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Peer Review File

Directed crystalline symmetry transformation of blue-phase liquid crystals by reverse electrostriction

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This work concerns liquid crystalline blue phases whose self-organized three-dimensional structures have been attracting considerable interest as a tunable soft-matter-based photonic crystal. The authors demonstrate the formation of monocrystalline blue phases within minutes by carefully controlling the applied electric field and temperature, in contrast to previous experimental attempts of obtaining monocrystalline blue phases requiring hours of relaxation (Supplementary Movie 1). They further show that much more variety of symmetries of the resulting blue phases can be realized than has been known for bulk thermodynamically stable blue phases; they can exhibit orthorhombic and tetragonal as well as cubic symmetry.

I read the manuscript with great interest, and I believe that the demonstration of a facile method of generating monocrystalline blue phases with various symmetry will attract broad readership of Nature Communications. However, I am afraid that the other reviewers and future interested readers might regard this work as one for a specialized audience who already knows about blue phases quite well: Reading this manuscript might require sufficient prior knowledge on blue phases and recent pertinent studies, and most of the papers in the reference list are on blue phases.

I believe that the authors' findings themselves deserve publication in Nature Communications as mentioned above, but the authors might want to rewrite the manuscript so that it is more easy accessible and appealing to broader audience. I also have several concerns on the interpretation and presentation of the experimental results, as listed below. Therefore I do not recommend the publication of this manuscript at least in its present form.

* Although I find the authors' analysis of Kossel diagrams interesting and carefully carried out, I understand that the possibility of a triclinic lattice is implicitly ruled out. I am wondering whether this possibility can be safely ruled out in the present study, and I am

afraid that this treatment might limit the applicability of the authors' method to future problems. I am also wondering whether this analysis can give information on the error bar of the lattice constant.

* Are the experimental and theoretical Kossel diagrams based on orthogonal projection? (See, e.g., Pieranski et al., J. Physique 42, 53 (1981).) If so, state this clearly.

* Figure captions should describe the experimental conditions; they should not be pushed out to Methods. The absence of temperatures, temperature gradients and electric fields there frustrated me a lot.

* The in-plane surface anchoring is employed in this work. Then the direction of the in-plane anchoring must be specified in figures and movies. The direction of the gradient temperature with respect to the anchoring direction might play some role.

* In Fig. 4, if the authors intend to claim that the lattice is cubic, a multiplied by sqrt(2) should be compared with b (or c).

* [The 3rd line of page 7] The trend "higher a, b, and c values at lower temperatures" is different from that of Fig. 4a. The authors should comment on it.

* The visibility of Fig. 5b is quite poor (especially when it is printed). The dashed line should be presented in a different color.

* I hesitate to accept the statement "the twins are the mirror images of each other" (The 1st paragraph of page 8) and "plane of symmetry" in Fig. 5c, because the liquid crystal is chiral.

* [The last paragraph of Sec. IV] I cannot be sure whether blue phases can be exploited for "dispersion engineering", especially for negative refraction.

* By Supplementary Movie 4 alone the authors cannot claim that they are observing a tetragonal lattice.

* [Supplementary Note 2] If the authors want to use the notations "dot product" (the last line of page 2) and "L1 norm" (page 4), they should give clearly their definition in the present context, and specify what vector space they are dealing with.

* [Supplementary Note 2, after eq. (2)] It should be made clear what "all four lattice planes" are.

* [Eq. 2 of Supplementary Note 2] I am wondering what the factor "2.5" comes from. I also note that the label "(2)" hides a part of the text.

* Some recent contributions on blue phases are missing in the reference list:

Oton et al., Sci. Rep., 10, 10148 (2020) (Demonstration of monocrystalline blue phase. This group publishes several other papers on blue phases)

Manda et al., NPG Asia Materials 12, 42 (2020) (Tunability of photonic band gap structure of blue phases)

Jin et al., Sci. Adv. 6, eaay5986 (2020); Liu et al., Nature Commun. 12, 3477 (2021); Yamashita and Fukuda, Phys. Rev. E 105, 044707 (2022) (twinning of blue phases)

* The information on Ref. 8 is incomplete. The authors should recheck the reference list so that all the information is complete and sufficient.

* The text is basically well written, but contains a few typographical/grammatical errors:

[Page 2, last line] "direct" -> "directs" (I also think this sentence is too long.)

[Page 4, the last paragraph of Sec. II] "an apply field" -> "an applied field"?

[Page 7, second paragraph] A verb is missing at "until they at E_D=..."

Reviewer #2 (Remarks to the Author):

This article reports on the fabrication of large-area monocrystalline blue-phase liquid crystals using a newly developed technology called reverse electrostriction-directed assembly. Notably, this method enables the modulation of crystal symmetry and lattice parameters. This work represents a significant improvement on the fabrication of structurally controlled BPLCs and may facilitate their photonic applications. The manuscript is suitable for publication in Nature Communications after minor revisions, which are detailed below.

