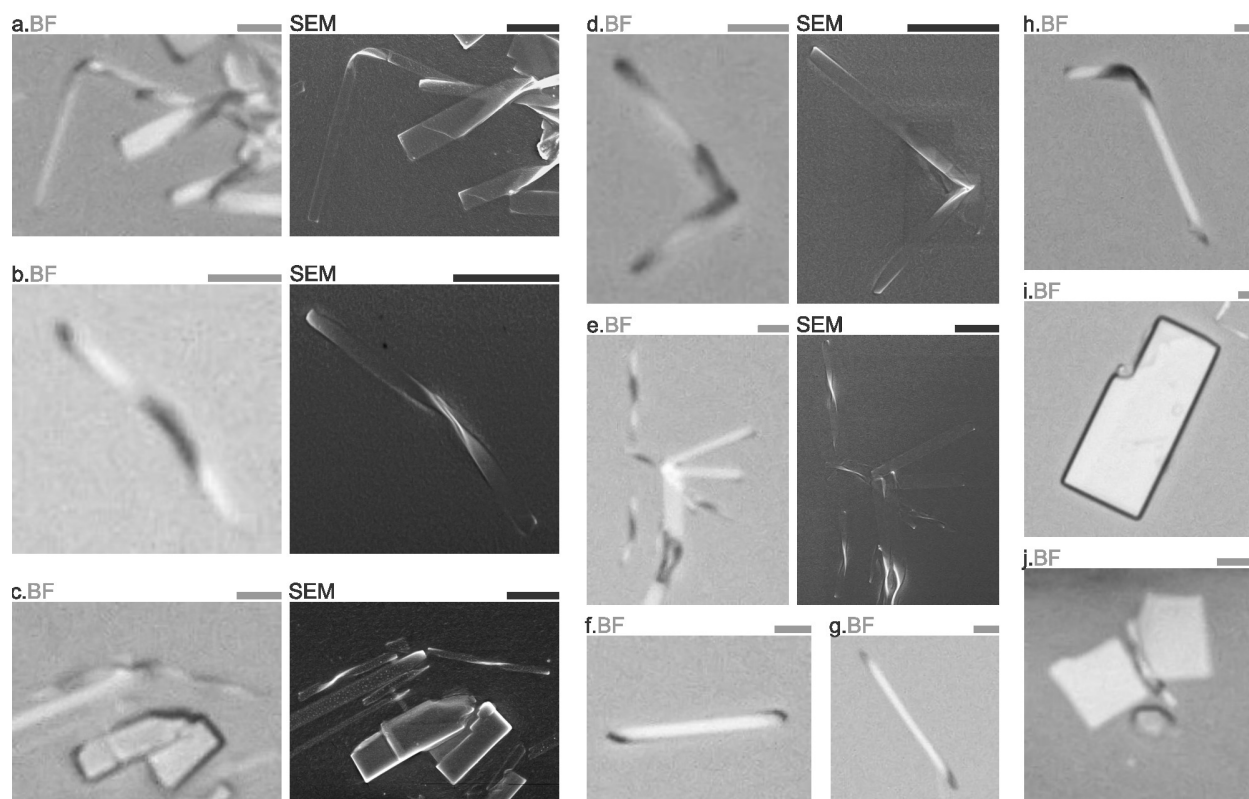
(BrCA3-Br), 2-(2-bromo-5-carboxyphenoxy)ethan-1-aminium bromide

- Materials: BrEs3-Boc (0.8572 mmol, 1 eq.), anhydrous dioxane (0.1 M), HBr (8.57 mmol, 10 eq.).

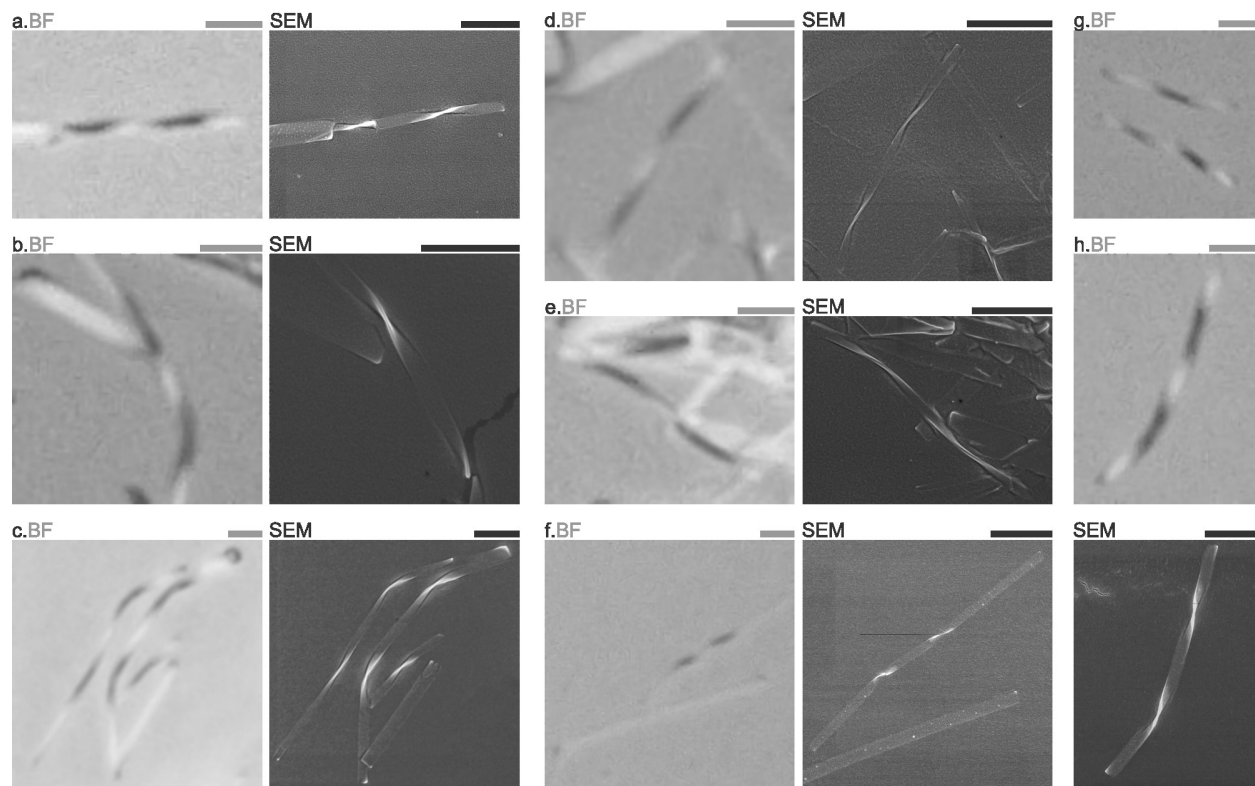
- Product reprecipitated with acetone/ether.
- Product: white powder. Yield: 81.9%.
- ^1H NMR (500 MHz, DMSO- d_6) δ 13.26 (s, 1H), 8.00 (s, 3H), 7.76 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 1.8 Hz, 1H), 7.51 (dd, J = 8.2, 1.8 Hz, 1H), 4.33 (t, J = 5.3 Hz, 2H), 3.29 – 3.26 (m, 2H).
- ^{13}C NMR (126 MHz, DMSO- d_6) δ 166.46, 154.21, 133.49, 131.71, 123.69, 116.84, 114.49, 66.03, 38.15.

(FCA3-Br), 2-(5-carboxy-2-fluorophenoxy)ethan-1-aminium bromide

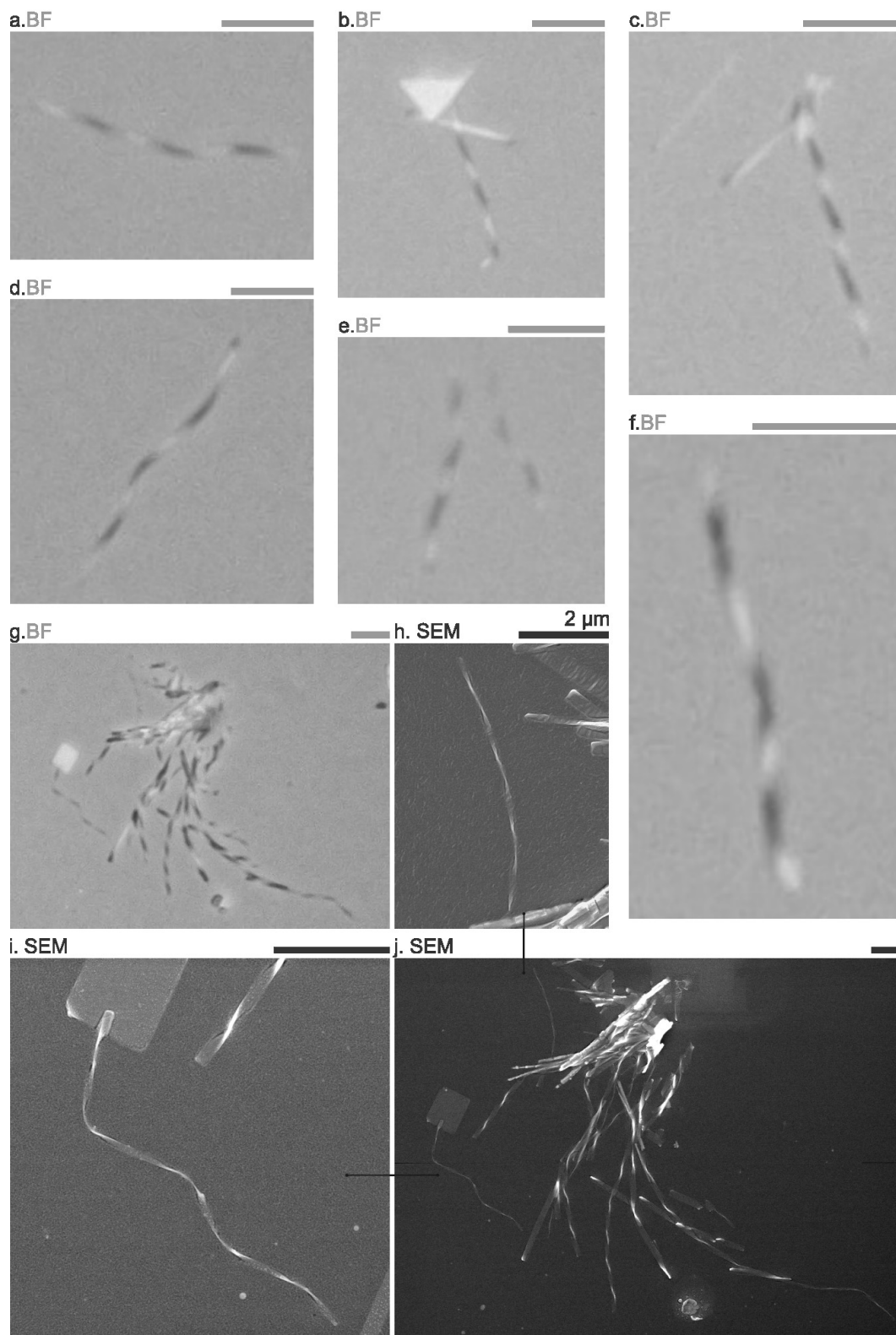
- Materials: FEs3-Boc (3 mmol, 1 eq.), anhydrous dioxane (0.1 M), HBr (30 mmol, 10 eq.).
- Product reprecipitated with acetone/ether.
- Product: white powder. Yield: 67.0%.
- ^1H NMR (500 MHz, DMSO- d_6) δ 13.14 (s, 1H), 7.96 (s, 3H), 7.70 (dd, J = 8.2, 1.8 Hz, 1H), 7.63 (ddd, J = 8.3, 4.4, 1.9 Hz, 1H), 7.39 (dd, J = 11.0, 8.5 Hz, 1H), 4.32 (t, J = 4.8 Hz, 2H), 3.27 (t, J = 4.7 Hz, 2H).
- ^{13}C NMR (126 MHz, DMSO- d_6) δ 166.25, 154.66 (d, JCF = 252.7 Hz), 145.58 (d, JCF = 11.2 Hz), 127.71 (d, JCF = 2.8 Hz), 123.75 (d, JCF = 7.8 Hz), 116.43 (d, JCF = 18.9 Hz), 116.22, 65.99, 38.23.
- ^{19}F NMR (470 MHz, DMSO- d_6 , uncalibrated) δ -127.05.



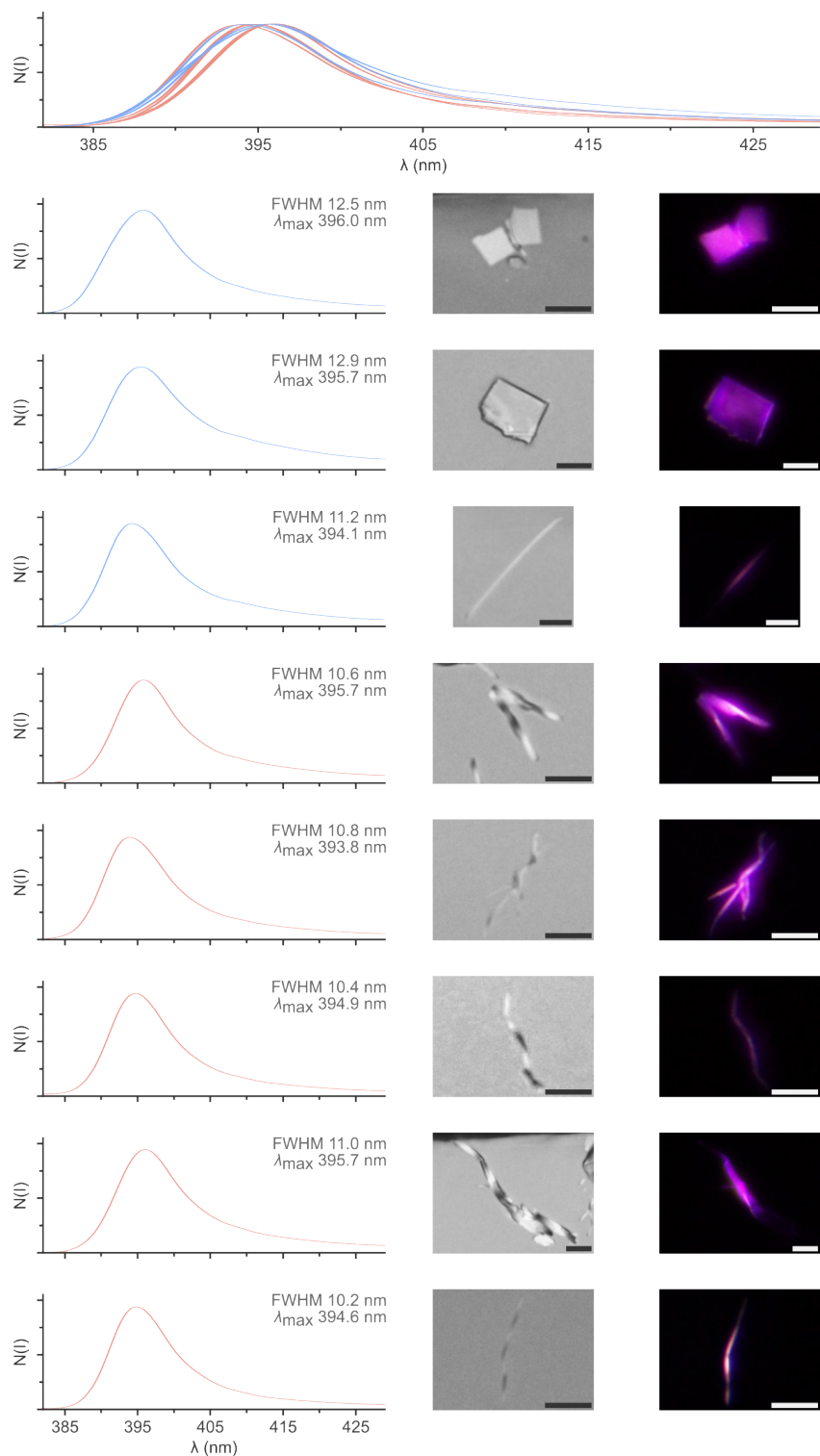
Supplementary Fig. S1. Flat microplates, bent, and twisted nanoribbons of $(\text{FCA3})_2\text{PbBr}_4$. All scale bars: 2 μm . BF stands for bright-field optical microscopy. SEM specifics: FEI Nova; Through-the-lens detector (TLD); 5.0 kV; spot size 5.0 (**b-e**); spot size 4.0 (**a**) no tilting.



Supplementary Fig. S2. Twisted nanoribbons of $(\text{FCA3})_2\text{PbBr}_4$ with 2 twist nodes.
 All scale bars: 2 μm . SEM specifics: FEI Nova; TLD; 5.0 kV; spot size 5.0; no tilting.

