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

Peer Review File

Axial Chirality-Induced Rigidification in Aminoboranes Enhances Persistent Room-Temperature Phosphorescence and Circularly Polarized Luminescence

Corresponding Author: Professor Pakkirisamy Thilagar

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript "Chirally-locked Aminoboranes: Molecular Persistent Room-Temperature Phosphorescence and Circularly Polarized Luminescence" presents a novel technique for improving the performance of persistent room-temperature phosphorescence (pRTP) by borylating and axially chirally locking aminoborane molecules. It also reveals for the first time that these compounds have the capacity to exhibit both pRTP and CPL properties at the same time. However, before publication, a few concerns still need to be resolved.

1. In fact, the article shows creativity in creating and refining organic compounds that exhibit persistent room-temperature phosphorescence (pRTP). The study successfully improves pRTP performance by combining borylation with axial chirality locking, and it also demonstrates how these compounds may exhibit circularly polarized luminescence (CPL).

(1): While the study shows how aminoboranes can improve performance, there isn't much discussion of how other techniques that improve phosphorescence or CPL performance compare in the literature. The originality and benefits of this study will be more effectively highlighted by strengthening the comparison with current metal-free PRTP material design methodologies, such as ligand modifications, hydrogen bonding, or halogen bonding.

(2): Although the study demonstrates the materials' fundamental optical characteristics, a more extensive discussion of their suitability and benefits for practical uses is possible. For example, these materials' potential in bioimaging, security devices, and OLEDs is not completely investigated.

2. The article uses multiple experimental techniques (such as spectroscopic analysis and time-dependent emission behavior testing) and theoretical calculations (DFT/TD-DFT) to explain material performance. The experimental design is sound, and the data is detailed. However, certain experimental parts can be further optimized to better support the paper’s central argument.

(1) Only a small number of concentrations were evaluated, despite the fact that the paper illustrates phosphorescence performance in PMMA sheets at various concentrations. Stronger proof, particularly with regard to concentration quenching at higher levels, would come from more systematic data demonstrating the link between concentration, phosphorescence quantum yield, and longevity.
(2) The impact of temperature on material performance is covered in the article, but other environmental parameters that are important in practical applications—like humidity and oxygen concentration—are not thoroughly examined. It would be beneficial to investigate the material's performance under different circumstances, particularly those that are pertinent to device functioning.

3. The article uses TD-DFT calculations to support experimental findings and analyze molecular orbitals and electronic transitions. However, the depth and connection of the theoretical analysis could be enhanced.

(1): While the paper uses TD-DFT to explain the improved luminescence performance, the theoretical analysis is somewhat complex, especially regarding higher-order transition states. Simplifying and presenting the interaction between energy levels more intuitively, perhaps through diagrams or tables, would make it easier to follow.
(2): Though the theoretical results align well with experimental data, further emphasizing the assumptions of the theoretical models and how they match real experimental conditions would enhance understanding of model applicability. For example,

more discussion on how the solvent models in TD-DFT relate to actual experimental environments could be helpful.

4. The article cites a wide range of relevant literature, particularly in the areas of metal-free phosphorescent materials, triplet states, and organic light-emitting devices. However, citations on recent developments are somewhat limited, especially those published in the last two years.

(1): The most cited references in the paper are classic. It would be beneficial to include more recent studies from the past two years, particularly the latest advancements related to axial-chirality-based organic luminescent materials. This would make the literature review more up-to-date and forward-looking.
(2): While the paper provides a detailed background in organic luminescent materials, discussions on cross-disciplinary fields, such as phosphorescence applications in biomaterials or gamma-ray detectors, are relatively lacking. Broadening the discussion into these areas would further enrich the potential application scope of the materials.

5. The paper is well-structured, and the language is fluent, but certain sections, such as theoretical calculations and complex spectroscopic analysis, seem slightly lengthy and too technical, which may affect the understanding of the results by some readers.

(1): To make the theoretical analysis portion more comprehensible to a wider audience, it is advised to simplify the language and use less scientific jargon.
(2): Optimize the abstract: Although the abstract summarizes the study, it could more clearly highlight the innovations and application prospects, especially with quantified descriptions of key results (e.g., pRTP lifetime, quantum yield) to attract readers' attention.