1. The authors have demonstrated the control of crystal symmetry of BPLCs through an electric field of varying strengths. Have the authors investigated other forms of stimuli?

2. The formation of different crystal symmetries in BPLCs was attributed to lattice deformation. The authors are encouraged to perform related simulations to elucidate the origin of this lattice deformation under the field effect.

General reply to the reviewers: We are thankful to the reviewers for their positive feedback about our manuscript. Their comments and questions are reproduced verbatim in this document, in black. Our responses are in blue below each comment. The modifications that we made in the text are highlighted in yellow.

Reviewer #1

This work concerns liquid crystalline blue phases whose self-organized three-dimensional structures have been attracting considerable interest as a tunable soft-matter-based photonic crystal. The authors demonstrate the formation of monocrystalline blue phases within minutes by carefully controlling the applied electric field and temperature, in contrast to previous experimental attempts of obtaining monocrystalline blue phases requiring hours of relaxation (Supplementary Movie 1). They further show that much more variety of symmetries of the resulting blue phases can be realized than has been known for bulk thermodynamically stable blue phases; they can exhibit orthorhombic and tetragonal as well as cubic symmetry.

I read the manuscript with great interest, and I believe that the demonstration of a facile method of generating monocrystalline blue phases with various symmetry will attract broad readership of Nature Communications. However, I am afraid that the other reviewers and future interested readers might regard this work as one for a specialized audience who already knows about blue phases quite well: Reading this manuscript might require sufficient prior knowledge on blue phases and recent pertinent studies, and most of the papers in the reference list are on blue phases.

I believe that the authors' findings themselves deserve publication in Nature Communications as mentioned above, but the authors might want to rewrite the manuscript so that it is more easy accessible and appealing to broader audience. I also have several concerns on the interpretation and presentation of the experimental results, as listed below. Therefore I do not recommend the publication of this manuscript at least in its present form.

***Author**:*

We sincerely appreciate Reviewer 1's thoughtful review, their recognition of the significance of our findings, and the potential for publication in Nature Communications.

In response to the reviewer's suggestion to make the manuscript more readable and appealing to a broader audience, we have reorganized, rewritten, and expanded the *Introduction* section, as well as reworded and rephrased several explanations in the main text. We have also *quoted 14 more references* (listed below) on the use of soft matter such as liquid crystals in optics, bio-medical, chemistry, and other areas. In the revised introduction, we discussed the advantages and potential of soft matter-based photonic crystals and introduced blue-phase liquid crystals (BPLC) as an important and intriguing class of such photonic crystals. We have included essential basics of BPLC and pointed out that BPLCs combine the unique advantages of photonic crystals (photonic bandgaps, strong band-edge dispersion, etc.) and liquid-crystal properties (birefringence, chirality, tunability, optical nonlinearity, etc.), thus presenting themselves as attractive materials for studies and applications in a *wide range of disciplines.*

New references quoted in the introduction section:

12 Rey, A. D. Liquid crystal models of biological materials and processes. *Soft Matter* **6**, 3402-3429, doi:10.1039/B921576J (2010).

15 Lowe, A. M. & Abbott, N. L. Liquid Crystalline Materials for Biological Applications. *Chemistry of Materials* **24**, 746-758, doi:10.1021/cm202632m (2012).

18 Martínez-González, J. A. *et al.* Directed self-assembly of liquid crystalline blue-phases into ideal single-crystals. *Nature Communications* **8**, 15854, doi:10.1038/ncomms15854 (2017).

19 Oton, E., Netter, E., Nakano, T., D.-Katayama, Y. & Inoue, F. Monodomain Blue Phase Liquid Crystal Layers for Phase Modulation. *Scientific Reports* **7**, 44575, doi:10.1038/srep44575 (2017).

20 Wang, M. *et al.* Bias-Polarity Dependent Bidirectional Modulation of Photonic Bandgap in a Nanoengineered 3D Blue Phase Polymer Scaffold for Tunable Laser Application. *Advanced Optical Materials* **6**, 1800409, doi:10.1002/adom.201800409 (2018).
23 Yang, J. *et al.* Fabrication and photonic applications of large-domain blue phase films. *Journal of Materials Chemistry C* **7**, 9460-9466, doi:10.1039/C9TC02938A (2019).
24 Manda, R. *et al.* Electrically tunable photonic band gap structure in monodomain blue-phase liquid crystals. *NPG Asia Materials* **12**, 42, doi:10.1038/s41427-020-0225-8 (2020).
25 Otón, E. *et al.* Orientation control of ideal blue phase photonic crystals. *Scientific Reports* **10**, 10148, doi:10.1038/s41598-020-67083-6 (2020).
27 Bisoyi, H. K. & Li, Q. Liquid Crystals: Versatile Self-Organized Smart Soft Materials. *Chemical Reviews* **122**, 4887-4926, doi:10.1021/acs.chemrev.1c00761 (2022).
28 Bagchi, K., Emeršič, T., Martínez-González, J. A., de Pablo, J. J. & Nealey, P. F. Functional soft materials from blue phase liquid crystals. *Science Advances* **9**, eadh9393, doi:10.1126/sciadv.adh9393 (2023).
29 Coles, H. J. & Pivnenko, M. N. Liquid crystal 'blue phases' with a wide temperature range. *Nature* **436**, 997-1000, doi:10.1038/nature03932 (2005).
30 Castles, F. *et al.* Blue-phase templated fabrication of three-dimensional nanostructures for photonic applications. *Nature Materials* **11**, 599-603, doi:10.1038/nmat3330 (2012).
31 Hu, W. *et al.* Ultrastable liquid crystalline blue phase from molecular synergistic self-assembly. *Nature Communications* **12**, 1440, doi:10.1038/s41467-021-21564-y (2021).
38 Pierański, P., Cladis, P. E., Garel, T. & Barbet-Massin, R. Orientation of crystals of blue phases by electric fields. *J. Phys. France* **47**, 139-143, doi:10.1051/jphys:01986004701013900 (1986).