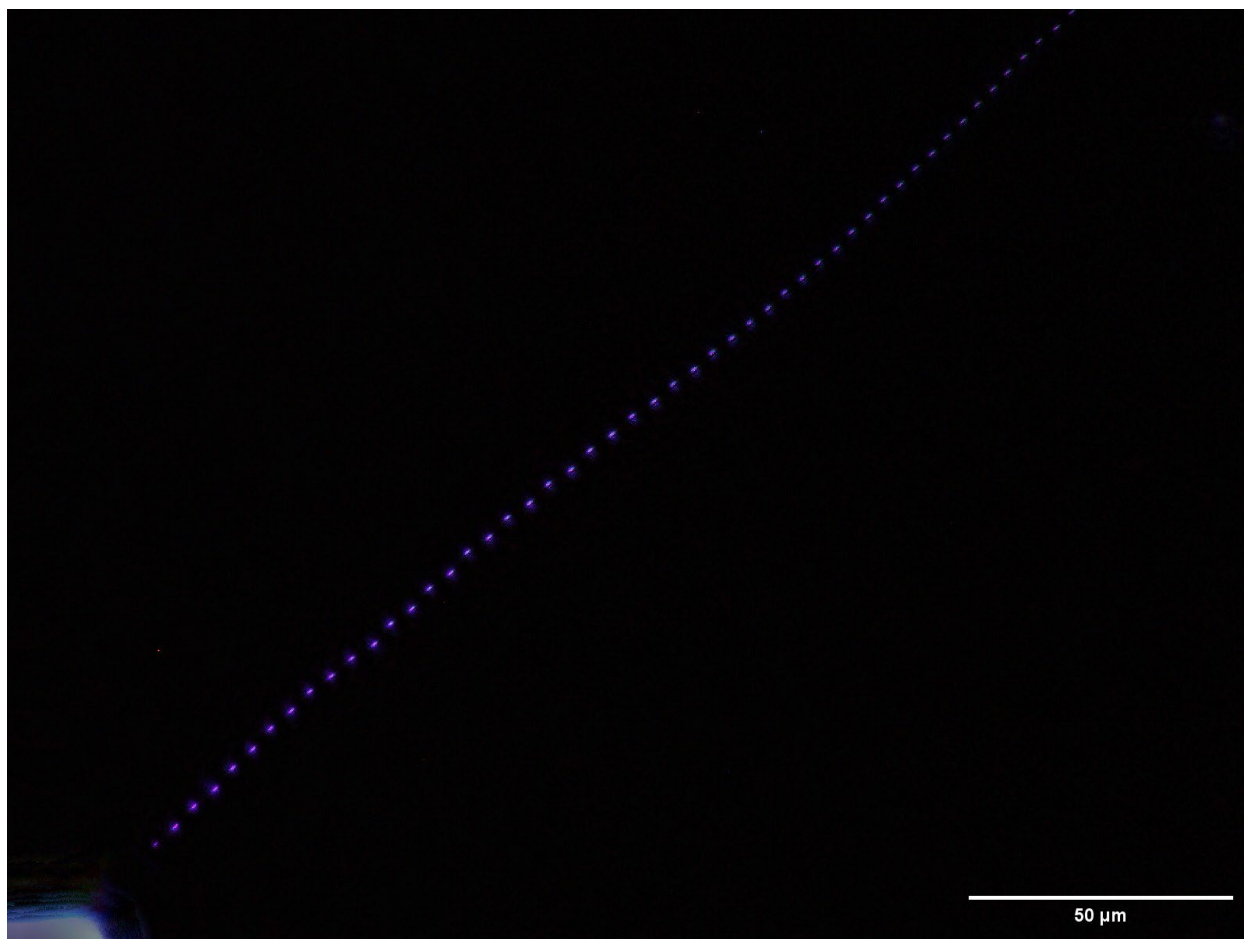


Supplementary Fig. S3. Twisted nanoribbons of $(\text{FCA3})_2\text{PbBr}_4$ with more than 2 twist nodes. All scale bars: 4 μm except H (2 μm). SEM specifics: FEI Nova; TLD; 5.0 kV; spot size 5.0; no tilting.



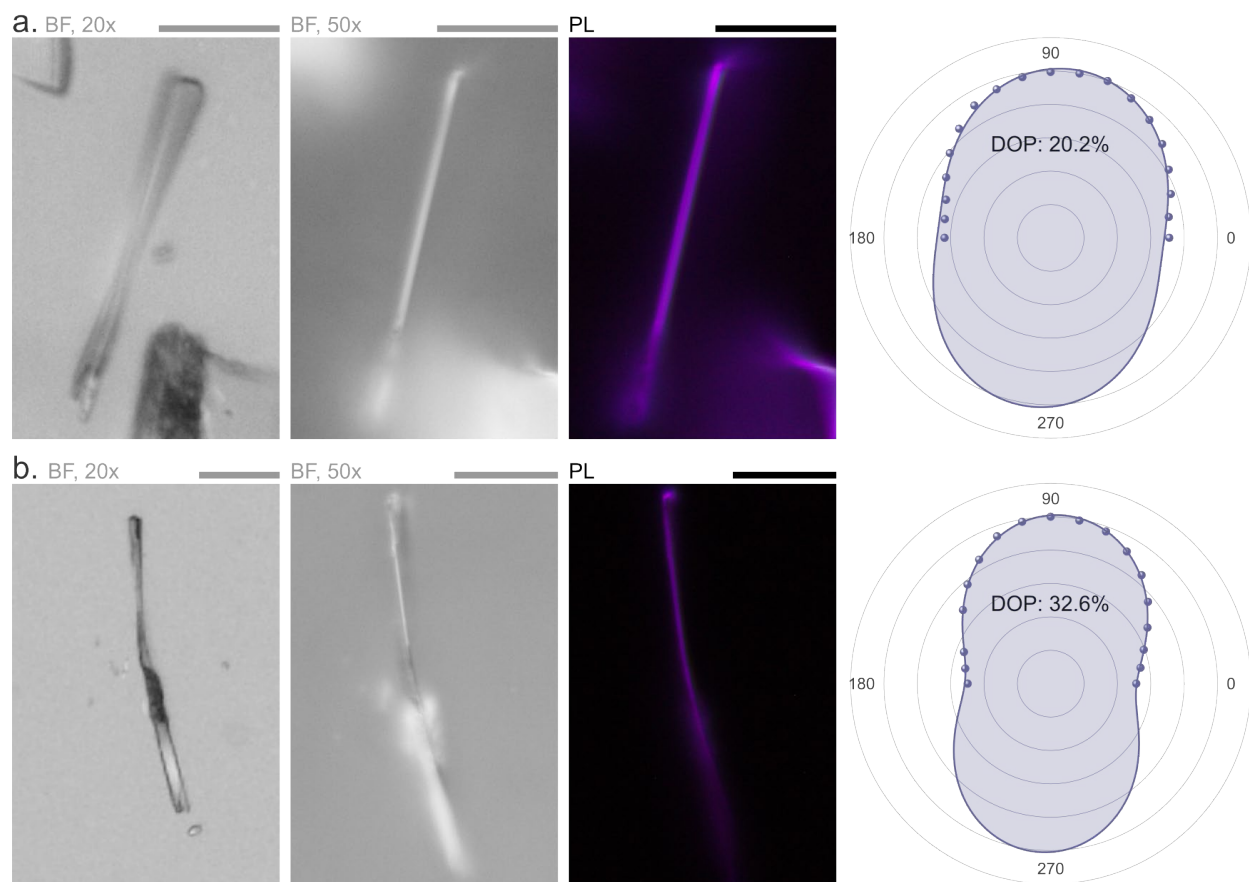
Supplementary Fig. S4. PL statistics across twisted and flat samples.

Both overlaid and individual PL spectra were included, along with individual BF and PL images. Only apparently thin crystals were selected to reduce effects from self-absorption. Minimal variations in PL λ_{max} and FWHM were observed. All scale bars: 5 μm .



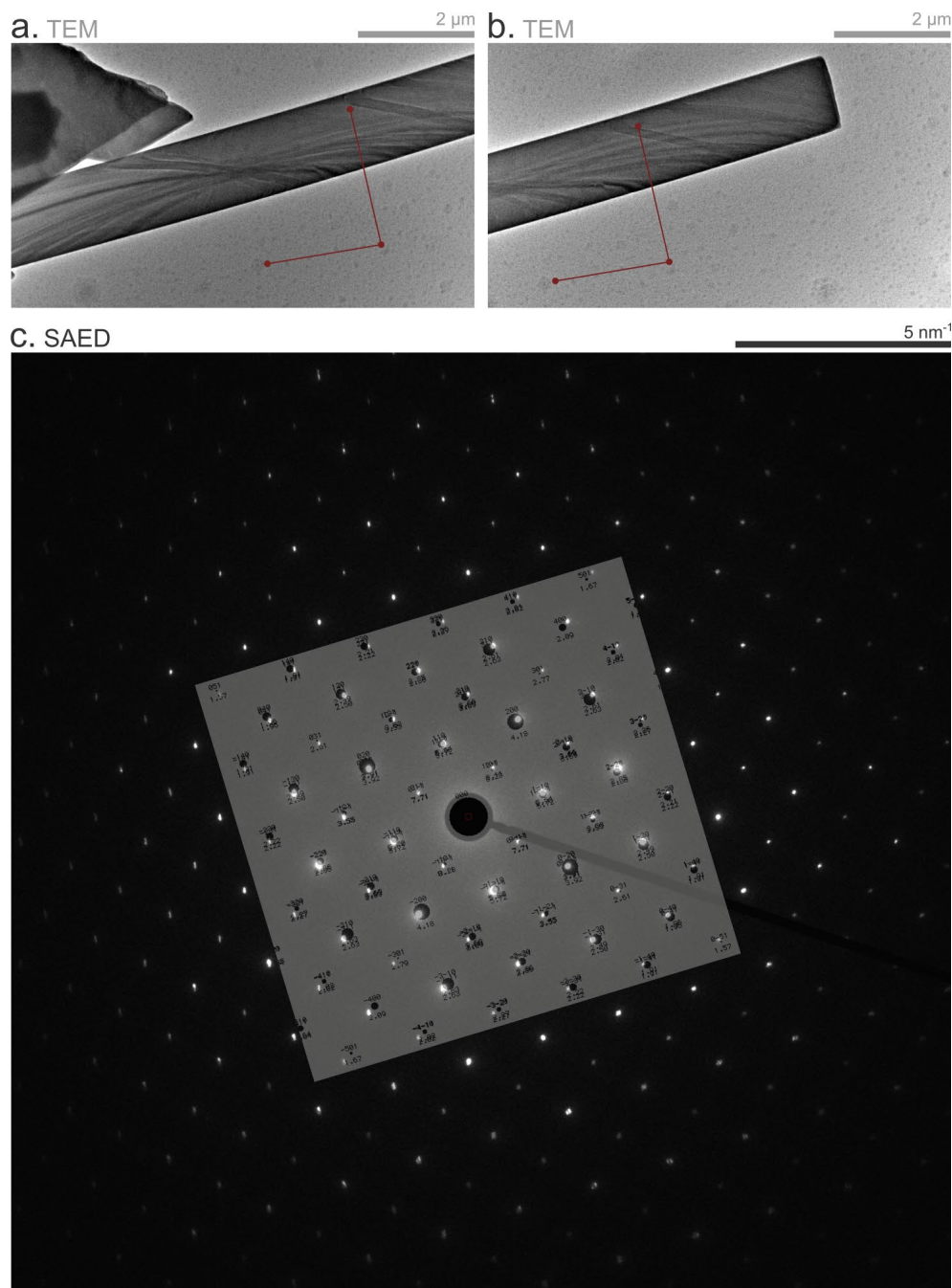
Supplementary Fig. S5. A $\sim 1\ \mu\text{m}$ wide, $\sim 1\ \text{mm}$ long ribbon with 86 twists – cross-polarized brightfield image.

This is a partial image of the lower section of the ribbon, taken using a $50\times$ objective under cross-polarized brightfield mode. Multiple images with various focal planes were captured and flattened using the Extended Depth of Field (easy mode) plugin in ImageJ. The bright spots correspond to the twist nodes. 51 nodes can be seen in this image.



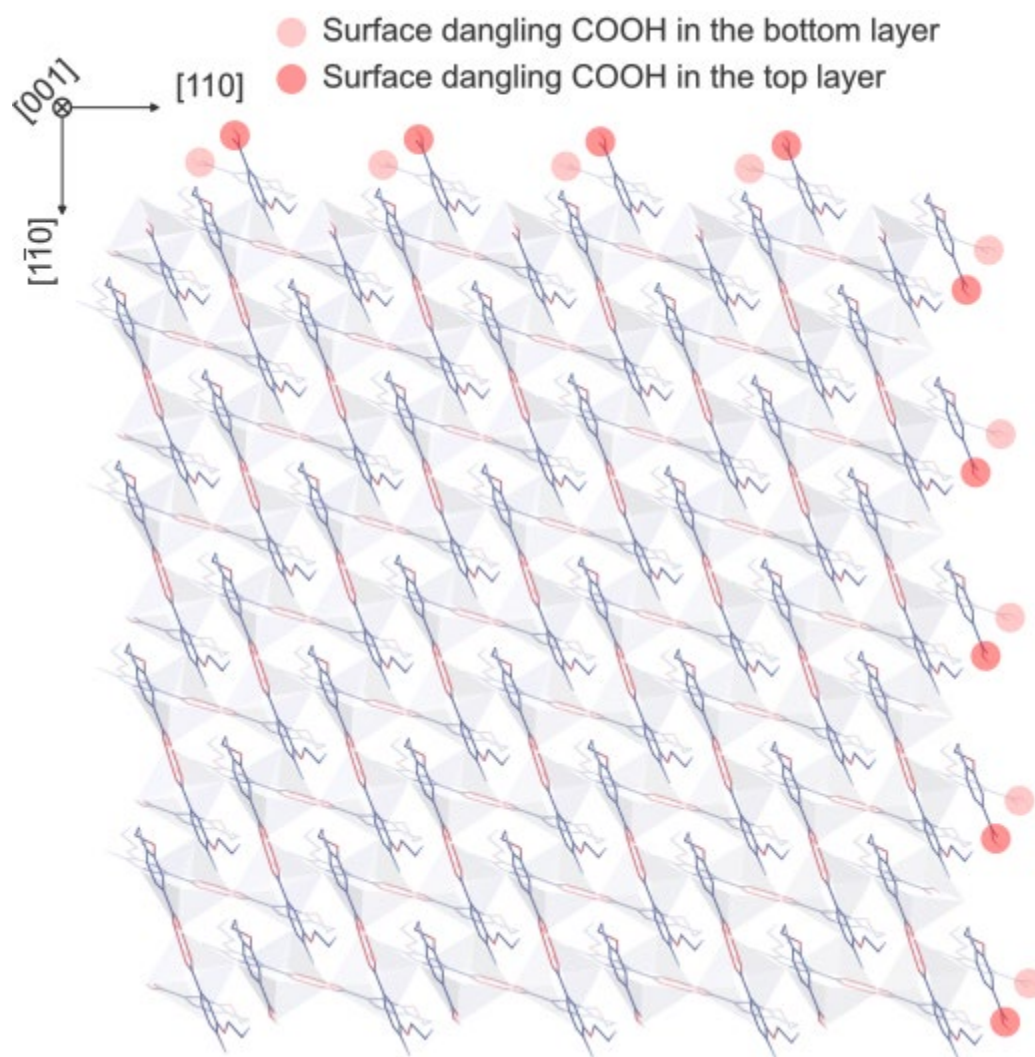
Supplementary Fig. S6. Linearly polarized PL from the twist nodes.

The linearly polarized PL profile was analyzed with the PL images taken using the 50× objective. All scale bars: 20 μm .