This paper has high academic value, particularly in its significant contribution to improving persistent room-temperature phosphorescence and circularly polarized luminescence performance through molecular design. However, the article could further expand on the discussion of application prospects, increase research on device performance and stability, and enhance the readability of the theoretical sections. Simplifying certain complex parts will make the article more understandable and accessible to a broader readership.

Reviewer #2

(Remarks to the Author)
This manuscript reports on the room temperature phosphorescence (RTP) emission from naphthyl-incorporated aminoboranes. The synthesized chiral R/S-(BN)2 molecules exhibited a phosphorescence quantum yield of 2.5% and a long lifetime of 0.9 seconds at room temperature. The authors attribute this to the restricted molecular motion induced by the more rigid and bulky structure of the R/S-(BN)2 molecules. This conclusion is supported mainly by simulations and photophysical analysis. Therefore, I recommend the manuscript for publication after the authors address the following points:

-The authors used the term “chirally-locked” to explain the origin of the enhanced RTP in R/S-(BN)2. However, the term seems inaccurate. While the restricted molecular motions of R/S-(BN)2 are an exact description, the chiral structure and its corresponding electronic configuration do not appear to directly contribute to the improvement in RTP. Additionally, circularly polarized luminescence (CPL) was not observed in the PMMA thin films, which actually exhibited the best RTP properties. The correlation between the "chirally-locked" structure and the RTP properties has not been fully substantiated.
-In Figure 2c, the absorption intensity of R-(BN)2 in different solvents varies, despite the concentrations being the same. What is the reason for this discrepancy?
Regarding the chiroptical properties, the dissymmetry factor (g-value) for absorption needs further explanation. Additionally, it would be helpful to discuss why CPL was not observed in the R-(BN)2 doped PMMA thin films.
-Was there any difference in the photophysical and RTP properties between the R- and S-(BN)2 enantiomers? It is recommended to include data for the S-(BN)2 enantiomer in the manuscript for comparison.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript entitled ' Axial Chirality-Induced Rigidification in Aminoboranes: Molecular Persistent Room-Temperature Phosphorescence and Circularly Polarized
Luminescence ' describes a unique method for borylating and axially chirally locking aminoborane molecules to enhance the performance of persistent room-temperature phosphorescence (pRTP). Additionally, it shows for the first time that these compounds can simultaneously display both pRTP and CPL characteristics. However, some issues still need to be addressed before publication.

1.The introduction offers a solid background on room-temperature phosphorescence (RTP), but the transition to your specific research approach can be made smoother. The discussion of the limitations of current systems, especially those relying on heavy metals or crystalline environments, can be emphasized earlier. This would give a clearer lead-in to the significance of your work in developing metal-free organic systems using axial chirality.

2.The following concerns should be addressed by the authors' revision and improvement of Figure 5's arrangement:
(1)Figure 5 is now arranged in an unclear and inconsistent manner, especially with regard to the images' alignment, spacing, and dimensions. Both the figure's legibility and overall visual impact are diminished by these problems.
(2)There are inconsistencies between the description of the figure notes and the content of the pictures in Figure 5, which may lead to readers' misunderstanding of the data.

Reviewer #2

(Remarks to the Author)
The manuscript has been revised according to the reviewer's comments, and most of major concerns have been properly addressed. So, it is recommended for publication in Communications Chemistry.

Reply to Reviewers' Comments for Manuscript COMMSCHEM-24-0535 for Communications Chemistry

Reply to the report of the Reviewer 1

General comment: *The manuscript "Chirally-locked Aminoboranes: Molecular Persistent Room-Temperature Phosphorescence and Circularly Polarized Luminescence" presents a novel technique for improving the performance of persistent room-temperature phosphorescence (pRTP) by borylating and axially chirally locking aminoborane molecules. It also reveals for the first time that these compounds have the capacity to exhibit both pRTP and CPL properties at the same time. However, before publication, a few concerns still need to be resolved.*

Author Reply: We thank the reviewer for appreciating our work and for the suggestions, which provide us an opportunity to further elaborate the scope of the article. We have now conducted several other experiments to support the significance of our material. Our point-by-point response is given below.