1. Although I find the authors' analysis of Kossel diagrams interesting and carefully carried out, I understand that the possibility of a triclinic lattice is implicitly ruled out. I am wondering whether this possibility can be safely ruled out in the present study, and I am afraid that this treatment might limit the applicability of the authors' method to future problems. I am also wondering whether this analysis can give information on the error bar of the lattice constant.

Author:

The reviewer raises an important point regarding the possibility of a triclinic lattice. Like monoclinic symmetry reported in our study, triclinic lattices have not been documented in blue-phase liquid crystals (BPLC) to date. *To address this concern, we have expanded and refined our numerical model to incorporate triclinic symmetry* by *allowing the c axis to deviate from the cell normal*. New paragraphs are added to the end of Supplementary Note 2 (pages 7 and 8) to explain how the triclinic symmetry and associated parameters are incorporated in the refined model. We have also added the new simulation result to Fig. 5d in the main text. We then use this refined model to fit the measured Kossel diagrams. Our analysis reveals that the *c* axis is highly aligned with the cell normal, with an uncertainty of only within half a degree. This suggests that triclinic symmetry can be safely excluded; a related discussion has been added to the end of sec. III.B in the main text (the second paragraph on page 9). The inclusion of triclinic symmetry in the model, however, demonstrates the potential applicability of our method to more complex systems in future investigations.

The new paragraphs in Supplementary Note 2 reads, "Although we could safely assume that the $\boldsymbol{c}$ axis is orthogonal to the $\boldsymbol{a}$ and $\boldsymbol{b}$ axes in the fitting process, a more rigorous way of analysis involves treating the angles between any two of the three axes as free parameters. We define the angle between $\boldsymbol{a}$ and $\boldsymbol{b}$ as γ (with $\gamma = 90° - \beta$), the angle between $\boldsymbol{c}$ and $\boldsymbol{a}$ as ζ, and the angle between $\boldsymbol{c}$ and $\boldsymbol{b}$ as α. As previously discussed, simulating a Kossel diagram requires knowing the orientation of the four lattice planes relative to the laboratory frame (Cartesian coordinates), described by their normal vectors $\boldsymbol{N}$. These normal vectors can be determined using three representative points (Q_1–Q_3) on each lattice plane, as shown in **Fig. 3e**. To transform each point $Q = (Q_a, Q_b, Q_c)$ from the crystallographic ($\boldsymbol{abc}$)

coordinates to Cartesian coordinates, it is written as a column vector $\boldsymbol{Q} = [Q_a, Q_b, Q_c]^{\mathrm{T}}$ and multiplied by a transformation matrix T:

$$T = \begin{bmatrix} 1 & 0 & 0 \\ \cos\gamma & \sin\gamma & 0 \\ \cos\zeta & \dfrac{\cos\alpha - \cos\zeta\cos\gamma}{\sin\gamma} & \sqrt{1 - \cos^2\zeta - \left(\dfrac{\cos\alpha - \cos\zeta\cos\gamma}{\sin\gamma}\right)^2} \end{bmatrix}.$$