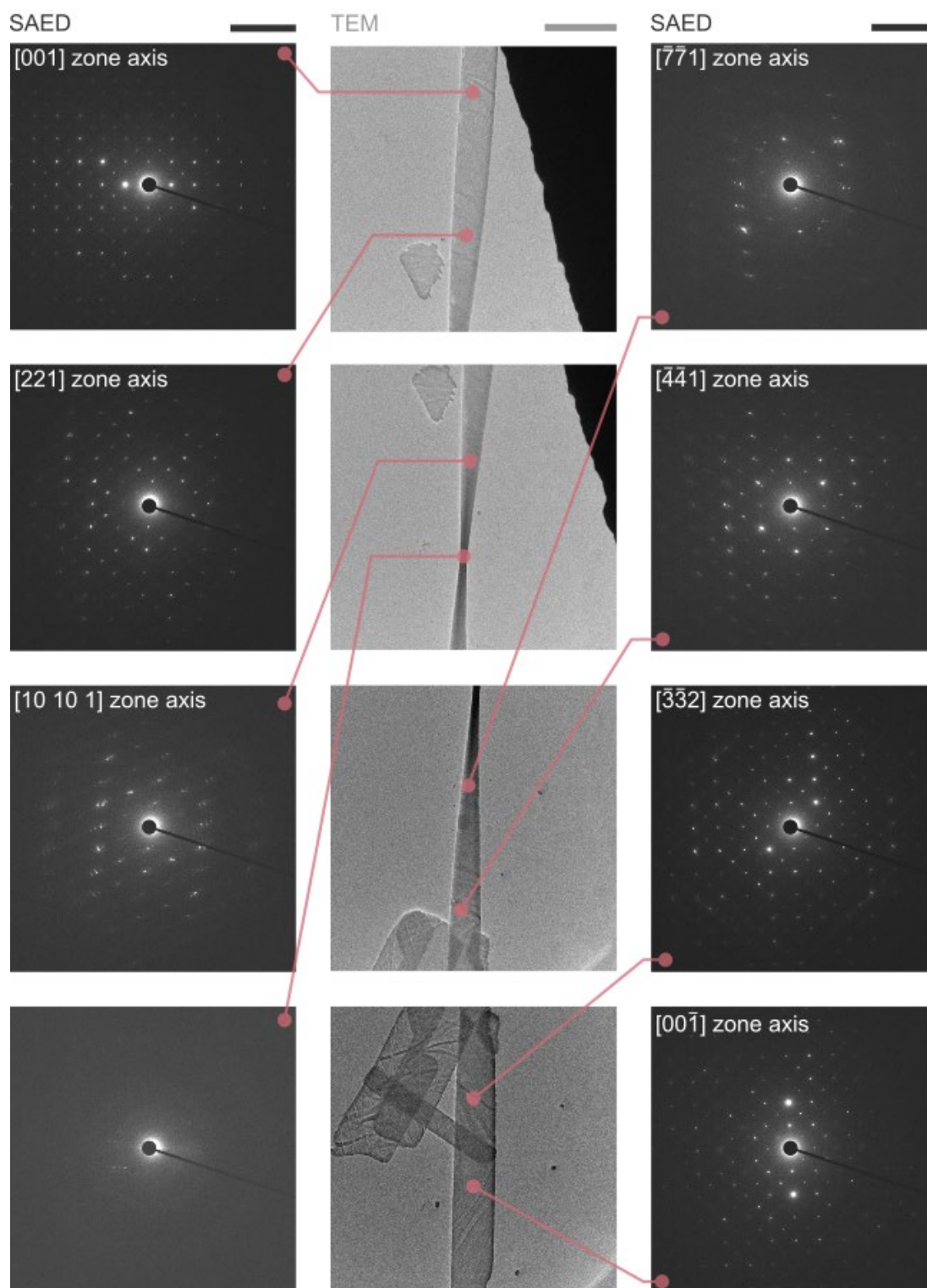
Supplementary Fig. S7. TEM and SAED of a flat (FCA3)₂PbBr₄ microribbon, continued from Fig. 2c.

(a) and (b) mark the relative location of dirty patterns on the substrate v.s. the fringes in the ribbon, showing that the relative location of fringes in the ribbon changes when moving the ribbon under the electron beam. The fringes resulted from bending of the sample and/or thickness variations within the single crystal, where local changes in crystal orientation or specimen thickness created varying diffraction conditions across the ribbon. (c) presented an overlay of experimental and simulated SAED pattern. Axis unit of the simulated pattern: nm⁻¹.

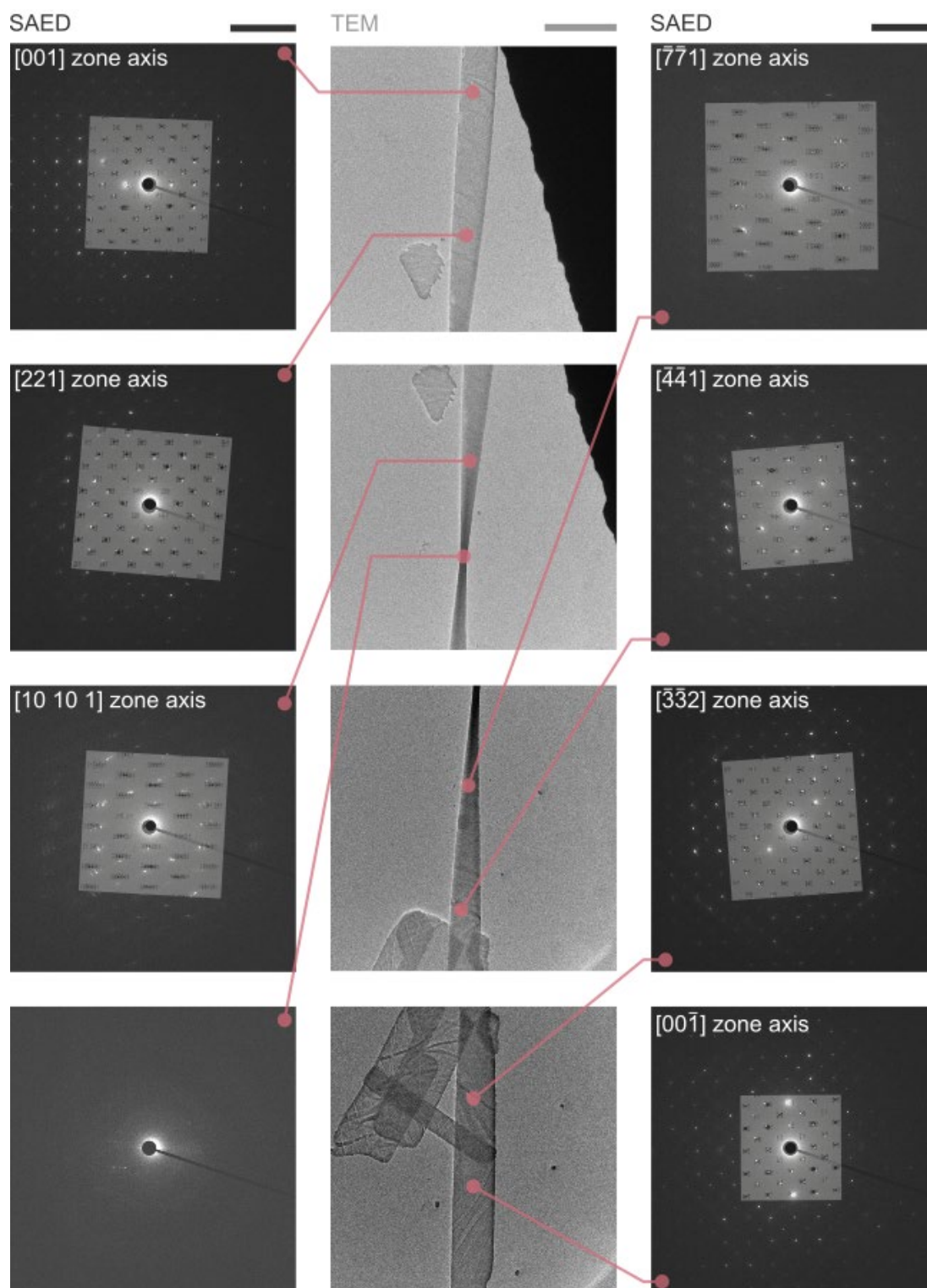


Supplementary Fig. S8. Surface dangling COOH.

The non-dimerized, surface-dangling COOH moieties have exactly the same density and orientation at the two termination edges $[110]$ and $[1\bar{1}0]$. According to our analysis in ref 12, surface-dangling COOH moieties can form robust H bonds with aqueous solvent molecules and thus modulate the surface energy. Surface density and orientation dictate how these directional antennas interact with the solvent molecules. Here, the two termination edges are similarly modulated, and hence $(\text{FCA3})_2\text{PbBr}_4$ is not expected to have a preferred growth direction along $[110]$ or $[1\bar{1}0]$.

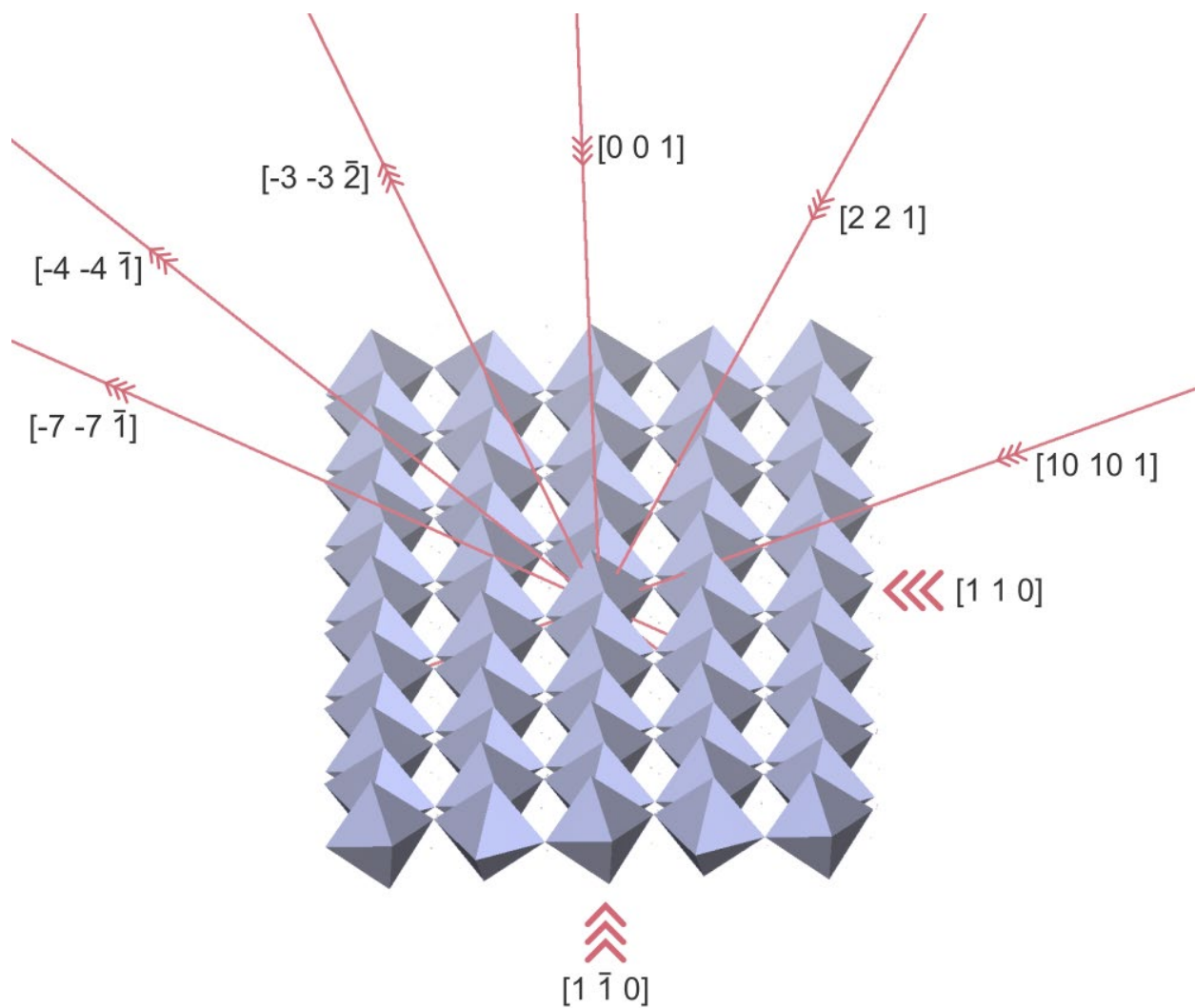


Supplementary Fig. S9. Low-temperature TEM and SAED images along a twisted ribbon. A zone axis was assigned to each SAED image. The assignment here assumed a longitudinal axis along $[1\bar{1}0]$. Scale bar for TEM: $2\ \mu\text{m}$; for SAED: $5\ \text{nm}^{-1}$.

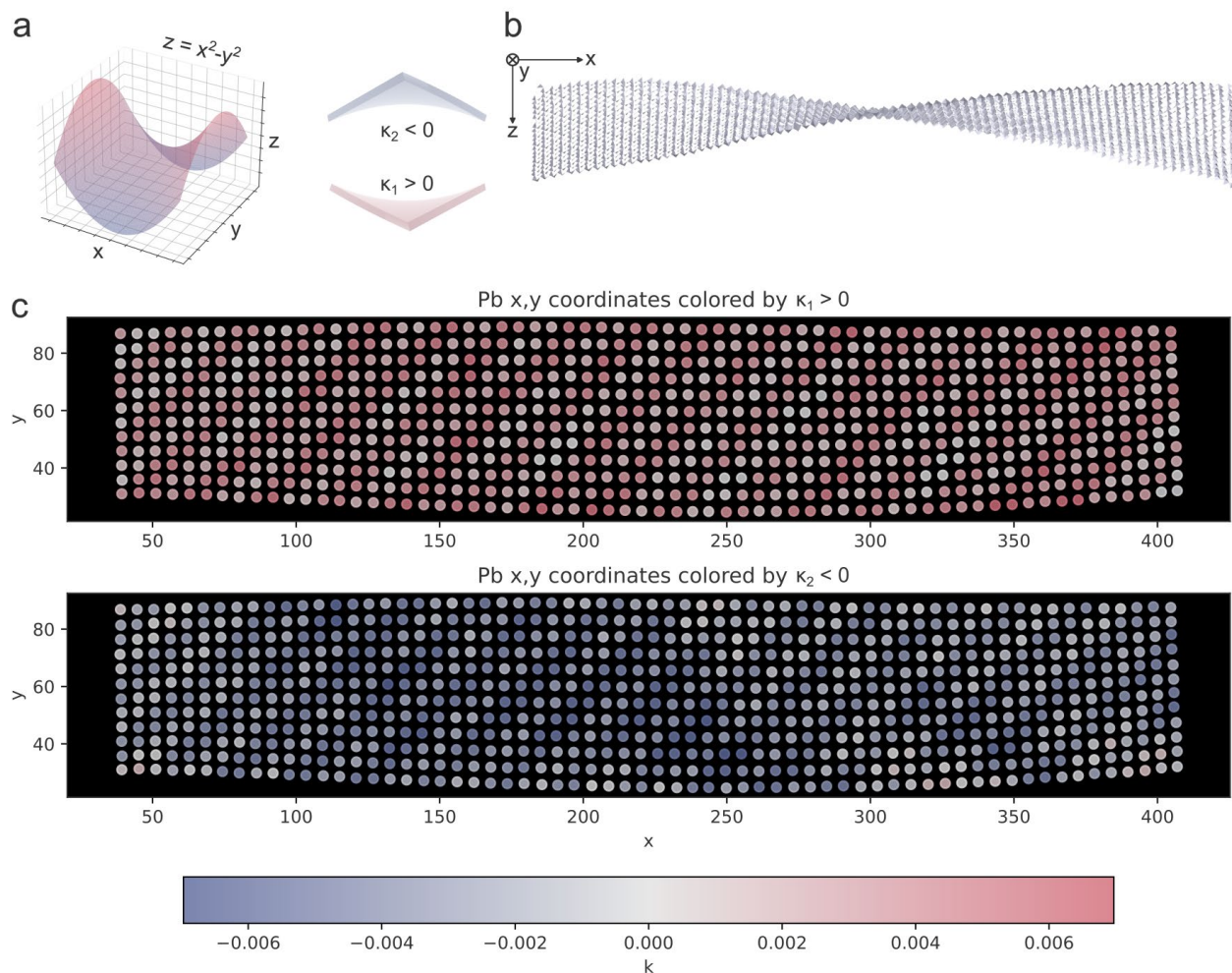


Supplementary Fig. S10. Low-temperature TEM and SAED images along a twisted ribbon, overlaid with simulated patterns.

A zone axis was assigned to each SAED image, though this assignment should be considered a qualitative estimation. For instance, due to continuous ribbon deformation, precisely identifying spots where the zone axis was exactly $[001]$ proved challenging.

