

Trans-scale crystal dynamics for controlling kinetic responses in organic molecular systems

Corresponding Author: Professor Shotaro Hayashi

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript presents a compelling interdisciplinary study on trans-scale crystal dynamics in anthracene derivatives, demonstrating innovative control of solid-state kinetics through chemical design and physical parameters (light direction, temperature). The work provides valuable mechanistic insights into photoinduced lattice strain and anisotropic responses. While scientifically sound and suitable for publication, minor revisions are required to enhance clarity, rigor, and presentation consistency.

1. In the manuscript, the crystal dynamics in photoreaction processes of crystal 1 was comprehensively studied. However, crystal 2-5 as control samples were rarely mentioned. The authors should add some discussion to explain the meanings of each crystal reported in the article.
2. The severe crystal collapse observed under UV light compared to visible light/LED is attributed to the light wavelength. However, UV light sources often have significantly higher photon energies and potentially higher intensities (power densities) than the visible light sources used (white LED, blue laser, sunlight). The manuscript does not report the incident light intensities/power densities for the different sources used in these comparative experiments. The authors should reconsider this issue.
3. In the temperature dependence of the photoreaction, the authors claimed that : "each temperature point represents the average response time of up to three crystals". Such sample size is not enough for statistical experiment, which is recommended to be increased to 10 or more.
4. Spelling mistake: "Date ware" (Fig.4 caption) → "Data were"
5. please confirm the format of the references.
6. Some literature (Research 2024, 7, 0411; Adv. Sci. 2025, 12, e09088) should be added to reflect the research breadth of the work.

Reviewer #2

(Remarks to the Author)

The manuscript presents an interesting study on anthracene-based crystals that show stimuli-responsive behavior through light-induced dimerization. Although this is a well-known photochemical reaction and have been previously used as a solid platform for exploring dynamic structural changes in the solid state, in this manuscript the authors introduce a dual control mechanism—using both heat and light—to modulate the crystal's response, allowing the visualization of intermediate states, which is a notable achievement.

However, despite these strengths, the manuscript has several issues that make it unsuitable for publication in a high-impact journal in its current form:

Comments

- 1) The abstract lacks specificity and fails to clearly state the focus on anthracene derivatives or highlight the key findings—namely, dual control and intermediate state visualization. Instead, it relies on vague references to biological systems, which are not directly relevant and overgeneralize the study's implications. It should be rewritten accordingly.
- 2) The rationale behind the selection and design of the anthracene derivatives is not explained. Although several

anthracene derivatives are synthesized and characterized, in the manuscript their specific roles are unclear. A schematic framework is needed to clarify how these derivatives contribute to the study's objectives.

3) As the author notes, identifying the relative orientation between light propagation and the molecular transition dipole moment as a control parameter in the photodynamic process is potentially significant. However, this concept is underdeveloped in the manuscript. To substantiate its importance, the authors should provide more robust theoretical/experimental evidence than simple statistics.

4) Several figures in the Supporting Information are either incorrectly referenced or not well integrated into the main text. This weakens the clarity and coherence of the experimental narrative. Proper cross-referencing and clearer integration are needed to improve consistency and readability throughout the manuscript. For example, in page 3 the authors mention: "Raman spectroscopy reveals changes in intra- and intermolecular vibrational modes (Supplementary Fig. 18), indicating modifications to both the chemical structure and crystal lattice (Supplementary Figs. 19–21 and Supplementary Table 8)". On the one hand, Supplementary Fig. 18 presents only two Raman spectra without any accompanying discussion of the observed differences, which limits its usefulness in supporting the claims made in the main text. On the other hand, Supplementary Figs. 19–20 primarily focus on the solid-state retro reaction, including thermal analysis (DSC and TGA), the experimental setup, and NMR characterization of the final product—none of which directly support the discussion on changes in chemical structure or crystal lattice. This misalignment highlights the need for more accurate and purposeful cross-referencing of the supplementary materials. Considering the substantial volume of Supporting Information provided, and to improve overall readability and coherence, the manuscript should be carefully revised to ensure that each supplementary figure and table is clearly and correctly cited in context, and that the integration of this material meaningfully supports the corresponding sections of the main text.

5) The authors study the transformation under different light sources; however, these reactions appear to proceed more rapidly and, in some cases, lead to the rapid breakdown of the crystals. It remains unclear whether the final phases obtained under these alternative light sources are the same as those formed under white LED light. The authors should clarify whether the photoproducts are structurally and chemically identical across different irradiation conditions, and, if not, provide a discussion on the observed differences and their implications.

In summary: While the results are of scientific interest a more focused presentation and clearer methodological framing are needed to meet the standards of a high-impact journal.

Reviewer #3

(Remarks to the Author)

In the manuscript titled "Trans-scale crystal dynamics for controlling kinetic responses in organic molecular systems", Hino et al. report temperature-dependent, photoinduced crystal dynamics in anthracene derivative crystals.

A key highlight of the study is the controlled modulation of crystal behavior through the relative orientation between the light propagation direction and the molecular transition dipole moment.

The work is intriguing and of have relevance to the field of dynamic molecular crystals. However, I recommend major revision before the manuscript can be considered for publication. The following points should be addressed to improve clarity, completeness, and presentation:

1. The abstract is too general and lacks a concise summary of the actual experimental work carried out. Instead of briefly stating the methodology or system studied, the abstract reads more like a conclusion. This diminishes clarity for readers attempting to understand the work from the outset.

2. The manuscript lacks a systematic description. For instance, it is not clearly stated how many anthracene derivatives were synthesized and studied, or the rationale behind their selection. The use of abbreviations should also be defined clearly at the beginning. From Figure 1 and the Supplementary Information (SI), it appears that five derivatives were investigated, but this should be clearly presented in the main text.

3. There is excessive referencing to the SI, which makes reading cumbersome. For example:

The sentence: "Depending on the choice of substituents, 1,8-diarylanthracene adopts either an ON (face-to-face) or OFF (edge-to-face) stacking structure (Supplementary Tables 1–6)" directs the reader across six different supplementary tables. A consolidated explanation in the main text summarizing this trend would help.

Similarly, the statement: "The minimum face-to-face π -stacked structure required for the ON reaction has been identified based on data from the crystal structure database, previous literature, and our own study using molecular electrostatic potential maps (Fig. 1a and Supplementary Figs. 1–13)" references 13 supplementary figures. Such heavy dependence on SI should be minimized by integrating key insights and summaries into the main text.