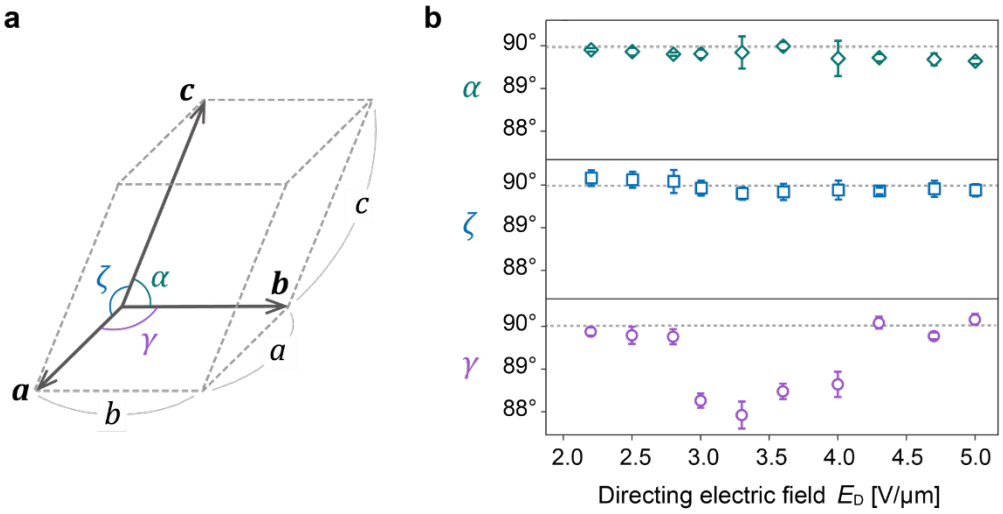

Fig. S5. Complementary analysis to Fig. 5d in main text. a Definition of angles γ ($= 90° - \beta$), ζ, and α. **b** Fitted γ, ζ, and α of monoclinic BPLC as a function of directing-field strength (E_D) used in the REDA process. These monoclinic crystals are obtained by directly cooling tetragonal single crystals that are formed by REDA under various E_D. Error bars represent the standard deviation.

We incorporate this refined treatment into our code and reanalyze the measured Kossel diagrams of what we previously identified as monoclinic crystals (characterized by $\zeta = \alpha = 90°$ and $\gamma \neq 90°$) [cf. Fig. 5d]. These crystals are obtained by two steps: first, reverse-electrostriction-directed assembly (REDA) of a BPLC under various directing-field strengths (E_D) form tetragonal single crystals of different a, b, and c; then, these crystals undergo direct cooling by ~1°C. Figure S5 shows the fitted angles γ, ζ, and α as a function of E_D, ranging from ~2 to 5 V/μm. The fitting process employs a genetic algorithm for optimization, and each data point represents the average of five independent searches. The results show that while ζ and α remain ~90.0° throughout the entire range of analysis, γ varies from ~90.0° (corresponding to $\beta \approx 0.0°$) to as low as ~87.5° ($\beta \approx 2.5°$). This confirms our initial characterization of the crystals as monoclinic. Incorporating all six fitting parameters (a, b, c, γ, ζ, α) expands the method's applicability to more intricate systems (e.g., triclinic crystals), but it also increases the computational complexity, time required for fitting, and risk of local optima. ”

The reviewer also inquired about the error bar in the lattice constant. This value is primarily influenced by two factors: the image quality of the measured Kossel diagram and the aberration of the imaging system. The latter can be effectively eliminated through calibration of the imaging system with a well-characterized reflective grating, as described in the Supplementary Information. The error bar for the lattice constant can be estimated by performing a full scan of the parameter space surrounding the optimal lattice constants identified. In the present study, the error bar for the lattice constant is ~ ±0.5 nm. This explanation has also been added to the second paragraph of page 6 in the Supplementary Information.

2. Are the experimental and theoretical Kossel diagrams based on orthogonal projection? (See, e.g., Pieranski et al., J. Physique 42, 53 (1981).) If so, state this clearly.

   Author: Yes, both the experimental and simulated Kossel diagrams presented in this paper are based on orthogonal projections. The orthogonal projection directly represents what is seen in the camera plane (Fig. S1). We have added this to relevant descriptions on the last paragraph on page 6 in the main text and the last paragraph on page 3 in the Supplementary Information.

3. Figure captions should describe the experimental conditions; they should not be pushed out to Methods. The absence of temperatures, temperature gradients and electric fields there frustrated me a lot.

   Author: We have added the experimental conditions to the captions of Figs. 2–6 and S1.

   The following have been added to the figure captions:

   In Fig. 2, temperature gradients are ~0.8°C/mm for the figures on the left-hand side. There are no temperature gradients for the figures on the right-hand side. The operating temperature is set at ~0.1°C below the BPI-BPII phase transition point (31.7 °C).

   In Fig. 3 and Fig. 4d, the operating temperature is set at 31.6°C (~0.1°C below the BPI-BPII phase transition point). The magnitude of applied fields E_D are 4.0, 2.6 and 0.0V/μm for the tetragonal, orthorhombic, and cubic symmetry, respectively (Fig. 3c).

   In Fig. 5, a BPLC with monoclinic symmetry is obtained by cooling a one with tetragonal symmetry. The cooling range is from 31.6°C to 30.7°C. For Figs. 5a,b, the applied field strength is 3.6 V/μm.

   In Fig. 6, the operating temperatures are 24.9°C, 31.6°C, and 37.9°C for purplish, greenish, and orangish BPLCs, respectively.

   In Fig. S1, the operating temperatures are set at 0.1°C and 1.0°C below the BPII–BPI phase-transition temperature (32.0°C) for Figs. S1a and S1b, respectively.