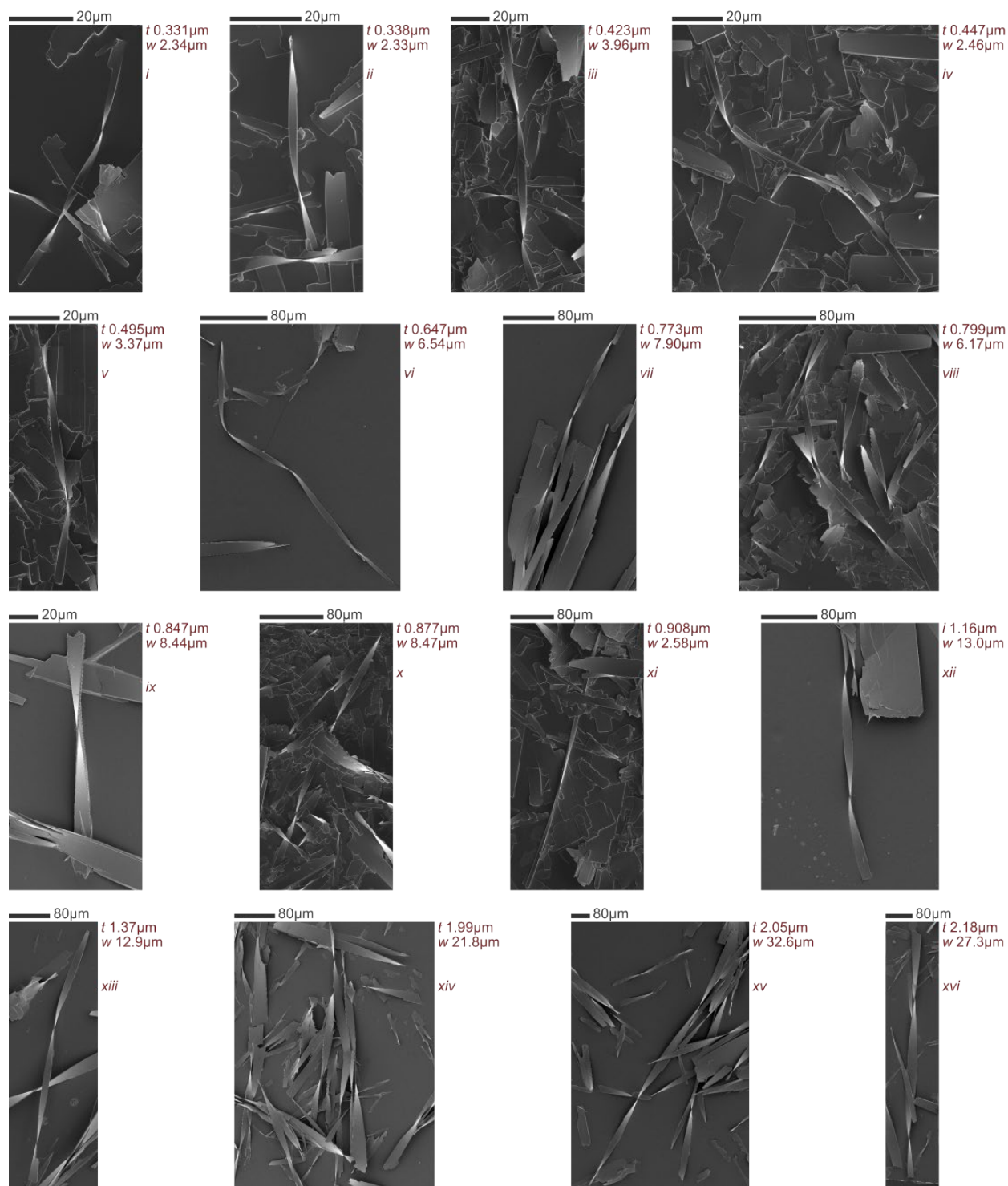


Supplementary Fig. S11. The rotating zone axes viewed in the actual lattice.



Supplementary Fig. S12. Curvature analysis of the *in silico* 10 nm × 40 nm monolayer ribbon.

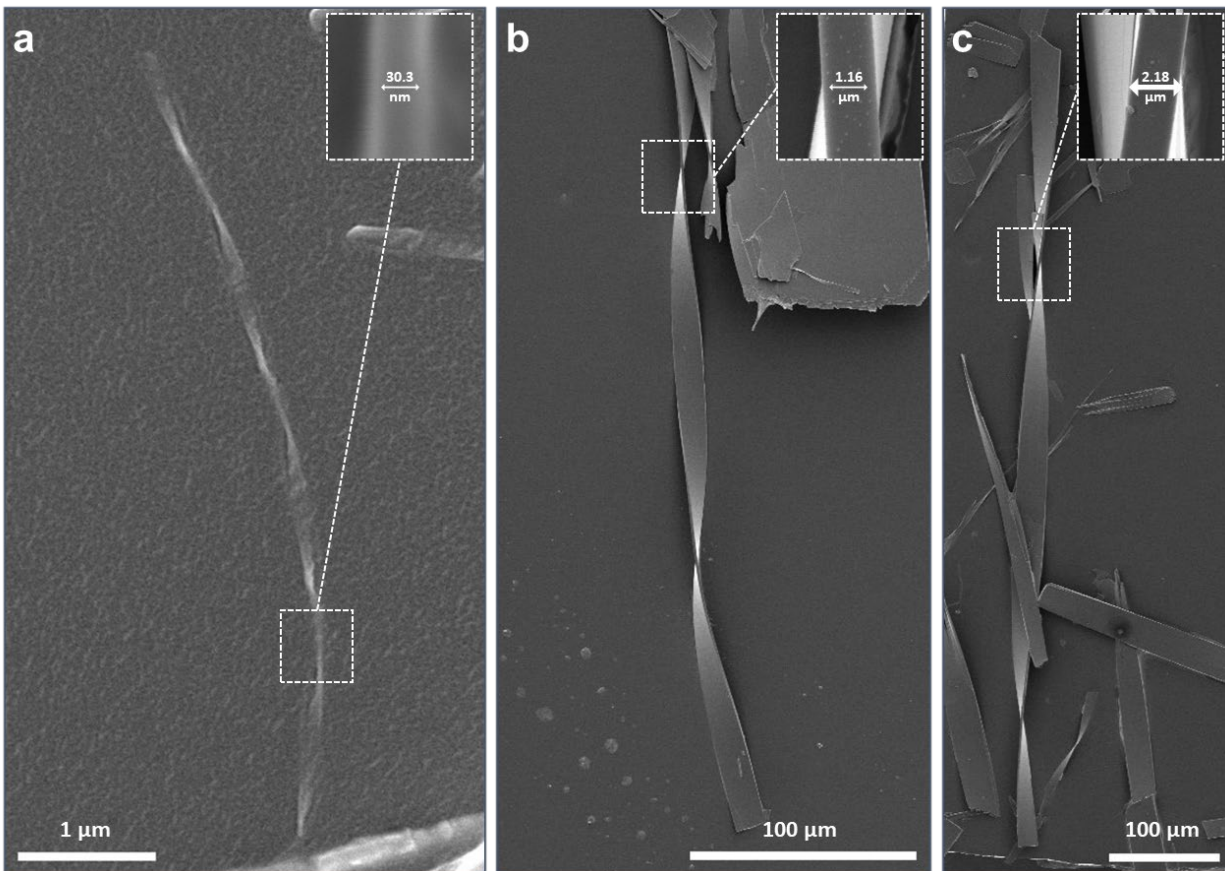
(a) Illustration of a mathematical saddle geometry, highlighting the characteristic principal curvatures $\kappa_1 > 0$ and $\kappa_2 < 0$. (b) Simulated twisted ribbon, displaying only Pb and Br atoms in polyhedral representation. The 10×40 nm ribbon corresponds to a 20×80 Pb atom grid. (c) x and y coordinates of Pb atoms, colored by κ_1 or κ_2 . Here, only a 12×64 atom subset is shown to exclude regions with unreliable curvature extraction near the edges. Despite local fluctuations in absolute curvature values, positive κ_1 and negative κ_2 are consistently observed throughout the ribbon.



Supplementary Fig. S13. Twisted microribbons of $(\text{FCA3})_2\text{PbBr}_4$ with thickness from 0.33 to 2.2 μm .

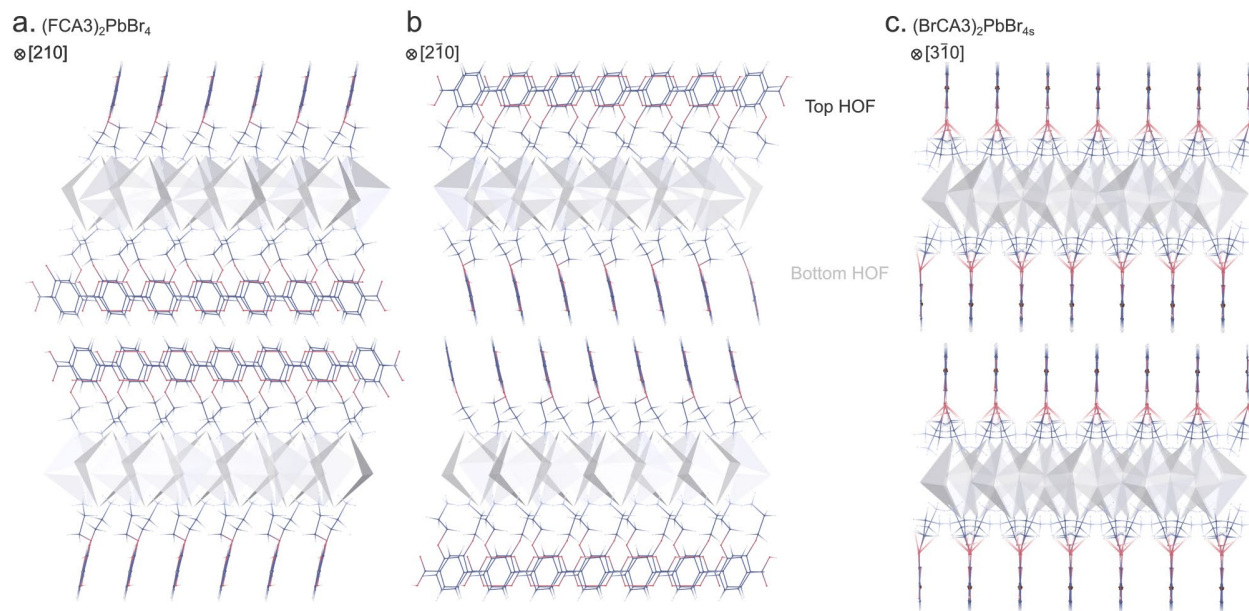
SEM images with thickness (t) and width (w) of each ribbon marked.

SEM specifics: (*i-v, viii, x, xi*) FEI Teneo; ETD; 5.0 kV; spot size 10.0; no tilting. (*vi, vii, xii-xvi*) FEI Nova; ETD; 5.0 kV; spot size 4.0; no tilting. (*ix*) FEI Nova; ETD; 5.0 kV; spot size 3.5; no tilting

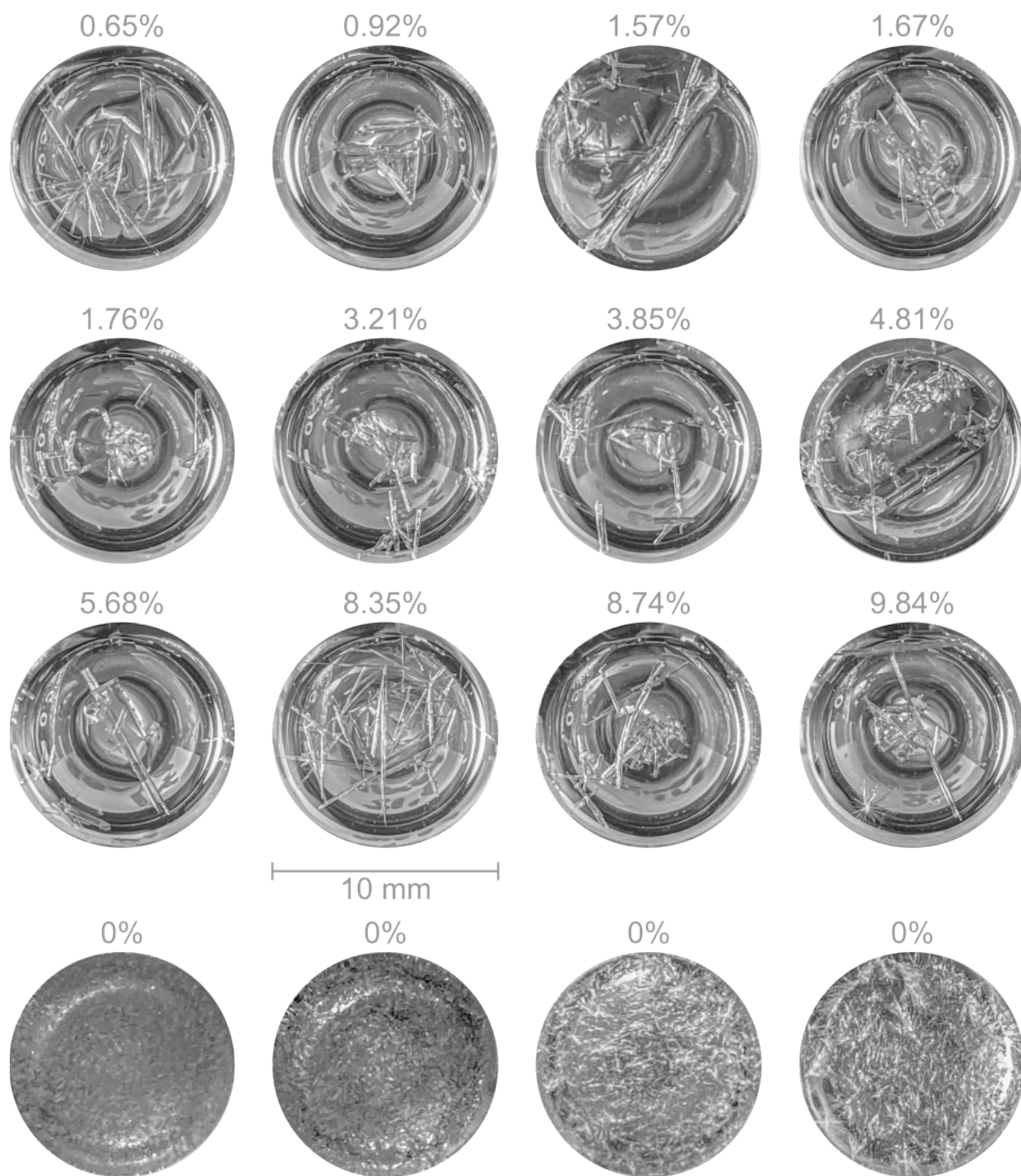


Supplementary Fig. S14. Thickness measurement of twisted ribbons.

SEM specifics: (a) FEI Nova; TLD; 5.0 kV; spot size 5.0; no tilting. (b and c) spot size 4.0.



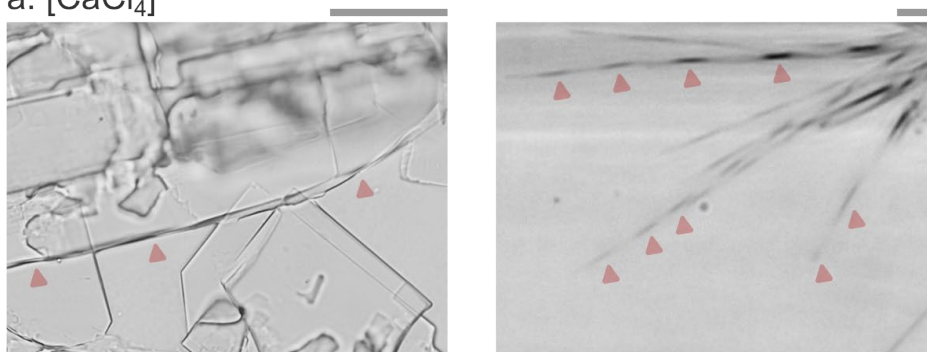
Supplementary Fig. S15. The alignment of HOF lattices in $(\text{FCA3})_2\text{PbBr}_4$ v.s. $(\text{BrCA3})_2\text{PbBr}_4$.



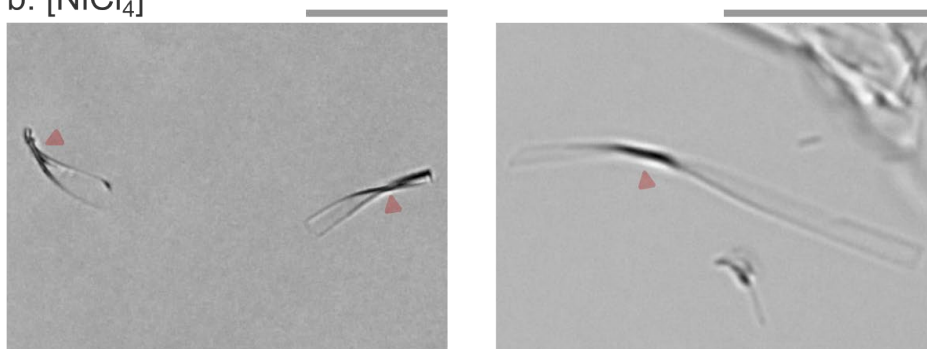
Supplementary Fig. S16. Morphology of $(\text{FCA3})_{2-2x}(\text{BrCA3})_{2x}\text{PbBr}_4$ at each doping percentage.

Images show crystals at the bottom of scintillation vials in their mother solutions. The BrCA3 doping percentage (x) is marked for each batch. Notably, all doped crystals grew as straight rods. Negative controls of pure $(\text{FCA3})_2\text{PbBr}_4$ crystals are included for comparison, demonstrating the typical appearance when spontaneous deformation is prevalent.