4. The sentence: "The discovery of crystal dynamics driven by visible light overcomes previous limitations related to light wavelength, enabling a more hierarchical and in-depth understanding of the dynamic process." is unclear and should be elaborated. What limitations were previously imposed by light wavelength, and how does visible light resolve them?

5. The manuscript would benefit from a more detailed explanation of what exactly constitutes the ON and OFF states in terms of molecular stacking and crystal structure. These structural transitions are central to the work but are only briefly

mentioned.

6. It is stated that UV light irradiation caused dramatic physical responses such as jumping, fragmentation, explosion, splintering, cracking, and splitting. But no detailed mechanism or conditions under which these movements occur is provided. Moreover, the photographic evidence (e.g., in the SI) is insufficient to clearly distinguish these effects.

7. The statement that “the crystal may exhibit varying phase transition ratios depending on the light wavelength” is not substantiated with any mechanistic explanation or data discussion. The authors should clarify the origin of this behavior.

8. Crucial details such as the intensity (power density) of the light sources used (UV, white LED, laser) are not provided. These are essential for reproducibility and understanding the kinetics.

9. Among three crystals irradiated, only one shows cracking. The authors should discuss why the other two did not respond similarly. Could crystal size or morphology be influencing the mechanical response? A brief analysis or hypothesis on size-dependence would add value.

10. The manuscript states that the transition dipole moment is oriented along the crystallographic b-axis. However, a more detailed explanation is needed on how μ is calculated or estimated from the crystal structure.

11. The manuscript focuses on the direction of the transition dipole moment but does not discuss how its magnitude might influence the photoinduced response. A brief discussion of whether higher μ would correlate with stronger or faster response would be useful, especially in the context of designing molecules for better dynamic behavior.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have carefully addressed all my issues and I suggest the acceptance of this manuscript in Nature Communications.

Reviewer #2

(Remarks to the Author)

The authors have satisfactorily addressed my concerns. I recommend acceptance of the manuscript in its current form.

Reviewer #3

(Remarks to the Author)

The manuscript titled “Trans-scale crystal dynamics for controlling kinetic responses in organic molecular systems” by Hayashi et al. has been thoroughly revised. The authors have addressed all the comments raised by the reviewers.

However, my comment regarding the excessive dependence on the Supporting Information appears to have been misunderstood. Earlier, the authors had cited numerous SI figures and tables within a single explanation, whereas in the revised version they have removed these citations altogether. My suggestion was not to eliminate references to the Supporting Information, but rather to combine a maximum of two to three related figures or tables in one explanation so that the reader does not lose track while going through the SI. The authors may wish to revisit this point.

With this minor revision, I would recommend acceptance of the manuscript for publication in Nature Communications.

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Point-by-Point Response to the Reviewers

To all Reviewers

We sincerely thank the reviewers for their insightful comments and constructive feedback on our study. Following their valuable suggestions, we have carefully revised the manuscript to enhance its clarity and rigor. We hope that the reviewers will find our responses and revisions satisfactory.

• Revised parts were highlighted by Yellow.

To the Reviewer: 1

This manuscript presents a compelling interdisciplinary study on trans-scale crystal dynamics in anthracene derivatives, demonstrating innovative control of solid-state kinetics through chemical design and physical parameters (light direction, temperature). The work provides valuable mechanistic insights into photoinduced lattice strain and anisotropic responses. While scientifically sound and suitable for publication, minor revisions are required to enhance clarity, rigor, and presentation consistency.

==== > Thank you for your understanding and your thoughtful review comments below.

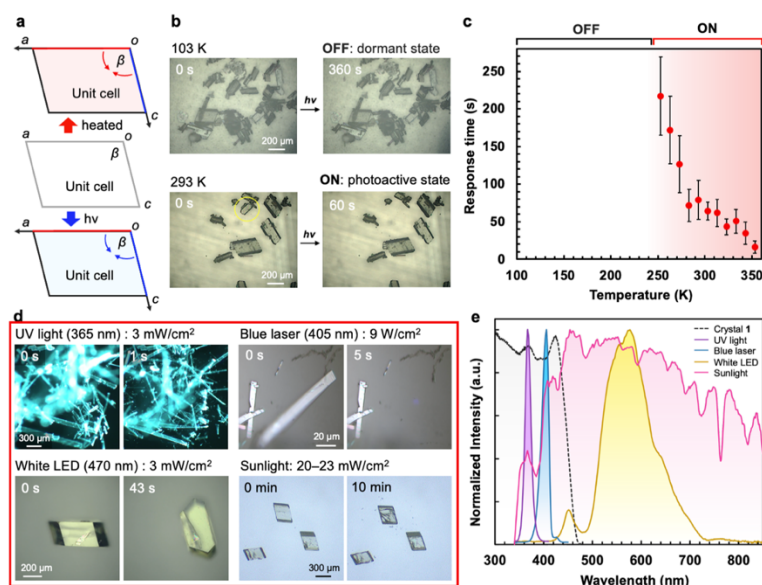
1. In the manuscript, the crystal dynamics in photoreaction processes of crystal 1 was comprehensively studied. However, crystal 2-5 as control samples were rarely mentioned. The authors should add some discussion to explain the meanings of each crystal reported in the article.

==== > We thank the reviewer for their insightful comments. Anthracene derivatives (1–5) reported here were designed and selected to identify the chemical control factors necessary for inducing *face-to-face* structures (Fig. 1). These substituent-induced assembly structures are not merely variations of crystal engineering; rather, they represent a branching point in crystal functions that govern the active (ON) and inactive (OFF) states of intermolecular photoreactions. Phenyl substitution introduces steric effects that favor the formation of *face-to-face* and *edge-to-face* arrangements between anthracene units. In contrast, the electronic effects of aryl substituents systematically shift the competitive balance of molecular assemblies, with increased electron-accepting properties promoting the selective formation of ON structures. Conversely, electron-donating substituents on the aryl groups contribute to the formation of OFF structures, underscoring the effectiveness of this chemical strategy for material design and functional control. Furthermore, as shown in Supplementary Fig. S15, we investigated the ground-state electrostatic potentials of compounds 1–5. The results indicate that electron-accepting substituents generate a negative relative charge density on the hydrogen atoms of the anthracene ring and along the short axis. This suggests that the electrostatic potential of the anthracene core plays a decisive role in guiding effective aggregate formation during molecular assembly. To strengthen the discussion, we have incorporated this evidence, along with comparative analyses and experimental data, into the revised manuscript and Supplementary Information. Please see *Pages 3-4* (Subtitle: **Chemical approaches for crystal dynamics**) in highlighted manuscript and Fig. 1.