4. The in-plane surface anchoring is employed in this work. Then the direction of the in-plane anchoring must be specified in figures and movies. The direction of the gradient temperature with respect to the anchoring direction might play some role.

   Author: In Figs. 2–6 and S1, as well as in Supplementary Movies 1, 2, 3 and 4, the surface-alignment directions to the optical micrographs are all from left to right. This information has been added to the figure captions and descriptions of the Supplementary Movies on the first page of Supplementary Information.

5. In Fig. 4, if the authors intend to claim that the lattice is cubic, a multiplied by sqrt(2) should be compared with b (or c).

   Author: The reviewer raises a valid point regarding the comparison for a cubic lattice claim in Fig. 4. To strengthen our argument, we have incorporated new data points representing $(\sqrt{2})a$ in both Figs. 4a and 4b. In Fig. 4a, at the phase transition point (32.1°C), the lattice parameter ratios for the formed cubic lattice are $c/a \approx 1.417$ and $b/a \approx 1.416$. These values are in close agreement with $\sqrt{2} \approx 1.414$, characteristic of a body-centered cubic (BCC) lattice. Similarly, in Fig. 4b, the c/a ratios (1.416, 1.431, 1.426, and 1.409) and b/a ratios (1.416, 1.401, 1.379, and 1.415) for data points ordered by decreasing temperature (32.1°C to 31.5°C) all show good agreement with $\sqrt{2}$. The observed standard deviation of

only 0.016 supports the conclusion of BCC symmetry in these lattices. We have included a corresponding explanation in the first paragraph on page 8 for improved clarity.

6. [The 3rd line of page 7] The trend "higher a, b, and c values at lower temperatures" is different from that of Fig. 4a. The authors should comment on it.

Author:

We would first like to clarify that, as mentioned in the same sentence that the reviewer quoted, the trend is observed for the data in Fig. 4b, *not* Fig. 4a.

The data points in Fig. 4b represent the lattice parameters *a*, *b*, and *c* of the blue-phase (BP) crystal directly formed by reverse electrostriction directed assembly (REDA) at each temperature in the diagram, whereas Fig. 4a shows how the lattice parameters of a crystal formed by REDA evolve upon cooling from 32.1°C to 30.9°C.

The first paragraph of page 8 in the main text describes the trend seen in Fig. 4b, which is a consequence of the reduction in twisting power of the chiral agent in the BP mixture with decreasing temperature. However, the trend in Fig. 4a is different: while *c* increases with decreasing temperature, *a* and *b* decrease. This never-before-seen phenomenon is referred to as the anisotropy of the lattice deformation during cooling, described in the only paragraph of page 7 in the main text. This is attributed to the fact that the boundary conditions and lattice dimensions are different in different directions. In the longitudinal direction (along the *c* axis), the BP lattice has a small dimension (~12 μm) and interfaces with the surface-alignment film on each side of the lattice. So, the longitudinal lattice deformation due to cooling is primarily subjected to the reduced twisting power of the chiral agent and the surface anchoring force exerted by the alignment films. In the lateral direction, however, the lattice and constituent DTCs are centimeter long. So, the lateral lattice deformation due to cooling is subjected to the elastic restoring force exerted by a nearly infinite number of unit cells. Such differences lead to the anisotropic lattice deformation observed.

To make the relevant descriptions clearer, we switched the order of the paragraphs on page 7 and 8 and also revised the text.

7. The visibility of Fig. 5b is quite poor (especially when it is printed). The dashed line should be presented in a different color.

Author: Since the twin lattices all have almost identical lattice constants along the cell normal, the color difference is indeed poor in Fig. 5b. In fact, in the original Fig. 5b, the contrast of the inset image has already been increased significantly. Therefore, to address this comment, we decided to replace the original inset with a gray-scale image with adjusted contrast. In this new inset, the twin boundary is much clearer, so the original dashed line is no longer needed and has been removed from the inset.

8. I hesitate to accept the statement "the twins are the mirror images of each other" (The 1st paragraph of page 8) and "plane of symmetry" in Fig. 5c, because the liquid crystal is chiral.

Author:

We agree that the terms "mirror images" and "plane of symmetry" used in reference to the twinned crystals (Fig. 5c) are not appropriate due to the chiral nature of the liquid crystal. In achiral materials, twinning often results in mirror-image relationships, but chirality prevents mirror symmetry because the twinned lattices exhibit the same handedness.

To address this, we have revised the text and figure caption to provide a more precise description. The revised sentence (the last sentence in the first paragraph of page 9) reads: "*As further illustrated in Fig. 5c, the twinned crystals have skew angles of equal magnitude but opposite signs*." In Fig. 5c, *the label "plane of symmetry" has been replaced with "twin boundary*".

9. [The last paragraph of Sec. IV] I cannot be sure whether blue phases can be exploited for "dispersion engineering", especially for negative refraction.