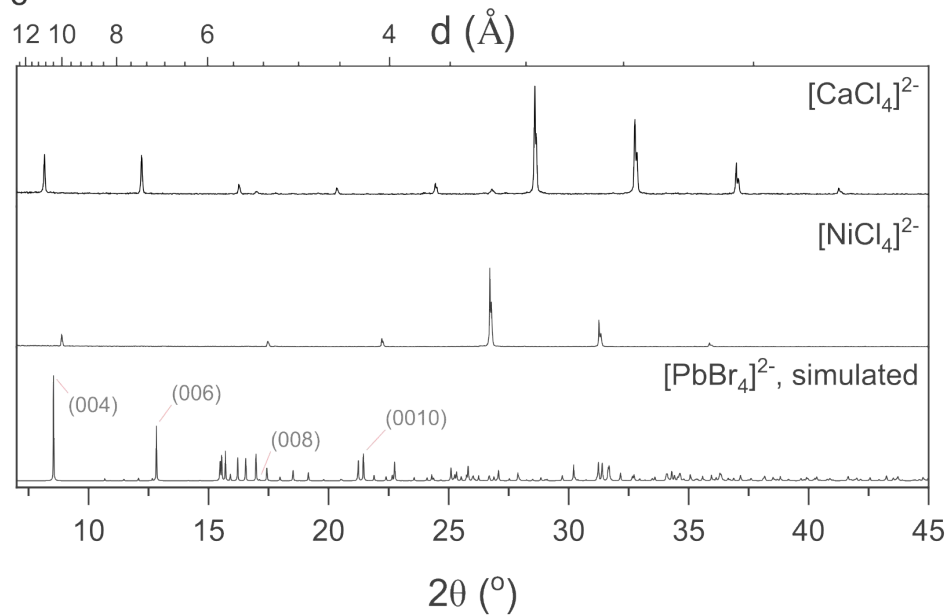
a. $[\text{CaCl}_4]^{2-}$



b. $[\text{NiCl}_4]^{2-}$



c



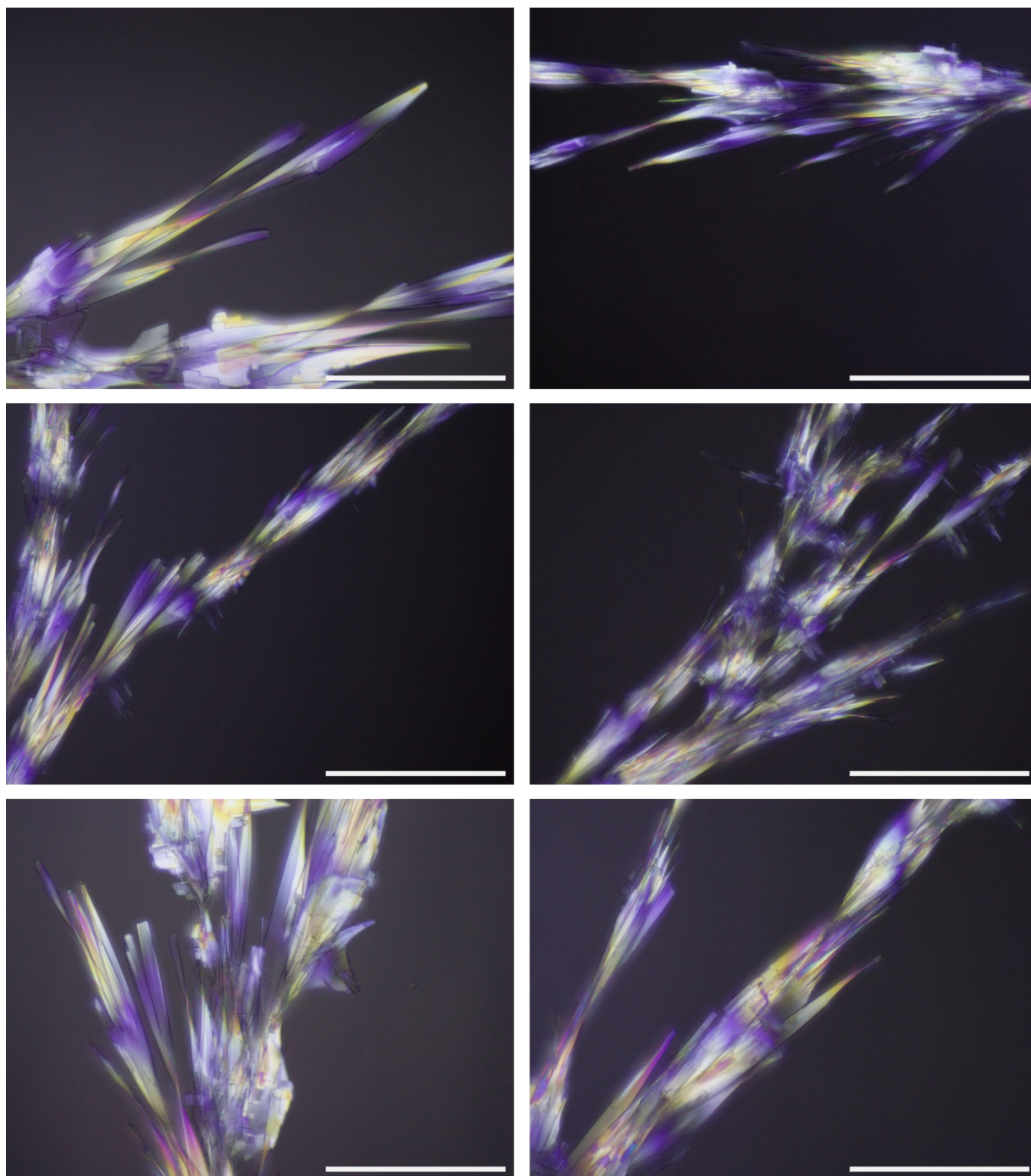
Supplementary Fig. S17. Spontaneously deformed $(\text{FCA3})_2\text{CaCl}_4$ and $(\text{FCA3})_2\text{NiCl}_4$.

Brightfield images of twisted (a) $(\text{FCA3})_2\text{CaCl}_4$ and (b) $(\text{FCA3})_2\text{NiCl}_4$ ribbons. Red arrows mark the twist nodes. Scale bars: 5 μm . (c) Powder X-ray diffraction spectra of each composition compared with the simulated spectrum from the room-temperature crystal structure of $(\text{FCA3})_2\text{PbBr}_4$.

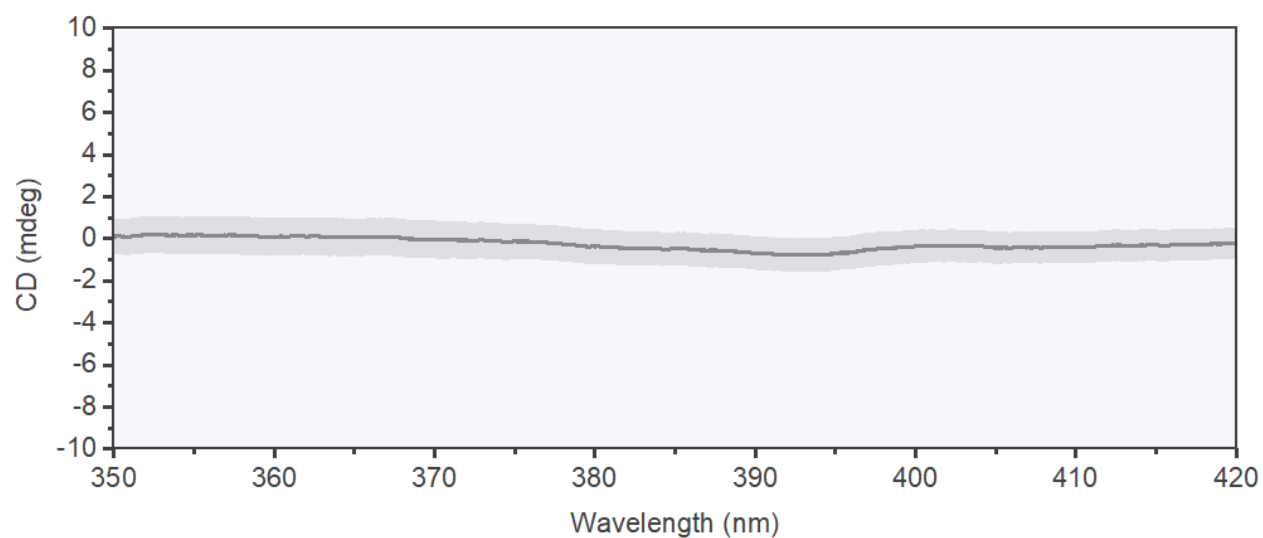
Batch	Growth rate (°C/min)	CCW	CW
1	0.010	207	136
2	0.010	46	47
3	0.010	315	184
4	0.010	92	72
5	0.044	176	235
All		836	674

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

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. Note, all batches were grown by free-space in-solution nucleation from vials. Only crystals that developed a visible twist (i.e. length $\geq$ half pitch) were counted. No external symmetry-breaking field (chiral template, circularly polarized light, or directional flow) is present, 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 [main text ref 23], 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.

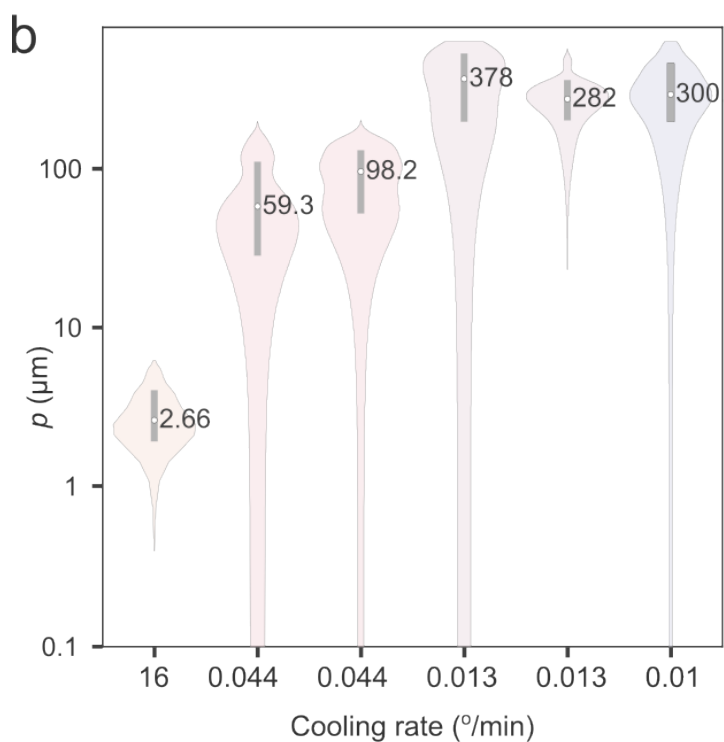
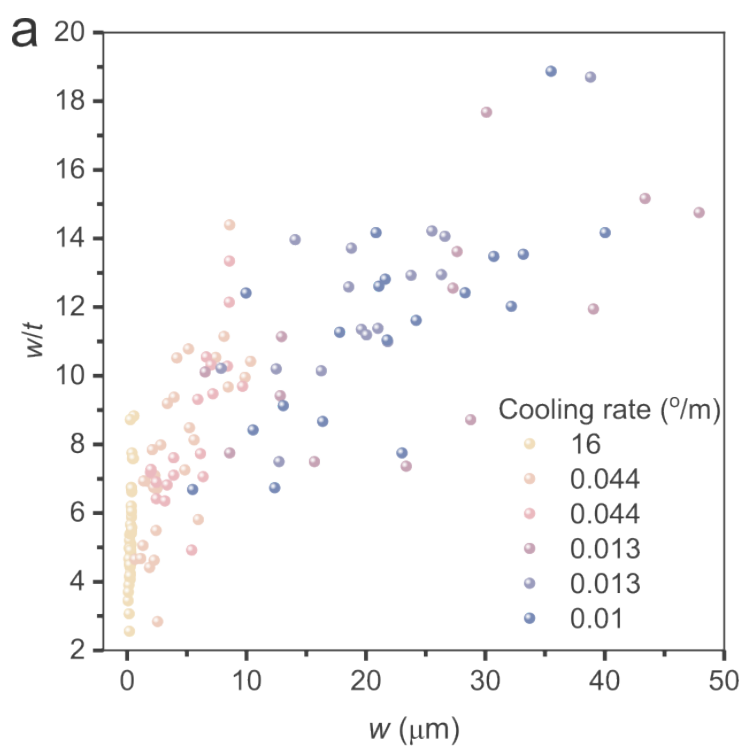


Supplementary Fig. S18. High-magnification ribbon forest regions of Extended Data Fig. 4a, cross-polarized.
Scale bars: 50 μm .



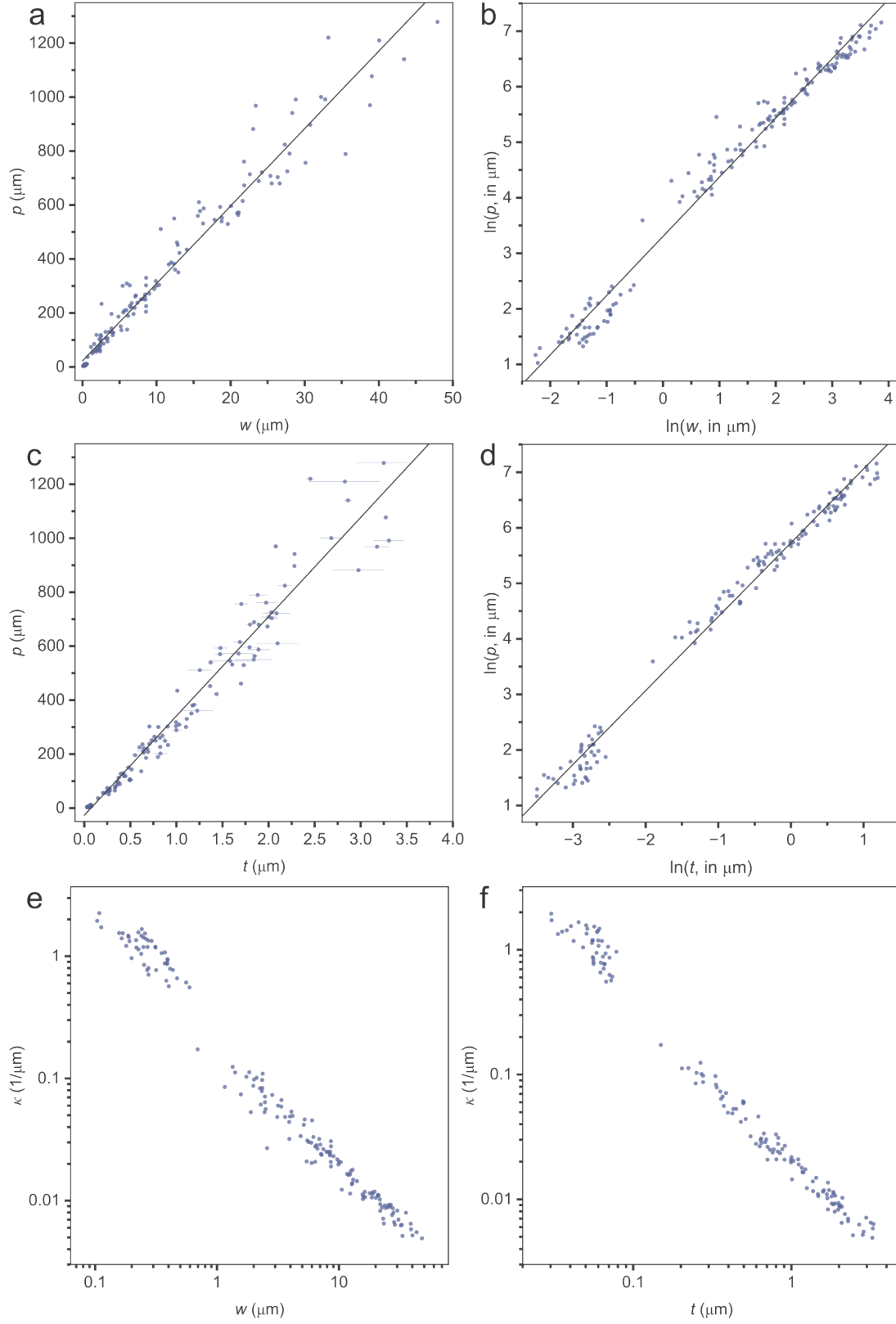
Supplementary Fig. S19. Ensemble averaged CD spectra of flat (FCA3)₂PbBr₄ crystals.

Abundant flat crystals obtained by free-space rapid growth were used for this measurement. CD spectra were obtained by averaging multiple measurements collected while the sample was rotated about the incident light axis and flipped. Error ranges (in shades) represent the standard deviation of each rotational-averaged dataset.