2. The severe crystal collapse observed under UV light compared to visible light/LED is attributed to the light wavelength. However, UV light sources often have significantly higher photon energies and potentially higher

intensities (power densities) than the visible light sources used (white LED, blue laser, sunlight). The manuscript does not report the incident light intensities/power densities for the different sources used in these comparative experiments. The authors should reconsider this issue.

====> The irradiation intensity/power density of each light source was specified, and the calculation method is described in the Supplementary Information (Supplementary Fig. S18). As shown in Fig. 3d, the following light sources were used: UV light (365 nm, 3 mW/cm²), blue laser (405 nm, 8 W/cm²), white LED (470 nm, 3 mW/cm²), and sunlight (20–23 mW/cm²). Despite their comparable intensities/power densities, significant crystal collapse was observed under UV irradiation compared with visible light (white LED). This behavior reflects differences in photon absorption efficiency and the resulting strain gradients within the crystal. In addition to the strong absorption of UV light by the reactants, the photoproducts also absorb within the same wavelength range. This overlap induces a steep strain gradient between the crystal surface and interior, leading to rapid crystal dynamics. By contrast, visible light (white LED) is more weakly absorbed by the reactants, and the strain arising from photoproducts accumulates gradually, resulting in a slower response of the crystal dynamics. To strengthen the discussion, we have incorporated this rationale, along with supporting experimental data, into the revised manuscript and Supplementary Information. Please see following revised figure.

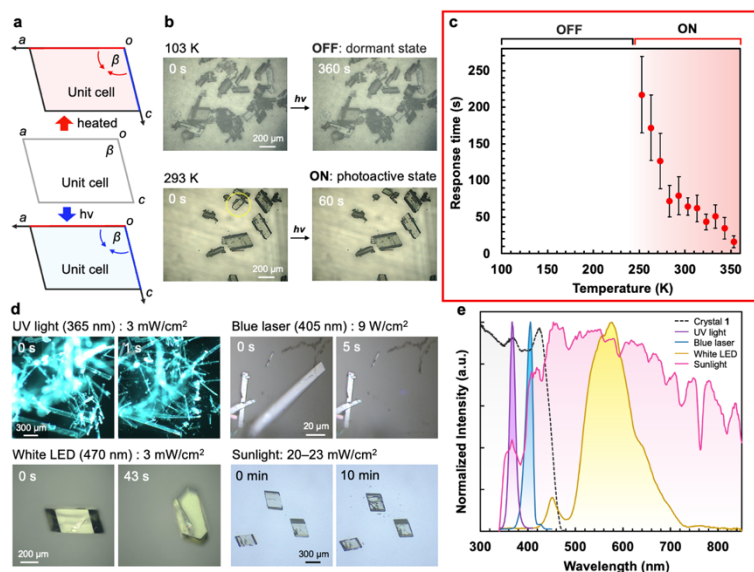


Revised figure (Fig.3)

3. In the temperature dependence of the photoreaction, the authors claimed that : “each temperature point represents the average response time of up to three crystals“. Such sample size is not enough for statistical experiment, which is recommended to be increased to 10 or more.

====> We investigated the average response time and its standard deviation (SD) as the number of samples increased at each temperature point (Fig. 3c). These experiments were conducted over a 5-minute observation period, during which a response of up to eight crystals was observed at the lowest temperature of 253 K (Supplementary Figs. S31-35). Accordingly, when the parameter for each temperature point was set to “maximum 8 crystals,” the average response time became progressively shorter with increasing temperature, consistent with the previous experiments (Fig. 3c). The revised Supplementary Material has been updated to

present the response of “maximum 8 crystals” in greater detail, and the original figure has been replaced with the revised version. Please see following revised figure.



Revised figure (Fig.3)

4. Spelling mistake: “Date ware” (Fig.4 caption) → “Data were”

==== > Based on your feedback, we have fixed the issue.

5. please confirm the format of the references.

==== > We have addressed the formatting issues in the references section, specifically including "all authors with 5 or fewer names in the reference list" and correcting the wording of "book citations."

6. Some literature (Research 2024, 7, 0411; Adv. Sci. 2025, 12, e09088) should be added to reflect the research breadth of the work.

==== > Thank you for the reference. We have incorporated the proposed reference on photoreactions in single crystals (Adv. Sci. 2025, 12, e09088) into the manuscript. This reference provides valuable background information and helps broaden the appeal of this work to readers interested in crystal dynamics.

To the Reviewer: 2

The manuscript presents an interesting study on anthracene-based crystals that show stimuli-responsive behavior through light-induced dimerization. Although this is a well-known photochemical reaction and have been previously used as a solid platform for exploring dynamic structural changes in the solid state, in this manuscript the authors introduce a dual control mechanism—using both heat and light—to modulate the crystal’s response, allowing the visualization of intermediate states, which is a notable achievement. However, despite these strengths, the manuscript has several issues that make it unsuitable for publication in a high-impact journal in its current form:

==== > Thanks for your understanding of our research contents and your constructive comments below.

1) The abstract lacks specificity and fails to clearly state the focus on anthracene derivatives or highlight the key findings—namely, dual control and intermediate state visualization. Instead, it relies on vague references to biological systems, which are not directly relevant and overgeneralize the study's implications. It should be rewritten accordingly.

==== > We would like to express our sincere gratitude to the reviewers for their constructive suggestions. Following their suggestions, we have revised the abstract to focus on anthracene derivatives and clarify the main achievements, such as "dual control and visualization of intermediate states."