   Author: Although blue-phase liquid crystals as photonic crystals can be used for guiding light propagation similar to negative-angle refraction, we deleted the sentence that mentioned dispersion engineering in the context of super prism and negative refraction as it detracts from the main theme/results of this paper.

10. By Supplementary Movie 4 alone the authors cannot claim that they are observing a tetragonal lattice.

    Author: The reviewer is correct that a definitive conclusion about the crystal's tetragonal structure cannot be based solely on Supplementary Movie 4. We would like to point out that the tetragonal lattice has also been confirmed by the measured Kossel diagram that was already included in the inset of Fig. 3b. In the revised description of Supplementary Movie 4 on the first page of Supplementary Information and the revised figure caption of Fig. 3b, we made a connection between the movie and the Kossel diagram insert.

11. [Supplementary Note 2] If the authors want to use the notations "dot product" (the last line of page 2) and "L1 norm" (page 4), they should give clearly their definition in the present context, and specify what vector space they are dealing with.

    Author:

    We agree with the reviewer that the dot product and L1 norm may be unclear to readers, so we revised the related text as follows:

    In the revised text in the first paragraph of page 5 in Supplementary Information, we have removed the term "dot product" and revised the statement around it as:

    "Each ring corresponds to a far-field diffraction of the narrowband probe from a specific lattice plane of the examined crystal, with its normal vector denoted as $\boldsymbol{N}$. This ring pattern can be simulated using the spectrum of the narrowband light source $S(\lambda)$ and the Bragg spectrum $R(\lambda, \varphi)$ of the photonic crystal across a range of reflection angles φ with respect to $\boldsymbol{N}$. $S(\lambda)$ is measured with a resolution of 0.3 nm across a wavelength range of 300 nm to 600 nm. $R(\lambda, \varphi)$ is discretized with respect to both wavelength (λ) and reflection angle (φ), and the discretization for λ matched the resolution of $S(\lambda)$ (0.3 nm). … When viewing along $\boldsymbol{N}$, the far-field intensity profile $I(\varphi)$ is calculated by integrating the product of $S(\lambda)$ and $R(\lambda, \varphi)$ over the entire wavelength range: $I(\varphi) = \int S(\lambda)R(\lambda, \varphi)\mathrm{d}\lambda$ [**Fig. S3d**]."

    Similarly, we have replaced the term "L1 norm" with a more descriptive explanation: the sum of the absolute intensity differences between corresponding pixels in the simulated and measured Kossel diagrams. This clarifies the concept without requiring familiarity with the technical term "L1 norm". The statement around it in the second paragraph of page 6 in Supplementary Information now reads:

    "Building upon the numerical simulations described earlier, we now focus on how these simulations are utilized to achieve the best fit with the experimentally measured Kossel diagram. Our primary goal here is to find the optimal values for a, b, and β, which define the simulated diagram. We achieve this by integrating the simulation with an optimization algorithm, such as an interior-point method or genetic algorithm. To ensure proper in-plane alignment between the simulated and measured Kossel

diagrams, the simulated diagram is first rotated to maximize the Pearson correlation coefficient with the measured one. The algorithm iteratively refines the simulated Kossel diagram to minimize its total intensity mismatch with the measured diagram. This mismatch is quantified by a cost function, calculated as the sum of absolute intensity differences between corresponding pixels in the two diagrams."

12. [Supplementary Note 2, after eq. (2)] It should be made clear what "all four lattice planes" are.

Author: Following the conventional definition of Miller indices in the body-centered cubic (BCC) crystal, if examining a BCC crystal with its [1 1 0] axis aligned with the *c* axis, the four rings correspond to four lattice planes (1 0 1), (1 0 −1), (0 1 1), and (0 1 −1). This has been added to the first paragraph on page 5 of the Supplementary Information, where we mentioned the four rings for the first time.

13. [Eq. 2 of Supplementary Note 2] I am wondering what the factor "2.5" comes from. I also note that the label "(2)" hides a part of the text.

Author: On the right-hand side of Eq. 2, the factor of 2.5 in the denominator of the second term arises from the normalization of $a^2 + b^2 + c^2$ to that in a body-centered cubic (BCC) lattice. In a BCC lattice, due to its symmetry, $c = b = (\sqrt{2})a$, leading to $a^2 + b^2 + c^2 = 2.5c^2$. This clarification has been added to the second paragraph of page 5 of Supplementary Information. In addition, the label (2) for Eq. 2 in the SI has been moved to the correct location.