Comment 1: *In fact, the article shows creativity in creating and refining organic compounds that exhibit persistent room-temperature phosphorescence (pRTP). The study successfully improves pRTP performance by combining borylation with axial chirality locking, and it also demonstrates how these compounds may exhibit circularly polarized luminescence (CPL).*

1. *While the study shows how aminoboranes can improve performance, there isn't much discussion of how other techniques that improve phosphorescence or CPL performance compare in the literature. The originality and benefits of this study will be more effectively highlighted by strengthening the comparison with current metal-free PRTP material design methodologies, such as ligand modifications, hydrogen bonding, or halogen bonding.*

Author Reply 1 (1):

We appreciate the reviewer's insightful comment. In our revised manuscript, we have modified introduction section and added a discussion section that positions our work in the context of other well-known methodologies like crystal engineering and heavy element incorporation.

Among the most explored methodologies for phosphorescence materials, ligand modifications and heavy element incorporation are employed to enhance phosphorescence by fine-tuning electronic properties and facilitating intersystem crossing. Similarly, hydrogen and halogen bonding strategies often rely on intermolecular interactions to stabilize the triplet state. In contrast, our approach utilizes the unique features of axial chirality and boron-nitrogen (BN) incorporation, which combine structural rigidity, enhanced ISC (facilitated by BN-induced spin-orbit coupling), and restricted molecular motion within a single system. This design enables both efficient phosphorescence and circularly polarized luminescence in a structurally robust framework.

Change in manuscript:

Introduction section: Recent times have seen a growing emphasis on persistent room temperature phosphorescent (pRTP) materials, which exhibit long-lasting emission with lifetimes (τ) greater than 0.1 seconds.[31] Among the commonly explored strategies for achieving prolonged organic afterglow, optimizing the incorporation of heavy elements[18] or modifying functional groups has been extensively studied, primarily to enhance intersystem crossing.[32] In other approaches, strong crystalline interactions such as hydrogen bonding or halogen bonding are utilized to stabilize the excited states.[33–35] In these materials, the rigid crystalline environment effectively suppresses non-radiative decay pathways by restricting molecular motions, thereby enhancing the phosphorescence efficiency.[36] Although these approaches are very propitious for developing metal-free organic phosphors, they still have limitations to practical applications because of the limited processability of crystalline materials. On the other hand, polymer-doped organic RTP materials offer several advantages due to its amorphous nature, improved processability, thermal and chemical stability. [37] Additionally, achieving pRTP with improved efficiency (in terms of lifetime and quantum yield) from chromophores doped at very low weight percentages in polymer media by reducing the aggregation caused quenching, opens an avenue for economically efficient emitters.

Discussion section: Compared to other conventional approaches that depend extensively on intermolecular interactions to stabilize excited states or the inclusion of heavy elements to facilitate ISC, our steric-hindrance-based strategy in aminoboranes offers a unique advantage. The combination of structural rigidity and enhanced spin-orbit coupling through BN inclusion achieves superior performance within a single molecular framework.

Comment 1:

2. *Although the study demonstrates the materials' fundamental optical characteristics, a more extensive discussion of their suitability and benefits for practical uses is possible. For example, these materials' potential in bioimaging, security devices, and OLEDs is not completely investigated.*

Author Reply 1 (2):

We appreciate the reviewer's suggestion. In response, we have currently expanded the discussion section to more thoroughly address the potential applications of our aminoborane-based materials in bioimaging, security devices, and light emitting displays. Additionally, to support the practical applicability of these materials, we have included a demonstration of the security writing by using the aminoborane materials.