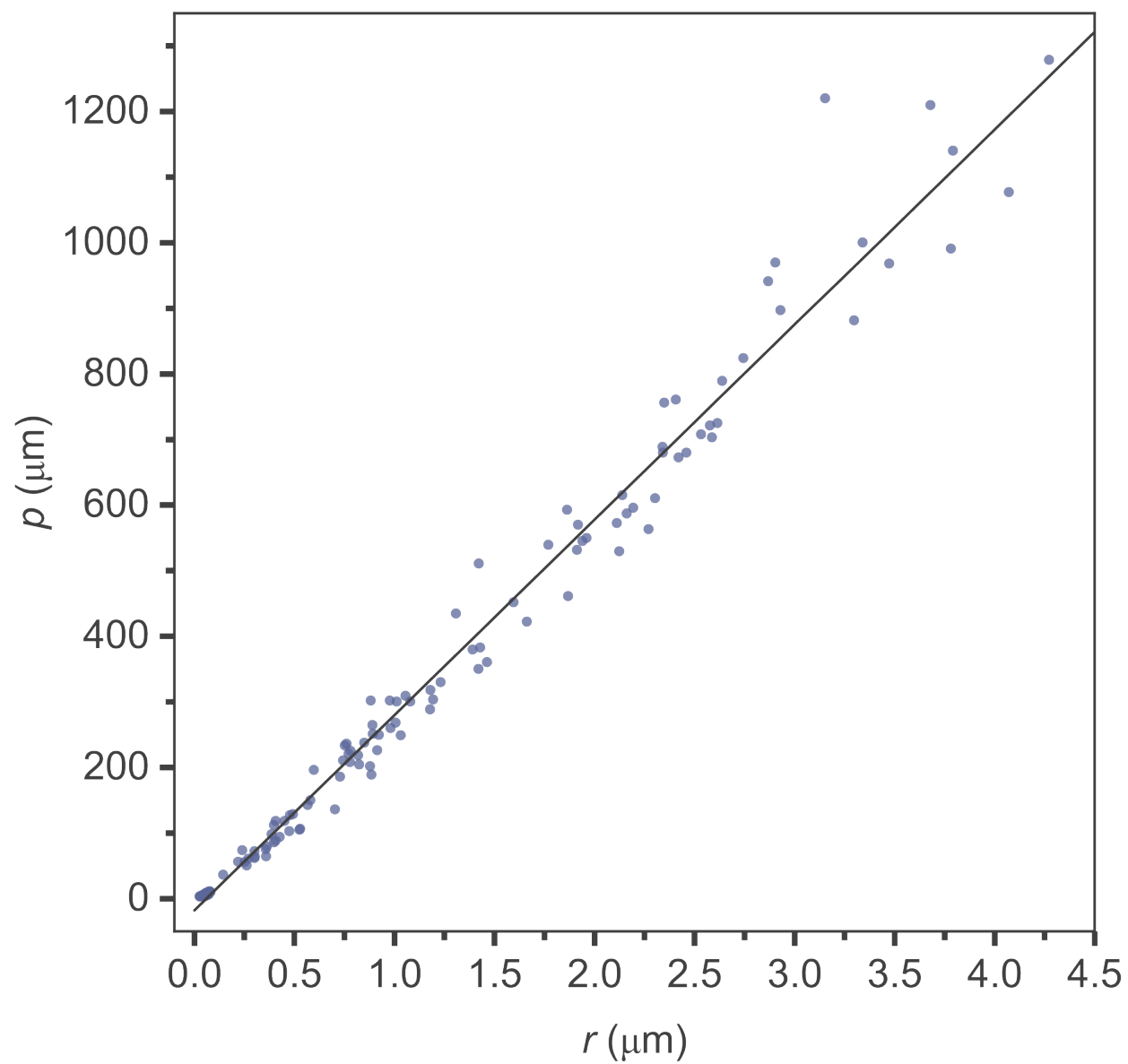
Supplementary Fig. S20. Twisted ribbon (a) w/t v.s. w distribution at various cooling rate and (b) p v.s. cooling rate distribution.

Population: full dataset ($n = 137$ ribbons) and each batch ($n = 41, 19, 29, 16, 13, 19$ from left to right in panel b)



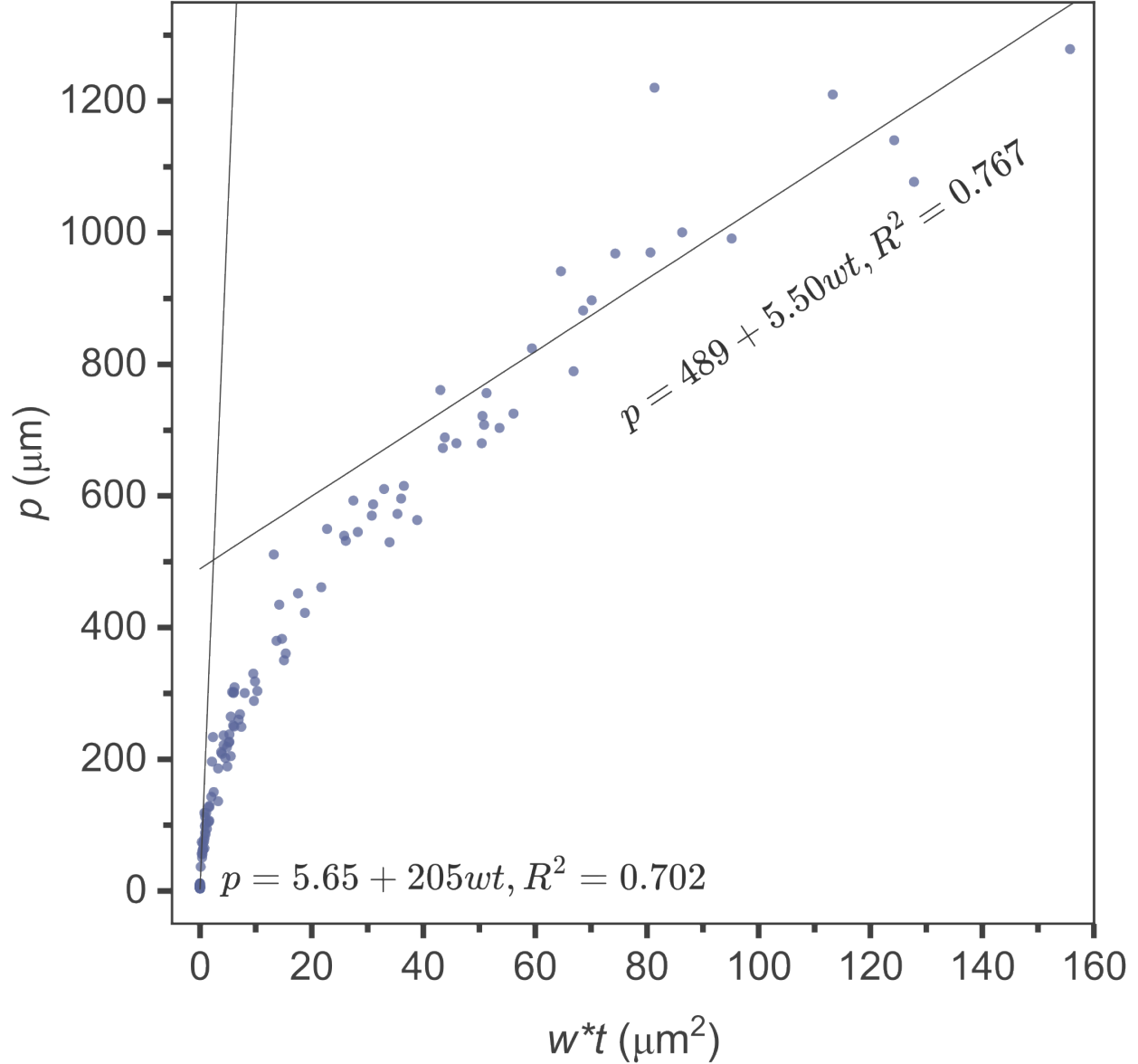
Supplementary Fig. S21. p - w , p - t , κ - w , and κ - t distributions.

All $n = 137$ ribbons were included in the analyses.



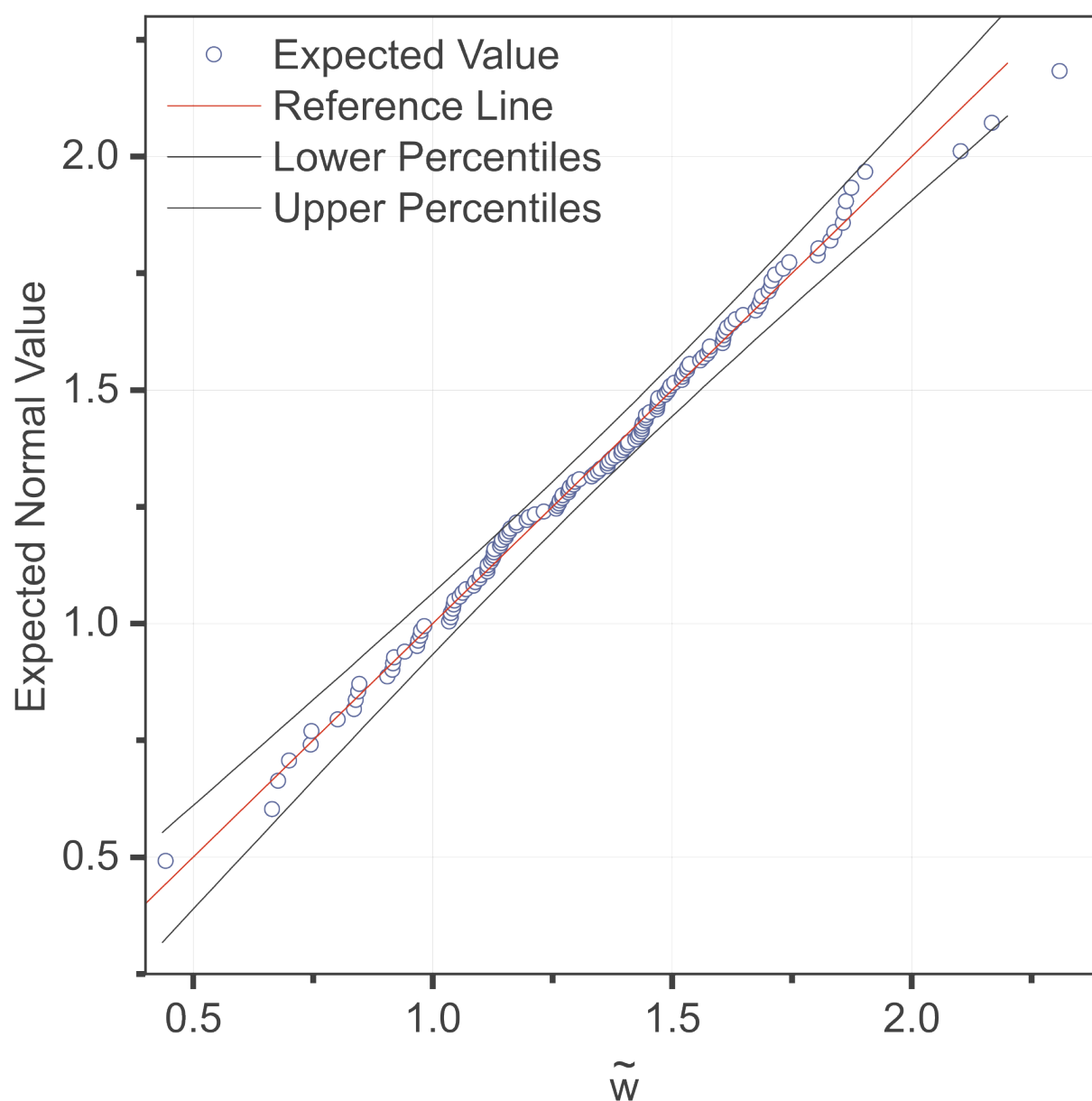
Supplementary Fig. S22. p - r distribution.

All $n = 137$ ribbons were included in the analyses.



Supplementary Fig. S23. p - wt distribution.

The attempt to fit the dataset under the Eshelby twist mechanism failed. According to Frank's theory (main text ref 31), twisting originates from screw dislocation-driven crystal growth, with the relationship $p = 2\pi k \frac{wt}{b}$, where k is a constant on the order of unity and b is the magnitude of the Burgers vector. However, the p - wt distribution clearly exhibited no linear relationship. Even if neglecting the considerable intercept and large R^2 values, attempt to fit a portion of the data where $wt > 50 \mu\text{m}^2$ gave $2\pi k/b = 5.50 \mu\text{m}^{-1}$ and $b = 1.14 \mu\text{m}$ assuming $k = 1$. Having a Burgers vector larger than a few lattice spacings indicates the formation of void/pipe inside the crystal. Assuming a rectangular cross-section with $w/t = 12.0$ typical for ribbons in this range of dimension (Supplementary Fig. S20a), an unreasonably large Burgers vector of $1.14 \mu\text{m}$ is essentially half of the thickness ($t = 2 \mu\text{m}$). A similar attempt to fit a portion of the data where $wt < 0.05 \mu\text{m}^2$ gave $b = 30.6 \text{ nm}$ for a thickness of 100 nm (assuming $w/t = 5$), which is unreasonable as well. All $n = 137$ ribbons were included in the analyses.



Supplementary Fig. S24. Quantile-quantile (Q-Q) plot of $\tilde{w}$ v.s. theoretical normal distribution.

The diagonal reference line represents the expected pattern if the data perfectly follows the theoretical distribution, which is normal distribution in this case. The region between the upper and lower percentile bands indicates the normal range of variation expected due to random sampling. All observed data points (shown as dots) fall precisely on the reference line and remain entirely within the confidence bands, indicating excellent agreement between the experimental observations and theoretical predictions. This result confirms that the data behaves as expected statistically and supports the validity of a normal distribution.

All $n = 137$ ribbons were included in the analyses.

Supplementary Table S2. Crystal data and structure refinement for (FCA3)₂PbBr₄, 150K

CCDC number	2485415
Moiety formula	(C ₉ H ₁₁ FNO ₃) ₂ PbBr ₄ ·0.5H ₂ O
Empirical formula	C ₃₆ H ₄₆ Br ₈ F ₄ N ₄ O ₁₃ Pb ₂
Formula weight	1872.43
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>c</i> (14)
<i>a</i> [Å]	16.897(8)
<i>b</i> [Å]	7.7711(19)
<i>c</i> [Å]	41.271(17)
α [°]	90
β [°]	98.49(3)
γ [°]	90
Volume [Å ³]	5360(4)
<i>Z</i>	4
ρ_{calc} [gcm ⁻³]	2.320
μ [mm ⁻¹]	12.310
<i>F</i> (000)	3496
Crystal size [mm ³]	0.166×0.176×0.710
Crystal colour	Colourless
Crystal shape	Needle
Radiation	MoK α (λ = 0.71073 Å)
2 θ range [°]	4.87 to 56.56 (0.75 Å)
Index ranges	-22 ≤ <i>h</i> ≤ 22 -10 ≤ <i>k</i> ≤ 10 -55 ≤ <i>l</i> ≤ 55
Reflections collected	143170
Independent reflections	13319; <i>R</i> _{int} = 0.0420; <i>R</i> _{sigma} = 0.0247
Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	13319 / 7 / 618
Absorption correction <i>T</i> _{min} / <i>T</i> _{max} (method)	0.0410 / 0.2280 (numerical)

Goodness-of-fit on F^2	1.100
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0361$; $wR_2 = 0.0802$
Final R indexes [all data]	$R_1 = 0.0412$; $wR_2 = 0.0822$
Largest peak/hole [$e\text{\AA}^{-3}$]	3.58/−2.31

Refinement details

The crystal exhibits pseudo-lattice translation along the a-axis. Exact translational symmetry is broken by the presence or absence of a water molecule, by different torsion angles for the ethyl ammonium groups of two cations (residues 1 and 3) and by a slight modulation of the Pb and Br atoms.

Water H atom positions were refined, and O-H and H $\cdots$ H distances were restrained to 0.84(2) and 1.36(2) Angstrom, respectively.

Carboxylic acid H atoms were placed in calculated positions and allowed to refine but were constrained to coplanar with the two COO fragments they are part of in the dimer structure.

Level B alerts from CheckCIF:

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.84Ang From Br7 3.47 eA-3

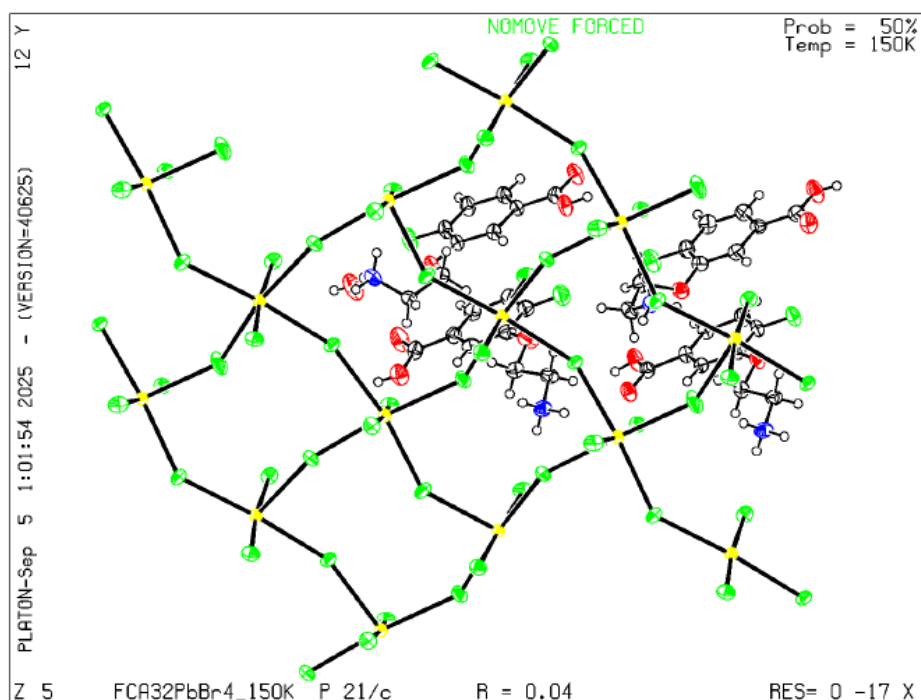
PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.67Ang From Pb2 3.07 eA-3

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.97Ang From Pb1 2.93 eA-3

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.76Ang From Pb1 2.93 eA-3

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.90Ang From Br4 2.77 eA-3

- The residue densities near the heavy inorganic layer are due to errors with absorption correction.