14. Some recent contributions on blue phases are missing in the reference list:

Oton et al., Sci. Rep., 10, 10148 (2020) (Demonstration of monocrystalline blue phase. This group publishes several other papers on blue phases)

Manda et al., NPG Asia Materials 12, 42 (2020) (Tunability of photonic band gap structure of blue phases)

Jin et al., Sci. Adv. 6, eaay5986 (2020); Liu et al., Nature Commun. 12, 3477 (2021); Yamashita and Fukuda, Phys. Rev. E 105, 044707 (2022) (twinning of blue phases)

Author:

The paper by Oton et al. has been added as ref. 25. In the second paragraph of the revised introduction section (on page 2 of the main text), we mention that: "Faster growth of BPLCs into mm^2- to cm^2-scale single crystals was also successfully demonstrated using special surface-alignment materials or nanostructures.[18,19,25]"

The paper by Manda et al. has been added as ref. 24. In the same paragraph (the 2nd paragraph of page 2 in the main text), we cited the paper at which monodomain BPLCs are discussed: "Alternatively, studies have also shown that a high-frequency (~ kHz) electric field[36,37] or proper surface alignment[24] can effectively transform a polycrystalline BPLC sample into the so-called 'monodomain' crystals in a short time of a few seconds to a minute with all the crystallites having the same crystalline axis (usually, $[110]_{BCC}$) along the applied field direction.[38]"

We have cited the three papers by Jin et al., by Liu et al., and by Yamashita and Fukuda as refs. 55, 56, and 57, respectively in section III.B of the main text. In the revised text (the 3rd paragraph on page 8), we point out that the twinning reported in the three papers and refs. 48, 54 has a completely different origin from the twinning reported in the present study. In the present study, the twinning originates from

cooling of a tetragonal single crystal, whereas the twinning reported in refs. 48, 54, 55, 56, 57 is induced by martensitic transformation from a simple-cubic lattice of BPII to a BCC lattice of BPI.

15. The information on Ref. 8 is incomplete. The authors should recheck the reference list so that all the information is complete and sufficient.

    Author: Thank you for pointing out an incomplete reference. We have conducted a careful check of the reference list to ensure that the format is correct, and the information is complete.

16. The text is basically well written, but contains a few typographical/grammatical errors:

    [Page 2, last line] "direct" -> "directs"

    [Page 4, the last paragraph of Sec. II] "an apply field" -> "an applied field"?

    [Page 7, second paragraph] A verb is missing at "until they at E_D=..."

    Author: Thank you for pointing out the errors. We have corrected these errors and did a comprehensive check/editing of the entire manuscript for other errors.

Reviewer #2

This article reports on the fabrication of large-area monocrystalline blue-phase liquid crystals using a newly developed technology called reverse electrostriction-directed assembly. Notably, this method enables the modulation of crystal symmetry and lattice parameters. This work represents a significant improvement on the fabrication of structurally controlled BPLCs and may facilitate their photonic applications. The manuscript is **suitable for publication in Nature Communications after minor revisions**, which are detailed below.

Author: We sincerely thank Reviewer 2 for the positive evaluation of our work and the recommendation for publication in Nature Communications after minor revisions.

1. The authors have demonstrated the control of crystal symmetry of BPLCs through an electric field of varying strengths. Have the authors investigated other forms of stimuli?

   Author: Besides the effect of electric field on controlling the crystal symmetry, we also studied how a subsequent *temperature change* (cooling) can further transform the crystal into new symmetry and structure, such as the unprecedented monoclinic symmetry in BPLCs. We believe this paper will stimulate new studies on manipulating the crystal symmetry and structure with other forms of stimuli, such as optical and magnetic fields.

2. The formation of different crystal symmetries in BPLCs was attributed to lattice deformation. The authors are encouraged to perform related simulations to elucidate the origin of this lattice deformation under the field effect.

   Author:

   Simulations of BPLC crystalline lattice transformation under the action of an applied electric fields subject to various boundary conditions and involving a long-timescale assembly of a large number of molecules (~10^7 or more) are non-trivial massive undertakings that nevertheless have been performed by various groups (*for examples, refs. 49, 50, 52, 53 in the main text*; see the next page for information).

   These studies on the *conventional electrostriction* provide valuable groundwork for understanding

and describing the underlying mechanisms by *reverse electrostriction*. [See detailed explanations and discussions given on last 2 paragraphs of page 2, the paragraph under Fig. 2 on page 4, the 5th and 6th paragraphs on page 5, the last paragraph on page 7, and the references quoted therein].

The mechanisms underlying the *conventional electrostriction*—lattice deformation under the action of an increasing applied electric field in the two principal blue phases—are quite well understood following simulations presented in these references (*ref. 49, 50, 52, 53*) and experimental studies (*refs. 46, 47, 48*). In short, in the case of BPII, the cubic crystal will deform under increasing electric field to orthorhombic and tetragonal symmetry but revert to the cubic symmetry when the applied field is removed. On the other hand, in BPI, the deformed crystal will relax to an intermediate metastable state when the applied field is turned off. In the limit of very high applied field, the double twist director axis arrangement in both BPI and BPII is completely unwound and all director axes are aligned parallel to the applied field (transitioned into the homeotropic *nematic* phase).