Change in manuscript:

Results section: **Demonstration of Security Writing Using pRTP Materials**

We also attempted to visually observe the pRTP signals from the 1 wt% PMMA thin films of **(BN)$_1$** and ***R/S*-(BN)$_2$** under an N□ atmosphere by exciting them with UV irradiation, aiming to unveil the potential of these materials for anticounterfeiting applications. Both samples exhibited blue fluorescence (CIE coordinates of (0.18, 0.18) for **(BN)$_1$** ; (0.18, 0.16) for ***R*-(BN)$_2$)** and green phosphorescence (CIE coordinates of (0.27, 0.48) for **(BN)$_1$**, (0.32, 0.56) for ***R*-(BN)$_2$)** (Fig. 8d). Notably, the prolonged green afterglow of the ***R/S*-(BN)$_2$** samples lasted up to 3.2 seconds, whereas **(BN)$_1$** exhibited a shorter afterglow duration of 0.8 seconds with lower intensity after the excitation ceased (Fig. 8a,8b, S26). This distinct difference in emission behavior inspired us to explore the security writing application. Using 1 wt% ***R*-(BN)□** and **(BN)□** doped PMMA inks, we created the digits ‘1180’ in a digital font. Under UV illumination, all digits displayed bright blue fluorescence (Fig. 8c). Upon turning off the UV light, after 1 second, the hidden message “IISC” became visible, highlighting the potential of these materials in anti-counterfeiting applications.