Supplementary Table S3. Crystal data and structure refinement for (FCA3)₂PbBr₄, 294K

CCDC number	2485416
Moiety formula	(C ₉ H ₁₁ FNO ₃) ₂ PbBr ₄ ·0.15H ₂ O
Empirical formula	C ₁₈ H _{22.29} Br ₄ F ₂ N ₂ O _{6.15} Pb
Formula weight	929.79
Temperature [K]	294(2)
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> [Å]	8.373(2)
<i>b</i> [Å]	7.8455(15)
<i>c</i> [Å]	41.44(2)
α [°]	90
β [°]	93.03(2)
γ [°]	90
Volume [Å ³]	2718.4(16)
<i>Z</i>	4
ρ_{calc} [gcm ⁻³]	2.272
μ [mm ⁻¹]	12.134
<i>F</i> (000)	1733.8
Crystal size [mm ³]	0.085×0.149×0.312
Crystal colour	colourless
Crystal shape	block
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	4.87 to 56.56 (0.75 Å)
Index ranges	-11 ≤ <i>h</i> ≤ 11 -10 ≤ <i>k</i> ≤ 10 -55 ≤ <i>l</i> ≤ 55
Reflections collected	67803
Independent reflections	6854 <i>R</i> _{int} = 0.1093 <i>R</i> _{sigma} = 0.0664
Completeness to θ = 25.242°	100.0 %
Data / Restraints / Parameters	6854 / 139 / 355

Absorption correction $T_{\min}/T_{\max}$ (method)	0.1410 / 0.6950 (numerical)
Goodness-of-fit on F^2	1.076
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0581$ $wR_2 = 0.1534$
Final R indexes [all data]	$R_1 = 0.0696$ $wR_2 = 0.1575$
Largest peak/hole [$\text{e}\text{\AA}^{-3}$]	4.30/−3.01

Refinement details

At lower temperature (150 K), the compound exhibited a well-defined superstructure with one water molecule for every four ammonium cations with pseudo-translation along the a-axis broken by presence or absence of the water molecule (and modulation of the associated ethyl ammonium group and of Pb and Br atoms). Upon warming to room temperature, the unit cell doubling along the a-axis disappears, together with development of worse peak shapes and onset of twinning. This is independent of whether crystals were cooled previously or were taken fresh from mother liquor without ever having been cooled.

Several crystals were investigated. Best data were obtained from a piece of the crystal of the 150 K structure determination after rewarming to RT. The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now¹⁰, with the two components being related by a 180-degree rotation around the real a-axis [100]. Attempts were made to integrate the two components using Saint (main text ref 39). Integration proved problematic due to excessive multiple overlap of reflections, resulting in excessive numbers of rejected reflections. Attempts were made to adjust integration parameters to avoid excessive rejections (through adjustments to integration queue size, integration box slicing and twin overlap parameters, and omission of box size optimization), which led to less but still substantial numbers of rejected reflections, or to complete but severely deteriorated data (no box size optimization).

With no acceptable quality complete data set obtainable through simultaneous integration of both twin domains, the data were instead handled as if not twinned, and twinning was handled using a TWIN transformation matrix in ShelXle (main text ref 45). The transformation matrix was obtained using Rotax (as embedded in WinGX)¹¹ and was TWIN

```
1.000 0.000 0.000
0.000 -1.000 0.000
-0.522 0.000 -1.000.
```

The minor twin ratio refined to only 0.0350(6) (likely an underestimation due to use of a TWIN command rather than separate domains) but led to substantial improvement of model and

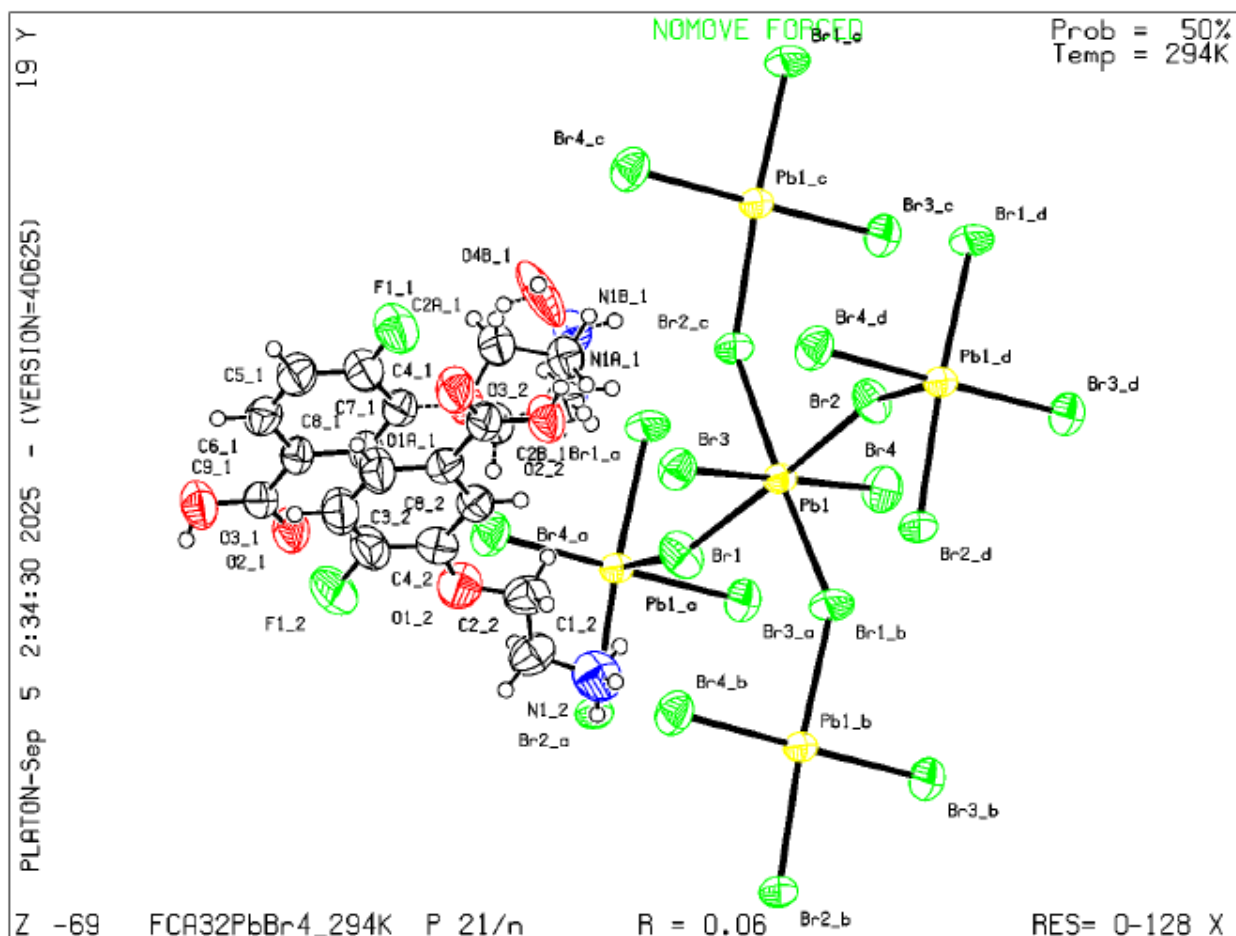
¹⁰ G. M. Sheldrick, "Cell_Now." University of Göttingen, Germany (2008).

¹¹ L. J. Farrugia, *J. Appl. Cryst.* **45**, 849-854 (2012).

refinement (R1 fell from 7.86 to 6.06 %; the largest hole rose from -4.54 to -3.00; ADPs of atoms, especially disordered C and N atoms, improved substantially).

One of the ammonium ethyl fragments (associated with the at 150 K ordered and modulated two ammonium ethyl fragments) was refined, initially as 1:1 disordered. Difference densities indicated a lower occupancy of the moiety associated with the water molecule, and occupancies were independently refined. The minor ammonium ethyl fragment and the water occupancy refined to similar values and a common value was thus used.

Water H atom positions were refined and O-H and H...H distances were restrained to 0.84(2) and 1.36(2) Angstrom, respectively. Some water H atom positions were further restrained based on hydrogen bonding considerations. The two disordered ammonium ethyl moieties were restrained to have similar geometries as the other not disordered moiety. U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 Angstrom were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.855(13) to 0.145(13), indicating that some water might have been lost from the structure after warming up from 150 K to RT, or that the remaining water is distributed within the structure in an ill-defined and not resolved manner.



Supplementary Table S4. Crystal data and structure refinement for (FCA3)_{1.821}(BrCA3)_{0.179}PbBr₄, 150K

CCDC number	2485417
Moiety formula	(C ₉ H ₁₁ FNO ₃) _{1.821} (C ₉ H ₁₁ BrNO ₃) _{0.179} PbBr ₄ ·0.64H ₂ O
Empirical formula	C ₁₈ H _{23.27} Br _{4.18} F _{1.82} N ₂ O _{6.64} Pb
Formula weight	949.57
Temperature [K]	150(2)
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
<i>a</i> [Å]	7.8223(4)
<i>b</i> [Å]	8.5746(5)
<i>c</i> [Å]	20.2961(10)
α [°]	86.372(3)
β [°]	82.391(2)
γ [°]	88.742(3)
Volume [Å ³]	1346.50(12)
<i>Z</i>	2
ρ_{calc} [gcm ⁻³]	2.342
μ [mm ⁻¹]	12.515
<i>F</i> (000)	886
Crystal size [mm ³]	0.108×0.138×0.510
Crystal colour	colourless
Crystal shape	rod
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	5.06 to 66.48 (0.65 Å)
Index ranges	-12 ≤ <i>h</i> ≤ 12 -13 ≤ <i>k</i> ≤ 13 -31 ≤ <i>l</i> ≤ 31
Reflections collected	74972
Independent reflections	10299 R_{int} = 0.0416 R_{sigma} = 0.0279

Completeness to $\theta = 25.242^\circ$	99.9 %
Data / Restraints / Parameters	10299 / 556 / 552
Absorption correction $T_{\min}/T_{\max}$ (method)	0.3461 / 0.7465 (multi-scan)
Goodness-of-fit on F^2	1.073
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0320$ $wR_2 = 0.0692$
Final R indexes [all data]	$R_1 = 0.0476$ $wR_2 = 0.0748$
Largest peak/hole [$\text{e}\text{\AA}^{-3}$]	2.23/−2.94

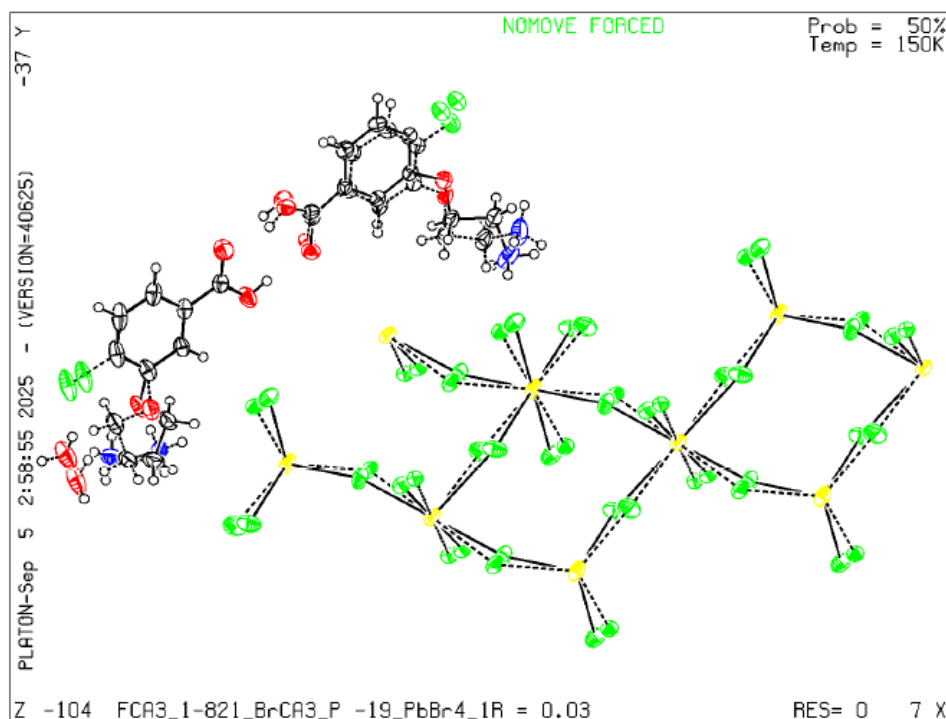
Refinement details

The structure was notably untwinned. It was modeled and refined with six types of disorder. The following explanation illustrates how the connectivity among these six disorders results in an FCA3:BrCA3 ratio of 1.821:0.179, as reflected in the moiety formula. Supplementary Fig. S25 visualizes all types of disorders in the unit cell with Mercury.

Level B alerts from CheckCIF:

PLAT972_ALERT_2_B Check Calcd Resid. Dens. 0.87Ang From Pb1 -2.61 eA-3

- The residue densities near the heavy inorganic layer are due to errors with absorption correction.



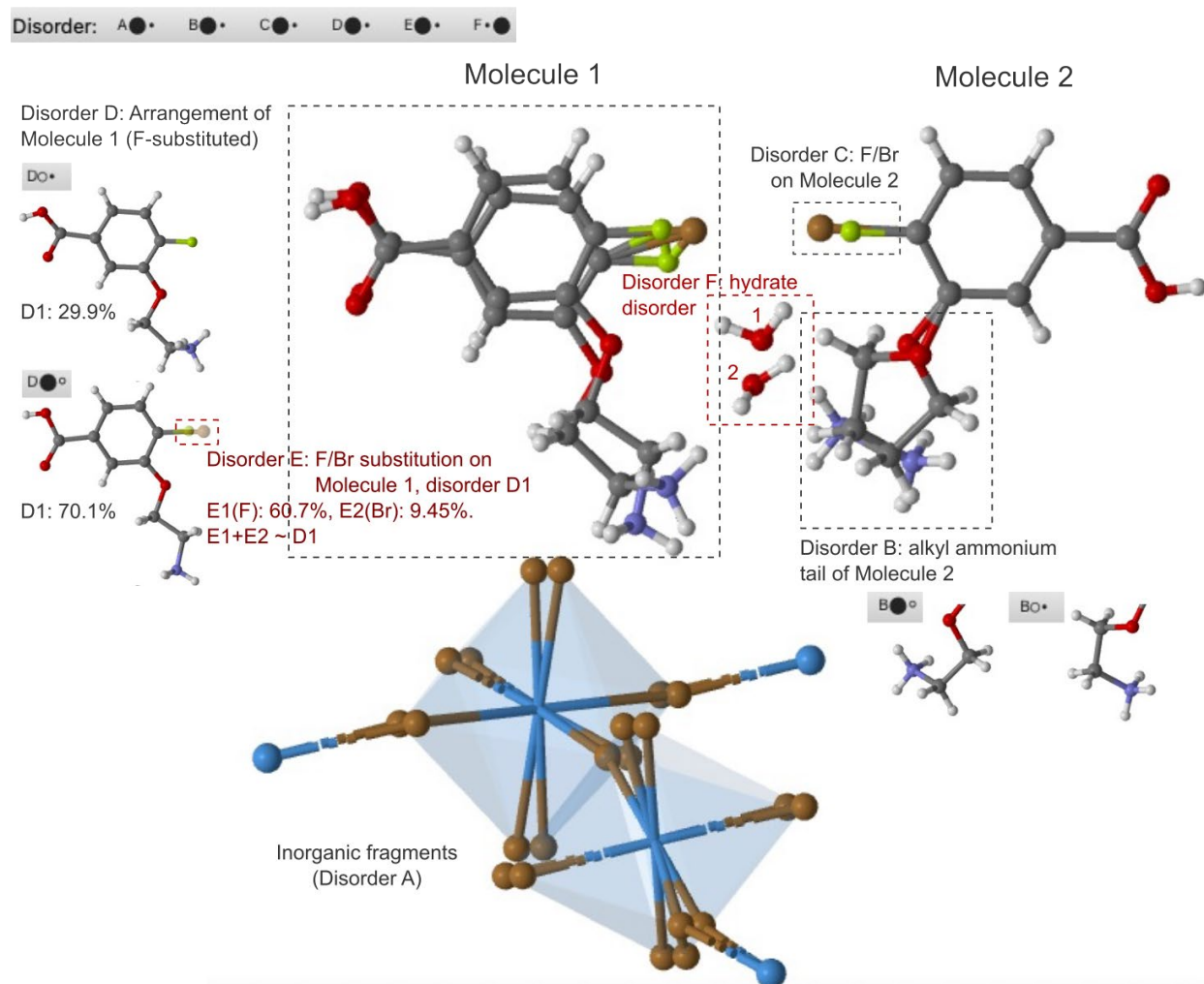
Occupancy of BrCA3

There are two organic cations in the unit cell (Molecule 1 and 2). Let's start from the disorder modeling of Molecule 1, which was the most challenging case. The entire Molecule 1 was disordered (#D) into two conformations (D1 and D2). Embedded in it, the D1 fragment has a sub-disorder #E representing the halide substitution disorder (F or Br). The D2 fragment was substituted with F only.