Revised Abstract:

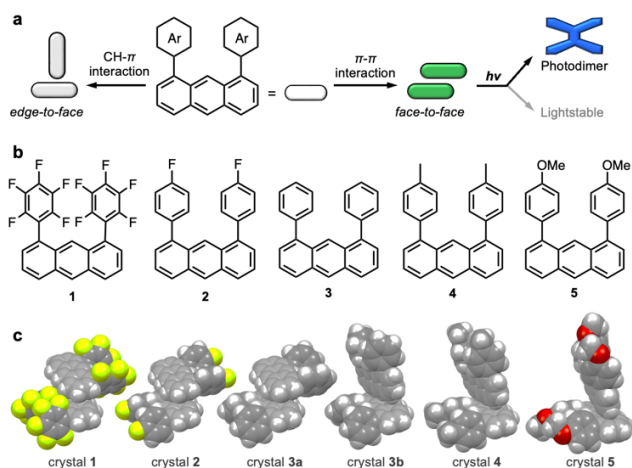
The origin and control of material dynamics are crucial for understanding functional systems, yet direct visualization of rapid changes in single crystals has remained challenging. We report an anthracene-based molecular crystal platform that enables dual physical control of solid-state [4+4] photocycloaddition through temperature and light. Chemically designed 1,8-bis(pentafluorophenyl)anthracene crystals formed photoactive face-to-face π -stacks, allowing visible-light-induced reactions. The crystals exhibited thermally switchable on/off states, governed by lattice strain accumulation. Weak LED light irradiation enabled direct observation of intermediate states in [4+4] photocycloaddition process, revealing a correlation between lattice strain and photoconversion rate. Moreover, reaction kinetics depended on light propagation direction and molecular transition dipole orientation, introducing a new anisotropic control parameter. This trans-scale approach, integrating molecular packing design, photo-thermal control, and directional anisotropy, offers a general strategy for tunable and observable crystal dynamics.

132 words (<150 words)

2) The rationale behind the selection and design of the anthracene derivatives is not explained. Although several anthracene derivatives are synthesized and characterized, in the manuscript their specific roles are unclear. A schematic framework is needed to clarify how these derivatives contribute to the study's objectives.

==== > We thank the reviewer for their insightful comments. Anthracene derivatives (1–5) were designed and selected to identify the chemical control factors necessary for inducing *face-to-face* structures (Fig. 1).

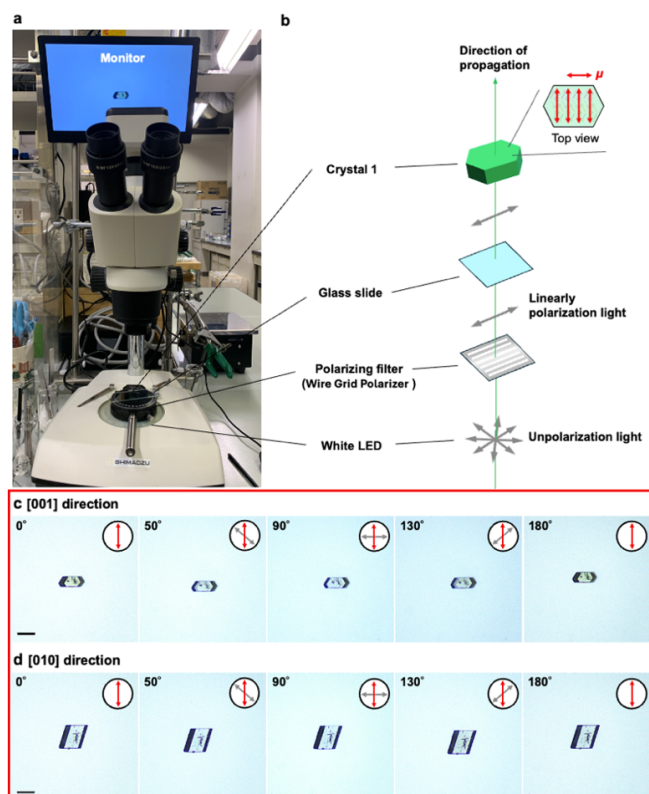
Photoinduced structural transitions in anthracene crystals proceed via photodimerization of the *face-to-face* packing motif. However, achieving photodimerization in single crystals requires precise control of molecular orientation and alignment to bring reactive sites into proximity. In this study, we successfully induced *face-to-face* structures by introducing electron-withdrawing groups along the short axis of anthracene. We believe these findings provide valuable molecular design guidelines for crystal dynamics and will contribute to the further development of this research field. To strengthen the discussion, we have incorporated this schematic diagram into the revised manuscript. Please see *Pages 3-4* (Subtitle: **Chemical approaches for crystal dynamics**) in highlighted manuscript. Please see following new figure.



Added figure (Fig. 1)

3) As the author notes, identifying the relative orientation between light propagation and the molecular transition dipole moment as a control parameter in the photodynamic process is potentially significant. However, this concept is underdeveloped in the manuscript. To substantiate its importance, the authors should provide more robust theoretical/experimental evidence than simple statistics.

==== > We appreciate the opportunity to clarify the correlation between the light transmission direction (polarization) and the molecular transition dipole moment (μ) in the crystal. Organic crystals adopt anisotropic molecular arrangements, allowing μ to be oriented in specific directions depending on the aggregation state. This orientation of μ leads to anisotropic optical absorption, since the efficiency of interaction between the electric field and μ depends on their relative orientation (parallel vs. perpendicular) to the polarization of incident light (Angew. Chem. 2020, 132, 4486–4493; Chem. Eur. J. 2023, 29, e202302351). This provides further evidence for the anisotropy observed in the response time and frequency of the crystal dynamics. Quantum chemical calculations (TD-DFT calculation) indicate that μ in bimolecular aggregates is aligned along the anthracene minor axis (Supplementary Fig. 46). Consistently, single-crystal X-ray diffraction analysis and indexing of crystal morphology (Supplementary Fig. 50) revealed that μ is oriented along the crystallographic b-axis (Supplementary Fig. 51). Experimental support for this assignment was obtained by examining the polarization dependence of incident white LED light for different crystal plane orientations ([001] and [010]) (Supplementary Fig. 52). Specifically, white light irradiation along the [010] direction exhibited no color regardless of polarization, suggesting isotropic absorption in this plane. By contrast, the irradiation along the [001] direction showed color at polarization angles of 0° and 180°, but not between 50° and 130°. This qualitatively demonstrates anisotropic absorption along [001] due to the in-plane orientation of μ on 001 facet, with polarization directions consistent with the theoretically predicted orientation of μ . We hope this additional information will help clarify that the relative configuration of polarization and μ is a key controlling parameter for crystal dynamics. To strengthen the discussion, we have incorporated this comparative analysis, experimental data, and references into the revised manuscript and Supplementary Information. Please see Pages 7-8 (188-, 195-) in highlighted manuscript. Please see following new figure.