However, the *reverse electrostriction* process and outcomes (the main theme of this work) have never been predicted by any numerical simulations and theoretical studies. Our experimental study of reverse electrostriction investigated the crystal symmetries that emerge when the applied field is reduced from the very high level (at which the system is in the homeotropic nematic phase) to intermediate field strengths. We discovered that near the BPI–BPII phase transition point, large areal size field-free BPLC monocrystalline crystal symmetries, including the never-seen-before monoclinic symmetry, can be obtained. Modeling of such field-driven processes involve simultaneous interactions of a vast number of molecules over extended timescales (10s to 100s of seconds), posing significant computational challenges in terms of both processing power and simulation time, is clearly outside the scope of the present study, and outside the expertise of this author group. Nonetheless, the findings/discoveries reported in this paper may motivate other more capable groups to perform such theoretical simulations/modellings.

Added references:

46 Heppke, G., Jérôme, B., Kitzerow, H.-S. & Pieranski, P. Electrostriction of the cholesteric blue phases BPI and BPII in mixtures with positive dielectric anisotropy. *J. Phys. France* **50**, 2991-2998 (1989).

47 Guo, D.-Y. *et al.* Reconfiguration of three-dimensional liquid-crystalline photonic crystals by electrostriction. *Nature Materials* **19**, 94-101, doi:10.1038/s41563-019-0512-3 (2020).

48 Zhang, Y. *et al.* Three-dimensional lattice deformation of blue phase liquid crystals under electrostriction. *Soft Matter* **18**, 3328-3334, doi:10.1039/D2SM00244B (2022).

49 Fukuda, J.-i. & Žumer, S. Field-induced dynamics and structures in a cholesteric-blue-phase cell. *Physical Review E* **87**, 042506, doi:10.1103/PhysRevE.87.042506 (2013).

50 Fukuda, J.-i. Simulation of a cholesteric blue phase cell with large but finite thickness. *Frontiers in Soft Matter* **2**, doi:10.3389/frsfm.2022.1011618 (2022).

52 Alexander, G. P. & Yeomans, J. M. Numerical results for the blue phases. *Liquid Crystals* **36**, 1215-1227, doi:10.1080/02678290903057390 (2009).

53 Tiribocchi, A., Gonnella, G., Marenduzzo, D. & Orlandini, E. Switching dynamics in cholesteric blue phases. *Soft Matter* **7**, 3295-3306, doi:10.1039/C0SM00979B (2011).

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The revised manuscript addresses all the comments of the two reviewers including me. Introduction is now more easily accessible and readable to broader audience, and the analysis of Kossel diagrams has been more carefully carried out. I agree with the authors' response that large-scale simulation of BP systems to investigate electrostriction is not at all a trivial task even for specialists.

Still I give several comments on the presentation. After these comments are addressed, I recommend the publication of this work in Nature Communications.

* The DOI's of Refs. 7 and 8 look strange. Again the reference list should be carefully checked.

* The caption of Fig. S4 still contains "L1 norm" that has been eliminated in the main text of Supplementary Note 2.

* [Supplementary Note 2] The three "2.5"'s in eq. (2) and the following sentences should be replaced by "(5/2)".

* [The paragraph before eq. (3) in Supplementary Note 2]

Should "Fig. 3e" be "Fig. S3e"?

"Q1-Q3" might be understood as "Q1 minus Q3".

Reviewer #2 (Remarks to the Author):

The authors have effectively addressed the concerns raised during the review process. I recommend this paper for publication.

Reviewer #1:

The revised manuscript addresses all the comments of the two reviewers including me. Introduction is now more easily accessible and readable to broader audience, and the analysis of Kossel diagrams has been more carefully carried out. I agree with the authors' response that large-scale simulation of BP systems to investigate electrostriction is not at all a trivial task even for specialists.

Still I give several comments on the presentation. After these comments are addressed, I recommend the publication of this work in Nature Communications.

***Author**:* We thank the reviewer for their thorough review and positive feedback of the revised manuscript. We have carefully addressed the additional comments as follows.

* The DOI's of Refs. 7 and 8 look strange. Again the reference list should be carefully checked.

***Author**:* We have checked the reference list. The DOIs of refs. 7 and 8 are correct.

* The caption of Fig. S4 still contains "L1 norm" that has been eliminated in the main text of Supplementary Note 2.

***Author**:* We have removed the term “L1 norm” from the caption of Fig. S4.

* [Supplementary Note 2] The three "2.5"'s in eq. (2) and the following sentences should be replaced by "(5/2)".

***Author**:* We have changed “2.5” to “5/2”.

* [The paragraph before eq. (3) in Supplementary Note 2]

Should "Fig. 3e" be "Fig. S3e"? ***Author**:* We have corrected it.

"Q1-Q3" might be understood as "Q1 minus Q3". ***Author**:* We have changed “Q_1–Q_3” to “Q_1, Q_2, and Q_3”.

Reviewer #2

The authors have effectively addressed the concerns raised during the review process. I recommend this paper for publication.

***Author**:* We appreciate the reviewer’s positive feedback and support of our work.