Bimodal disorder phases were each assigned a part # in ShelXle but only one shared free variable (FVAR) denoting the contribution of one phase to be refined. The contribution of the other phase was simply calculated as 1-FVAR. However, in this "disorder within disorder" case, it's no longer possible to only use two parts during structural refinement. We therefore assigned D1 and D2 as part 5 and 6, respectively, while sharing a FVAR (#5). Afterwards, the disorder phase E1 (part 3), the F-substituted D1, and E2 (part 4), the Br-substituted counterpart, were each assigned a separate FVAR (#3 and #4) and let refined on its own. The FVAR of E1, E2, and D1 were refined to 0.60662, 0.09452, and 0.70114, respectively, which matched our initial hypothesis that D2, the other disordered phase of Molecule 1, was substituted with F only. Note that during this process, part 3&4 were both bind to Molecule 1 using the BIND command.

On the other hand, Molecule #2 exhibited disorder both for the alkyl ammonium tail (Disorder B) and the halide substitution (C). They were each assigned a FVAR and refined separately. The occupancy of F-substituted Molecule 2 was refined to be 0.91547.

In other words, the occupancy of BrCA3 in Molecule 1 was 0.09452. In other words, the total occupancy of BrCA3 was calculated to be $(0.09452 + 1 - 0.91547)/2 = 0.08953$.



Supplementary Fig. S25. Types of disorder in a unit cell.

Notably, the occupancy of Br in either Molecule 1 or 2 was too low for the accurate calculation of its atomic displacement parameter (ADP). The EADP command was used to unite the ADP for F and Br in each molecule since their bonding environments are similar.

Supplementary Table S5. Disorder type, part #, and occupancy.

Disorder #	Type	Part# in shelx res file	FVAR#
A1	Inorganic framework	1	2: 63.9%
A2	Inorganic framework	2	-2: 36.1%
B1	Alkylammonium tail on Molecule 2	1	7: 62.7%
B2		2	-7: 37.3%
C1	F substituted Molecule 2	1	6: 91.5%
C2	Br substituted Molecule 2	2	-6: 8.45%
D1	Conformations of Molecule 1	5	5: 70.1%
D2		6	-5: 29.9%

E1	F-substituted D1	3	3: 60.7%
E2	Br-substituted D1	4	4: 9.45%
F1	Water 1	7	8: 33.8%
F2	Water 2	8	9: 29.7%

Hydrate disorder

Water H atom positions were refined, and O-H and H···H distances were restrained to 0.84(2) and 1.36(2) Angstrom, respectively.

The hydrate split into two conformations (water 1 and 2) which did not add up to 1.0 occupancy and thus, part of the structure had water loss. The need to split water molecules is due to the originally poorly refined ADP and the compatibility between the unsplit hydrate molecule and the nearby cation fragments. Based on the potential H bonds between water and nearby molecule 1 or 2, additional restraints were added during refinement to restrain the distance from water H atoms to possible H bonding acceptors:

DFIX 2.3 H7D F2 (water 1 to Molecule 2)

DFIX 2.3 H7D O2A (water 1 to Molecule 2)

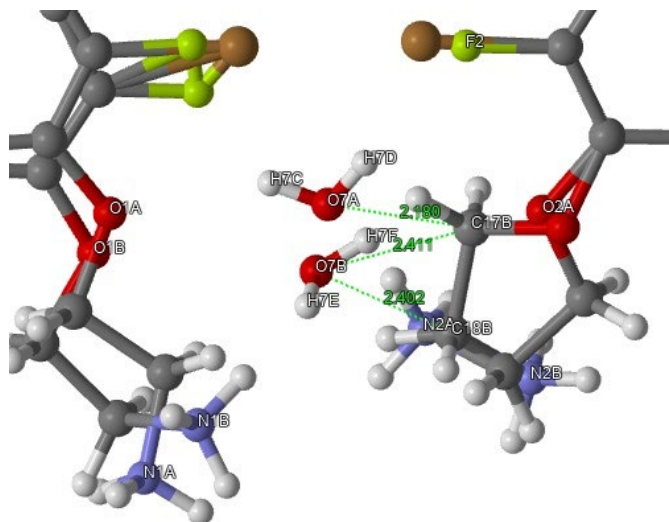
DFIX 2.4 H7C O1A_\$1 (water 1 to Molecule 1)

DFIX 2.9 H7F F2 (water 2 to Molecule 2)

DFIX 2.6 H7F O2A (water 2 to Molecule 2)

DFIX 2.4 H7E O1B_\$1 (water 2 to Molecule 1)

These distance values were obtained as follows. First, find to which atoms the water is likely H bonded to. Then measure the distance from the water O atom to the acceptor. Subtract 0.84 Å (for a linear O-H···Acceptor bond) or some less for a bifurcated (nonlinear) H bond. Adjust if needed.



Supplementary Fig. S26. Disordered hydrates and the surrounding cation fragments.

Water 1&2 were assigned part #7&8 and FVAR #8&9, respectively, and were freely refined without binding with certain cation fragments. Occupancy of water 1 was refined to 0.33832 and water 2 as 0.29750, giving a total water occupancy of 0.63582.

Notably, the total hydrate occupancy is very similar to the occupancy of the disorder phase B1 of Molecule 2's alkylammonium tail. This result is expected since both hydrate conformations are incompatible with the disorder phase B2. In detail, water 2 is incompatible with B2 of Molecule 2's alkylammonium tail since the distance between O7B and C17B (2.41 Å) or C18B (2.40 Å) is too short. Also, water 1 is incompatible with this disorder phase B2 since O7A is too close to C17B (2.18 Å).

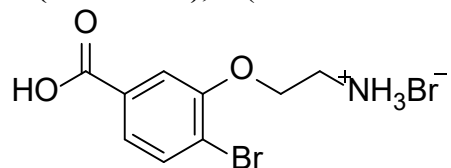
Other refinement details

Carboxylic acid H atoms were placed in calculated positions and allowed to refine but were constrained to coplanar with the two COO fragments they are part of in the dimer structure (using the FLAT command).

The FCA3 cation in disorder D2 and E1 of Molecule 1 was restrained to have the same bond distances (each type of bond restrained to have the same distance using the SADI command). All atoms were restrained to have similar APDs using the SIMU command with esd = 0.01 Å². Similar restraint was applied to the disordered alkylammonium of Molecule 2 (B1 and B2).

NMR Spectra

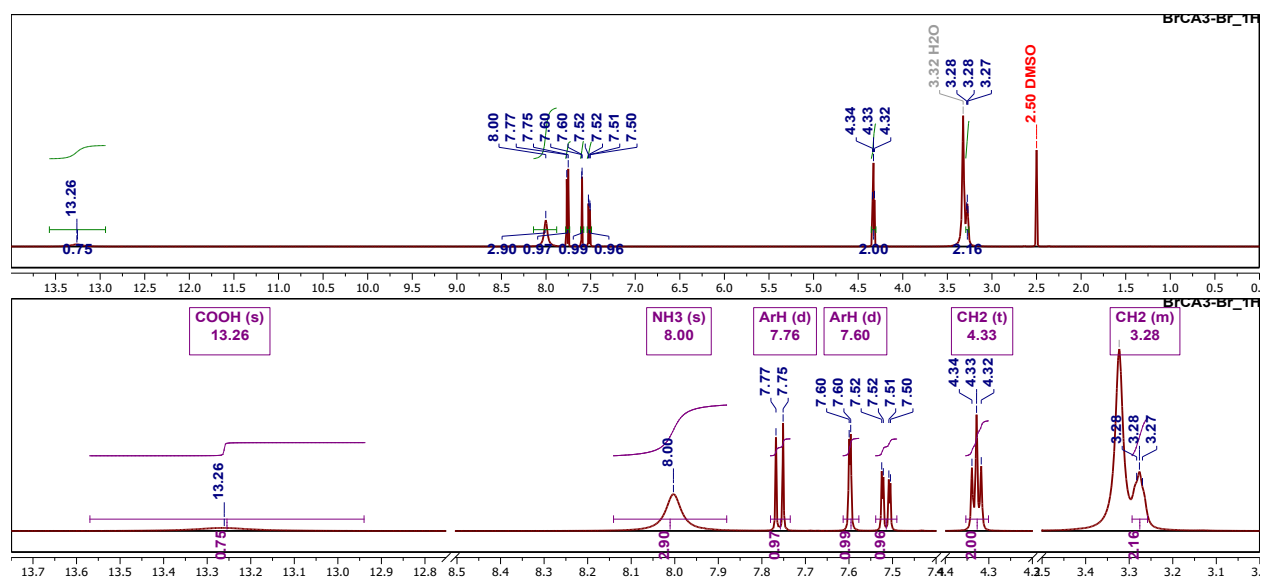
- (BrCA3-Br), 2-(2-bromo-5-carboxyphenoxy)ethan-1-aminium bromide



BrCA3-Br

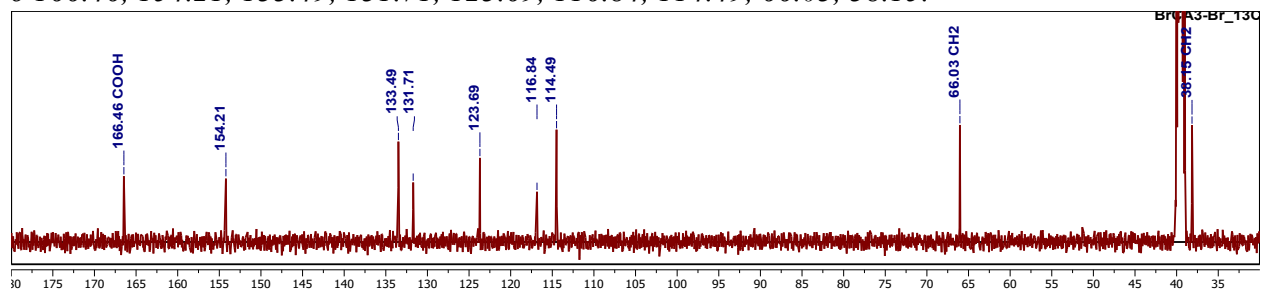
^1H NMR (500 MHz, DMSO- d_6)

δ 13.26 (s, 1H), 8.00 (s, 3H), 7.76 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 1.8 Hz, 1H), 7.51 (dd, J = 8.2, 1.8 Hz, 1H), 4.33 (t, J = 5.3 Hz, 2H), 3.29 – 3.26 (m, 2H).

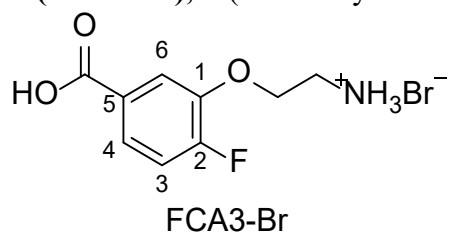


^{13}C NMR (126 MHz, DMSO- d_6)

δ 166.46, 154.21, 133.49, 131.71, 123.69, 116.84, 114.49, 66.03, 38.15.

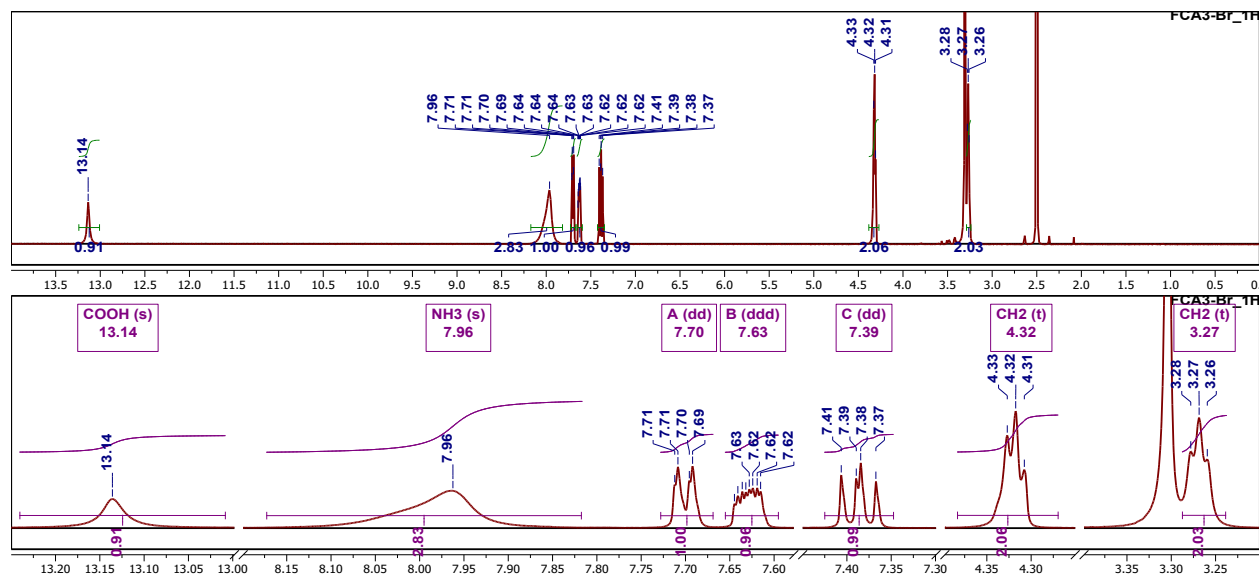


- **(FCA3-Br)**, 2-(5-carboxy-2-fluorophenoxy)ethan-1-aminium bromide



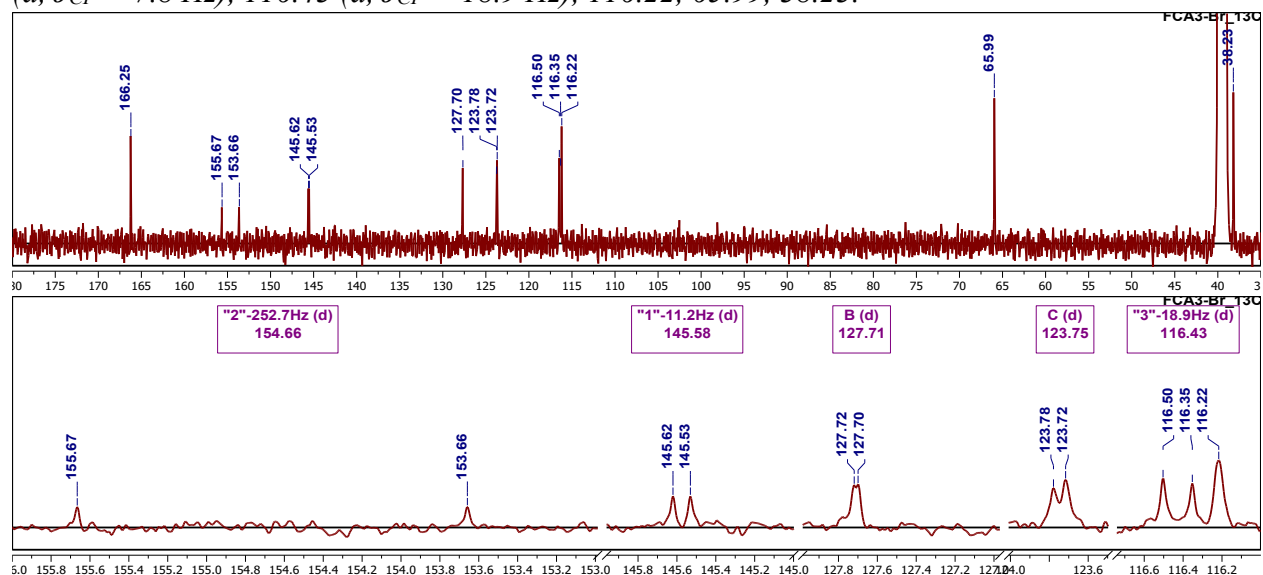
*¹H NMR (500 MHz, DMSO-*d*₆)*

δ 13.14 (s, 1H), 7.96 (s, 3H), 7.70 (dd, $J = 8.2, 1.8$ Hz, 1H), 7.63 (ddd, $J = 8.3, 4.4, 1.9$ Hz, 1H), 7.39 (dd, $J = 11.0, 8.5$ Hz, 1H), 4.32 (t, $J = 4.8$ Hz, 2H), 3.27 (t, $J = 4.7$ Hz, 2H).



^{13}C NMR (126 MHz, DMSO- d_6)

δ 166.25, 154.66 (d, $J_{\text{CF}} = 252.7$ Hz), 145.58 (d, $J_{\text{CF}} = 11.2$ Hz), 127.71 (d, $J_{\text{CF}} = 2.8$ Hz), 123.75 (d, $J_{\text{CF}} = 7.8$ Hz), 116.43 (d, $J_{\text{CF}} = 18.9$ Hz), 116.22, 65.99, 38.23.



^{19}F NMR (470 MHz, DMSO- d_6) *uncalibrated

δ -127.05.