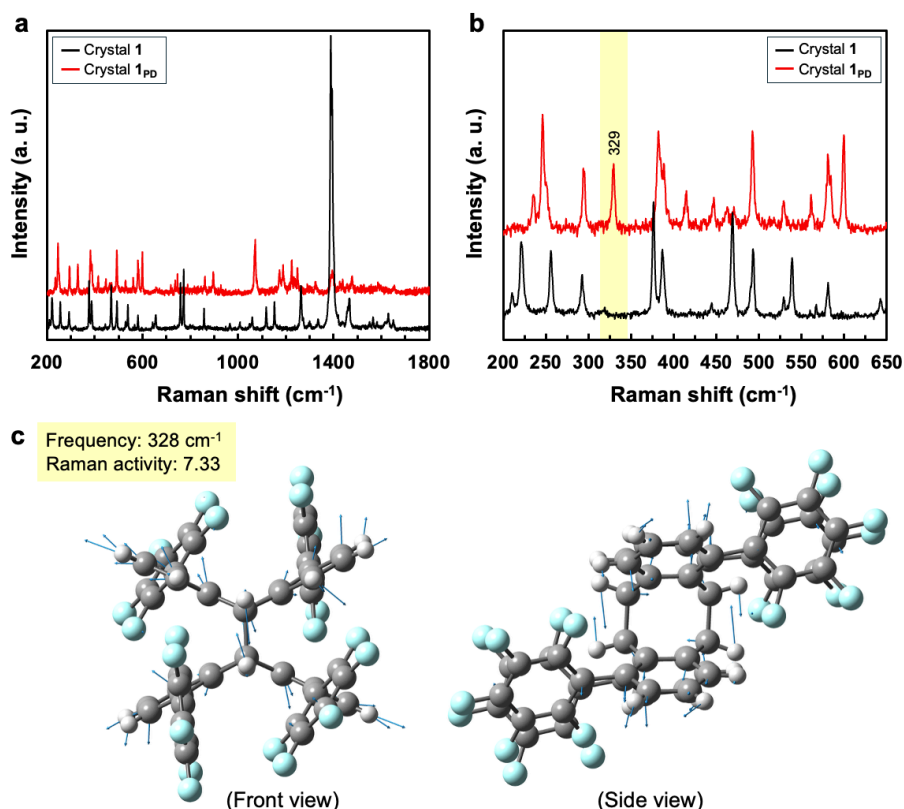
Revised figure (Fig. S2 in SI)

4) Several figures in the Supporting Information are either incorrectly referenced or not well integrated into the main text. This weakens the clarity and coherence of the experimental narrative. Proper cross-referencing and clearer integration are needed to improve consistency and readability throughout the manuscript.

====> Thank you very much for your constructive comments. We regret unable to cite properly due to the large amount of additional information. We have checked and revised everything to improve the consistency and readability of the entire manuscript. We have also minimized excessive citations.

For example, in page 3 the authors mention: “Raman spectroscopy reveals changes in intra- and intermolecular vibrational modes (Supplementary Fig. 18), indicating modifications to both the chemical structure and crystal lattice (Supplementary Figs. 19–21 and Supplementary Table 8)”. On the one hand, Supplementary Fig. 18 presents only two Raman spectra without any accompanying discussion of the observed differences, which limits its usefulness in supporting the claims made in the main text. On the other hand, Supplementary Figs. 19–20 primarily focus on the solid-state retro reaction, including thermal analysis (DSC and TGA), the experimental setup, and NMR characterization of the final product—none of which directly support the discussion on changes in chemical structure or crystal lattice. This misalignment highlights the need for more accurate and purposeful cross-referencing of the supplementary materials. Considering the substantial volume of Supporting Information provided, and to improve overall readability and coherence, the manuscript should be carefully revised to ensure that each supplementary figure and table is clearly and correctly cited in context, and that the integration of this material meaningfully supports the corresponding sections of the main text.

==== > We thank the reviewer for their careful attention to detail. In response to their comments, we have corrected the issues regarding references and the integration of Supplementary Information into the text. The changes in intramolecular and intermolecular vibrational modes observed by Raman spectroscopy in this study provide spectroscopic evidence that photoirradiation induces chemical structural transformations in the crystal, leading to subsequent structural transitions. A previous study reported that Raman spectroscopy measurements during solid-state photoreactions of 9-methylanthracene revealed the appearance of a new intramolecular band near 330 cm^{-1} , attributed to photodimer formation (J. Raman Spectrosc. 2017, 48, 271–277). To further clarify this point, we performed quantum chemical calculations to analyze the vibrational modes of the photoproduct **1_{PD}**. The Supplementary Information (Supplementary Fig. 21) has been updated accordingly. The results show a Raman-active intramolecular vibrational mode at 329 cm^{-1} , arising from the newly formed C–C single bond upon photodimerization. This provides theoretical support for the two experimentally observed Raman spectra. Furthermore, we demonstrate that the reverse reaction from crystal **1_{PD}** back to crystal **1** is possible. This process is likely based on flash vacuum pyrolysis, in which specific molecular bonds are cleaved under instantaneous high-temperature treatment (Chem. Rev. 2006, 106, 12, 4868–4884). These results suggest that crystal dynamics can, in principle, be driven reversibly through the combined use of light and heat. To improve the consistency and readability, we incorporated these experimental data into the revised manuscript (*Pages 4-5 (100-)*) and Supplementary Information.

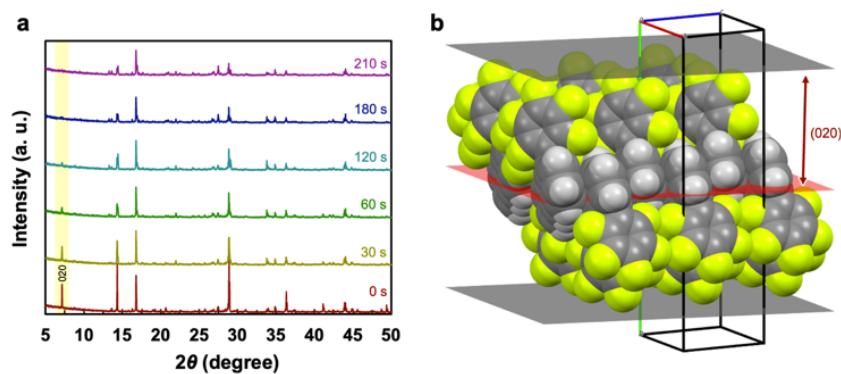


Revised figure (Fig. 21 in SI)

5) The authors study the transformation under different light sources; however, these reactions appear to proceed more rapidly and, in some cases, lead to the rapid breakdown of the crystals. It remains unclear whether the final phases obtained under these alternative light sources are the same as those formed under

white LED light. The authors should clarify whether the photoproducts are structurally and chemically identical across different irradiation conditions, and, if not, provide a discussion on the observed differences and their implications.

====> The final product obtained under white LED irradiation was identified as the photodimer **1_{PD}**. However, it remained unclear whether the products generated under different light sources were identical to that obtained under white LED light. To address this issue, we carried out X-ray diffraction measurements under UV irradiation. Powder X-ray diffraction at room temperature revealed a gradual disappearance of the {020} reflection of crystalline **1** with increasing irradiation time (Supplementary Fig. 40), suggesting a structural transition from crystalline **1** to crystalline **1_{PD}** under UV light. To further clarify this point, we performed single-crystal X-ray structural analysis. The crystals obtained under UV irradiation (CCDC reference number: 2483421) were identified as **1_{PD}** and confirmed to be structurally and chemically identical to the final product obtained under white LED light. We believe these additional experiments enhance the clarity and accuracy of our identification of the final product under different light sources. Please see *Page 6* (147-) in highlighted manuscript.



Added figure (Fig. 40 in SI)

In summary: While the results are of scientific interest a more focused presentation and clearer methodological framing are needed to meet the standards of a high-impact journal.

====> We would like to express my sincere gratitude for the evaluation and comments on this research. Based on the valuable advice, we have carefully revised the paper to provide a more focused description of the research results and organize the methodology.

To the Reviewer: 3

In the manuscript titled “Trans-scale crystal dynamics for controlling kinetic responses in organic molecular systems”, Hino et al. report temperature-dependent, photoinduced crystal dynamics in anthracene derivative crystals.

A key highlight of the study is the controlled modulation of crystal behavior through the relative orientation between the light propagation direction and the molecular transition dipole moment.

The work is intriguing and of have relevance to the field of dynamic molecular crystals. However, I recommend major revision before the manuscript can be considered for publication. The following points

should be addressed to improve clarity, completeness, and presentation:

==== > Thanks for your understanding of the content and your constructive comments below.

1. The abstract is too general and lacks a concise summary of the actual experimental work carried out. Instead of briefly stating the methodology or system studied, the abstract reads more like a conclusion. This diminishes clarity for readers attempting to understand the work from the outset.

==== > Considering that the abstract was too general, we have specifically included the experimental subjects and main results (such as dual control of crystal dynamics by heat and light, and direct observation of crystallographic intermediate states) in the abstract. We hope that this revision will address the reviewer's concerns and more clearly convey the outline and novelty of our research.

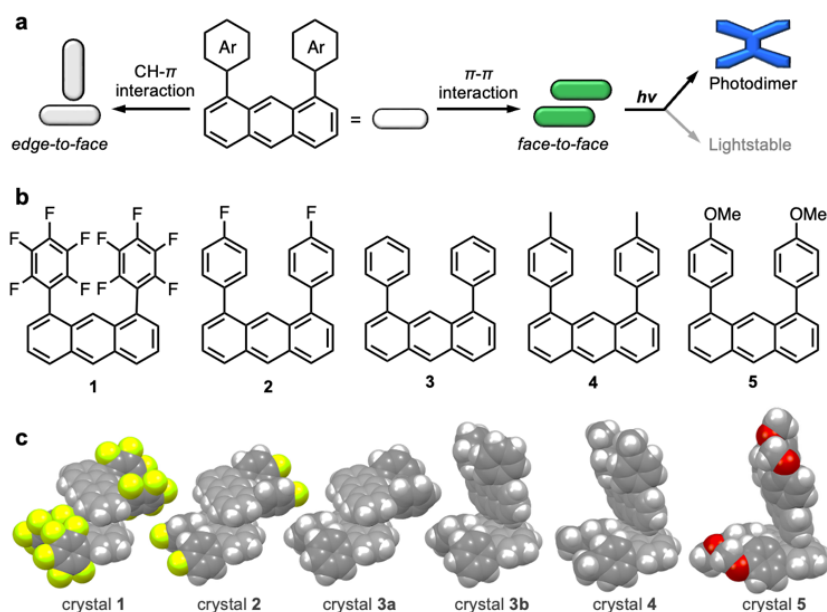
Revised Abstract:

The origin and control of material dynamics are crucial for understanding functional systems, yet direct visualization of rapid changes in single crystals has remained challenging. We report an anthracene-based molecular crystal platform that enables dual physical control of solid-state [4+4] photocycloaddition through temperature and light. Chemically designed 1,8-bis(pentafluorophenyl)anthracene crystals formed photoactive face-to-face π -stacks, allowing visible-light-induced reactions. The crystals exhibited thermally switchable on/off states, governed by lattice strain accumulation. Weak LED light irradiation enabled direct observation of intermediate states in [4+4] photocycloaddition process, revealing a correlation between lattice strain and photoconversion rate. Moreover, reaction kinetics depended on light propagation direction and molecular transition dipole orientation, introducing a new anisotropic control parameter. This trans-scale approach, integrating molecular packing design, photo-thermal control, and directional anisotropy, offers a general strategy for tunable and observable crystal dynamics.

132 words (<150 words)

2. The manuscript lacks a systematic description. For instance, it is not clearly stated how many anthracene derivatives were synthesized and studied, or the rationale behind their selection. The use of abbreviations should also be defined clearly at the beginning. From Figure 1 and the Supplementary Information, it appears that five derivatives were investigated, but this should be clearly presented in the main text.

==== > A systematic description of the anthracene derivatives and definitions of abbreviations have been added to the text. It should first be emphasized that the activity or inactivity of intermolecular photoreactions in crystals is determined by the association mode and crystal structure of the compound. To clarify the underlying chemical factors, five anthracene derivatives were designed and selected to identify structural features that promote face-to-face arrangements. This study demonstrates that the introduction of electron-withdrawing groups provides an effective chemical strategy for inducing face-to-face structures, which are a prerequisite for photodimerization. Please see *Pages 3-4* (Subtitle: Chemical approaches for crystal dynamics) of highlighted manuscript and following new figure.



Added figure (Fig. 1)

3. There is excessive referencing to the SI, which makes reading cumbersome. For example:

The sentence: “Depending on the choice of substituents, 1,8-diarylanthracene adopts either an ON (face-to-face) or OFF (edge-to-face) stacking structure (Supplementary Tables 1–6)” directs the reader across six different supplementary tables. A consolidated explanation in the main text summarizing this trend would help.

====> To avoid excessive SI dependence, we have made the relationship and tendency between the substituents and bimolecular structures correspond to Fig. 1c. Please see *Pages 4 (76-)* in highlighted manuscript.

Similarly, the statement: “The minimum face-to-face π -stacked structure required for the ON reaction has been identified based on data from the crystal structure database, previous literature, and our own study using molecular electrostatic potential maps (Fig. 1a and Supplementary Figs. 1–13)” references 13 supplementary figures. Such heavy dependence on SI should be minimized by integrating key insights and summaries into the main text.

====> To focus on the main points, we have narrowed down the citations to those that are particularly relevant.

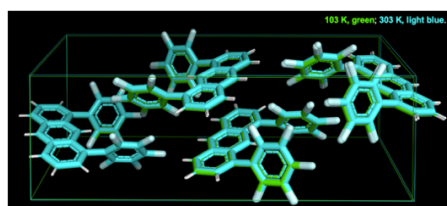
4. The sentence: “The discovery of crystal dynamics driven by visible light overcomes previous limitations related to light wavelength, enabling a more hierarchical and in-depth understanding of the dynamic process.” is unclear and should be elaborated. What limitations were previously imposed by light wavelength, and how does visible light resolve them?

====> Previously, [4+4] photocycloaddition reactions (photodimerization) in solids were largely limited to ultraviolet light (Chem. Soc. Rev., 2023, 52, 3098–3169). This limitation is attributed to the near-UV absorption bands of anthracene derivatives, which exhibit very low absorption efficiency in the visible light range. Moreover, UV light-induced crystal dynamics often lead to rapid crystal collapse, making it difficult to

capture gradual changes in lattice strain. In this study, we overcame the previous wavelength limitation by extending the π -conjugation of anthracene via aryl substitution on the short axis, thereby enhancing visible-light absorption and inducing a photoreactive crystal structure. Crystal **1** undergoes efficient photodimerization under white light (visible light), enabling direct visualization of intermediate states during the structural transition. This approach overcomes the previous UV light-dependence and allows direct observation of lattice strain changes, which is crucial for elucidating the origin of crystal dynamics. We hope that these explanations address the reviewer's concerns and more clearly communicate the significance of our research. Please see *Page 6* (143-) of highlighted manuscript.

5. The manuscript would benefit from a more detailed explanation of what exactly constitutes the ON and OFF states in terms of molecular stacking and crystal structure. These structural transitions are central to the work but are only briefly mentioned.

====> We appreciate the opportunity to clarify the dual control (ON/OFF) of crystal dynamics. First, we note that crystal dynamics is driven by the external release of lattice strain accumulated in the crystal as a result of photoreaction. Both heating and photoreaction were found to decrease the lattice axis angle β (Fig. 3a), indicating that the accumulation of lattice strain due to photoreaction is accelerated by heating. The temperature-dependent lattice strain was characterized by X-ray diffraction measurements. Temperature-variable single-crystal X-ray analysis of crystal **1** between 103 K and 303 K revealed an elongation of the π -stacking distance and an increase in molecular volume with increasing temperature. These molecular stacking displacements induced lattice deformations, resulting in a decrease of the axis angle β . To clarify the temperature dependence of molecular stacking and crystal structure, we compared the crystal structures at 103 K and 303 K. The updated Supplementary Information (Supplementary Fig. 30) clearly visualizes these differences in crystal structures based on molecular stacking displacements. We believe that these additional comparisons enhance the clarity and accuracy of the correlation between the ON/OFF states and the molecular stacking and crystal structures. To further enrich the discussion, we have incorporated this rationale, comparative analysis, and experimental data into the revised manuscript and Supplementary Information.

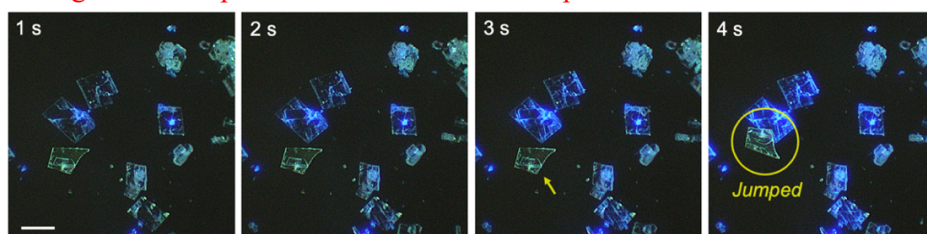


Added figure (Fig. 30 in SI)

6. It is stated that UV light irradiation caused dramatic physical responses such as jumping, fragmentation, explosion, splintering, cracking, and splitting. But no detailed mechanism or conditions under which these movements occur is provided. Moreover, the photographic evidence (e.g., in the SI) is insufficient to clearly distinguish these effects.

====> To avoid confusion, we have added a description of an additional jumping mechanism under UV light irradiation to the Supplementary Information (Supplementary Fig. 37). The diverse responses observed under

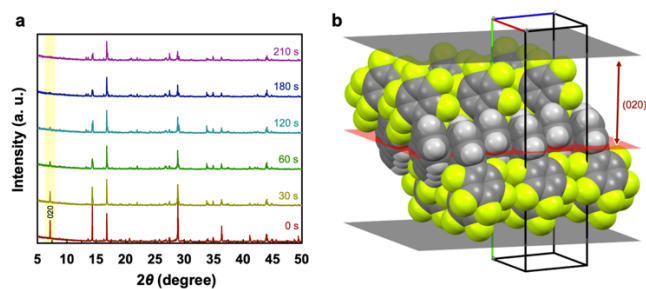
UV light, shown in Fig. 3d and Supplementary Fig. 37, arise from the accumulation of lattice strain due to photodimerization. The different modes of stress release give rise to complex crystal responses. When photodimerization proceeds unevenly within the crystal, the lattice strain becomes biased in one direction, generating a driving force that causes the crystal to jump. When stress is concentrated on a specific crystal plane, localized fracture occurs, forming cracks. Furthermore, when stress simultaneously exceeds the cohesive strength of the crystal lattice in multiple regions, the crystal partially collapses, resulting in local fracture. Finally, if photodimerization occurs rapidly throughout the crystal, causing a large volume change and overwhelming the stress-relaxation capacity, the crystal fractures all at once, leading to explosive scattering of fragments (total fracture). However, the conditions required to independently achieve jumps, fractures, explosions, or crack formation remain unclear. In future work, we plan to investigate the relative orientation of the UV light propagation direction (polarization) and the molecular transition dipole moment, aiming to achieve precise control over these responses.



Added figure (Fig. 37 in SI)

7. The statement that “the crystal may exhibit varying phase transition ratios depending on the light wavelength” is not substantiated with any mechanistic explanation or data discussion. The authors should clarify the origin of this behavior.

====> As you pointed out, the original manuscript lacked sufficient mechanistic explanation and supporting data for the wavelength-dependent phase transition rate. To address this, we have provided additional explanations and supplementary data. Specifically, powder X-ray diffraction measurements under room-temperature UV irradiation showed that the {020} reflection from crystal **1** completely disappeared after approximately 210 seconds, indicating a quantitative transformation to crystal **1_{PD}** (Supplementary Fig. 40). In contrast, under white LED irradiation, the phase transition (conversion) rate remained at approximately 50% over a similar irradiation period. This difference is attributed to the higher absorption coefficient of UV light compared with visible light, confirming that the phase transition rate depends on the light wavelength. However, UV irradiation also induces responses such as fracture, explosion, and cracking, making it impossible to determine the phase transition rate from single-crystal X-ray analysis of the same crystal. We hope that these explanations address the reviewer’s concerns and more clearly convey the mechanism underlying the wavelength-dependent phase transition rate. Please see *Page 6* (147-) in highlighted manuscript.



Added figure (Fig. 40 in SI)

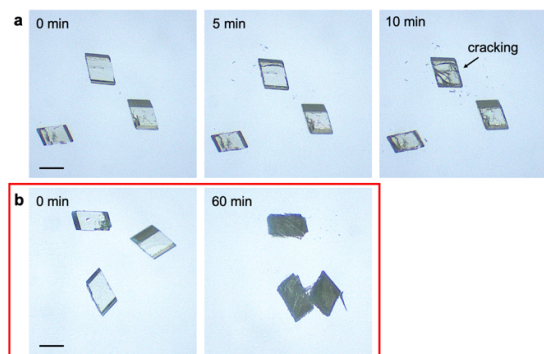
8. Crucial details such as the intensity (power density) of the light sources used (UV, white LED, laser) are not provided. These are essential for reproducibility and understanding the kinetics.

==== > Thank you very much for your valuable comment. Following your suggestion, we have revised Fig. 3d (caption) to clarify:

"Optical microscopy images of crystal **1** under UV light (365 nm, 3 mW/cm²), blue laser (405 nm, 9 W/cm²), white LED (470 nm, 3 mW/cm²), and sunlight (20–23 mW/cm²) at 298 ± 5 K."

9. Among three crystals irradiated, only one shows cracking. The authors should discuss why the other two did not respond similarly. Could crystal size or morphology be influencing the mechanical response? A brief analysis or hypothesis on size-dependence would add value.

==== > Our initial observations showed that only one of three crystals exposed to sunlight for 10 minutes exhibited a crack, while the other two remained intact (Fig. 3d). This difference may have been due to insufficient light exposure time. In a follow-up experiment, after exposing the crystals to sunlight for 1 hour, all crystals exhibited clear collapse (Supplementary Fig. 39b). These results suggest that the response time of crystal dynamics depends on both internal factors (e.g., crystal size and morphology) and external factors (e.g., wavelength and exposure time). Notably, even among three crystals derived from the same crystal structure, only one exhibited a crack after 10 minutes of sunlight exposure. These observations motivated us to perform a statistical analysis of the response time and frequency of crystal dynamics under white LED irradiation. The rationale, comparative analysis, and experimental data are provided in the Supplementary Information.



Added figure (Fig. 39 in SI)

10. The manuscript states that the transition dipole moment is oriented along the crystallographic b-axis. However, a more detailed explanation is needed on how μ is calculated or estimated from the crystal structure.

==== > We apologize for the insufficient description in our previous manuscript. The direction of the transition dipole moment (μ) was estimated based on crystal structure and electronic structure analyses. Specifically, we first performed TD-DFT calculations on the bimolecular aggregate (Unit 1 and Unit 2) of crystal **1** to identify the major electronic transitions corresponding to the absorption bands. The μ associated with the S_0 – S_2 transition was found to lie along the short axis of the anthracene skeleton, determined by defining the obtained x, y, and z coordinates using dummy atoms. Next, we aligned the molecular orientation obtained from single-crystal X-ray structure analysis to the crystal coordinate system and projected on this molecular axis onto the crystal axes (Supplementary Fig. 46). As a result, we confirmed that the μ direction primarily coincides with the crystallographic *b*-axis (Supplementary Fig. 51). In this revised manuscript, we have added this analysis procedure to the Methods section and Supporting Information. We believe that this clarification demonstrates that our estimation method is based on a combination of TD-DFT calculations and crystallographic orientation analysis. Please see *Pages 10* (270-) in highlighted manuscript.

11. The manuscript focuses on the direction of the transition dipole moment but does not discuss how its magnitude might influence the photoinduced response. A brief discussion of whether higher μ would correlate with stronger or faster response would be useful, especially in the context of designing molecules for better dynamic behavior.

==== > While this paper has focused on the directionality of the transition dipole moment (μ), we would like to add that its magnitude is also important. In general, the magnitude of μ is proportional to the absorption efficiency, and molecules with a larger μ will generate more photoexcited states or photoproducts under the same irradiation conditions. As a result, photoreactions and structural transitions in the crystal are promoted, suggesting that the response of crystal dynamics is strong and appears quickly. Therefore, considering both the "direction" and "magnitude" of μ is an important guideline for dynamic crystal design. Please see *Page 8* (212-) in highlighted manuscript.