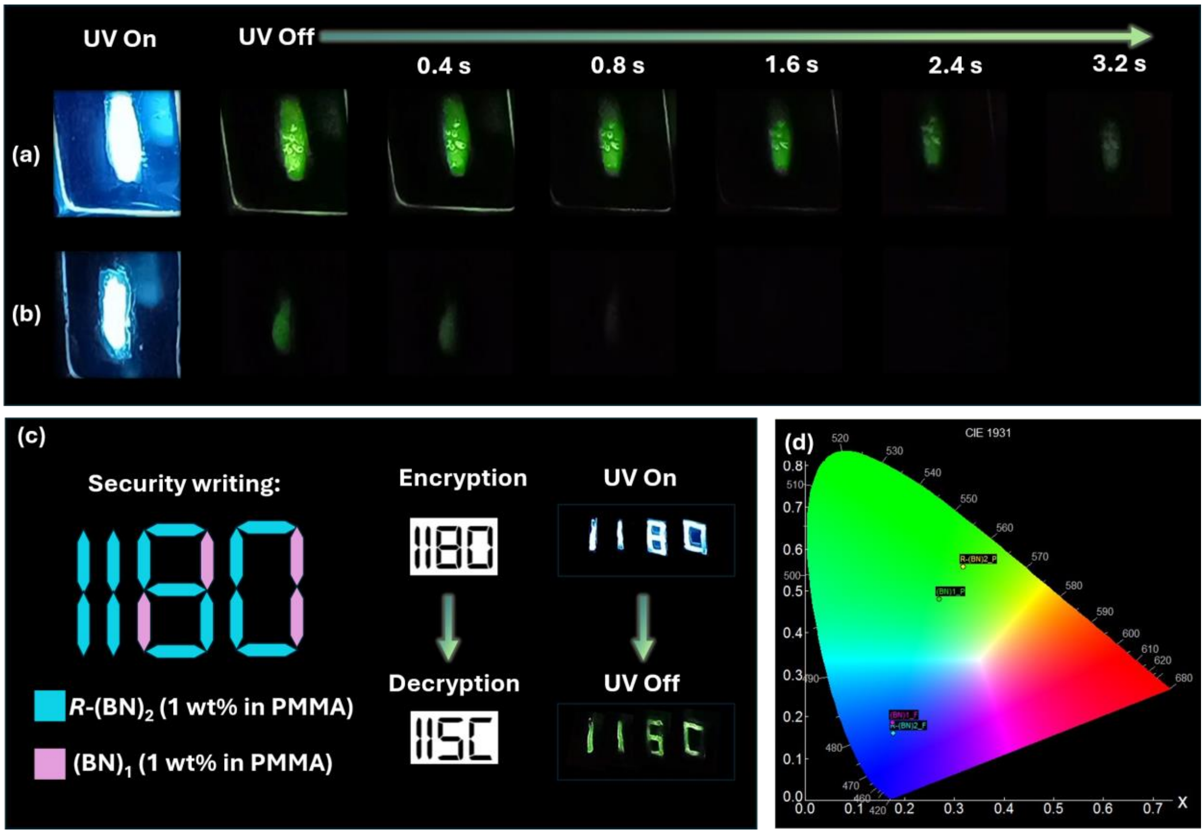

Fig. 8. Luminescence photographs of pRTP samples with UV-340 nm irradiation and after removal of irradiation: (a) 1 wt% ***R*-(BN)$_2$)** in PMMA (b) 1 wt% **(BN)$_1$** in PMMA; (c) Demonstration of security writing using ink formulated from 1 wt% ***R*-(BN)□** or **(BN)□** in PMMA. (Background reflections under UV illumination were removed to enhance clarity) (d) Chromaticity diagram with CIE 1931 coordinates for 1wt % in PMMA doped films of ***R*-(BN)$_2$)** and **(BN)$_1$** The samples are showing identical fluorescence, yet the chiral framework induced brighter phosphorescence and prolonged afterglow at 298 K in N_2 atmosphere

Comment 2: *The article uses multiple experimental techniques (such as spectroscopic analysis and time-dependent emission behavior testing) and theoretical calculations (DFT/TD-DFT) to explain material performance. The experimental design is sound, and the data is detailed. However, certain experimental parts can be further optimized to better support the paper's central argument.*

1. *Only a small number of concentrations were evaluated, despite the fact that the paper illustrates phosphorescence performance in PMMA sheets at various concentrations. Stronger proof, particularly with regard to concentration quenching at higher levels,*

would come from more systematic data demonstrating the link between concentration, phosphorescence quantum yield, and longevity.

Author Reply 2 (1):

At lower doping levels, we prepared and analyzed multiple concentrations (1, 3, 6, 10, 25, 50 wt%) to optimize and identify the highest-performing doping level. Our observations indicate that all lower doping levels exhibit good molecular pRTP performance. However, the 1 wt% doping level showed the highest emission intensity and lifetime, which are highlighted in the manuscript (Figure 3) and supporting information (Figure S3).

One critical finding from this experiment is the significantly improved phosphorescence quantum yield at 1 wt%, which was measured as 9.2 % for ***R*-(BN)$_2$**. In the initial submission of the manuscript, this value was reported as 2.5 %. Noticing this discrepancy, we repeated all the measurements multiple times with freshly prepared samples. The 9.2 % value was found to be reproducible within an acceptable error margin.

We suspect that the previously reported lower quantum yield value resulted from an undetected issue with the cryostat used during the initial phosphorescence QY measurements. This equipment was later repaired and confirmed to be functioning correctly. To ensure the reliability of our data, we repeated all measurements conducted during the period of this error multiple times. We sincerely regret any confusion caused by this discrepancy and have since implemented all necessary precautions to guarantee the accuracy and reproducibility of the measurements presented in the current version of the manuscript.

Change in manuscript:

Results section: The emission properties of PMMA-based thin films with varying doping concentrations (1, 3, 6, 10, 25, 50 wt %, and neat film) of samples were investigated to determine the optimal doping concentration and analyse the effect of concentration-induced quenching in phosphorescence.

As the doping concentration is increased in the PMMA matrix, the fluorescence spectra displayed significant variation in the intensity ratio of LE and CT contributions. At higher doping levels, an increase in the CT contribution was observed for both the ***R*-(BN)$_2$** and **(BN)$_1$** sample. The rigid geometry of ***R*-(BN)$_2$** resulted in a consistently higher LE contribution compared to **(BN)$_1$** across all doping levels. At elevated doping concentrations, the reduced PMMA content in the thin films limited the interaction between the phosphor molecules and the polymer chains, thereby increasing the detrimental intermolecular interactions. These interactions could have favoured the adoption of a CT geometry over the LE geometry.

The optimum phosphor doping concentration was found to be 1 wt % for ***R*-(BN)$_2$** and **(BN)$_1$** in the PMMA matrix, as shown in Figures 4c-h. At higher phosphor concentrations, self-quenching is likely responsible for the observed reduction in phosphorescence quantum yield, with a complete disappearance of the phosphorescence band in the neat film (100 wt%) for ***R*-(BN)$_2$** and 50 wt % for **(BN)$_1$** (Table S6). We also analysed the phosphorescence lifetime of various concentrations of phosphors dispersed into PMMA. A significant decrease in the average lifetime was observed as the phosphor concentration exceeded 10 wt %, attributed to dominant non-radiative self-quenching pathways at higher concentrations.

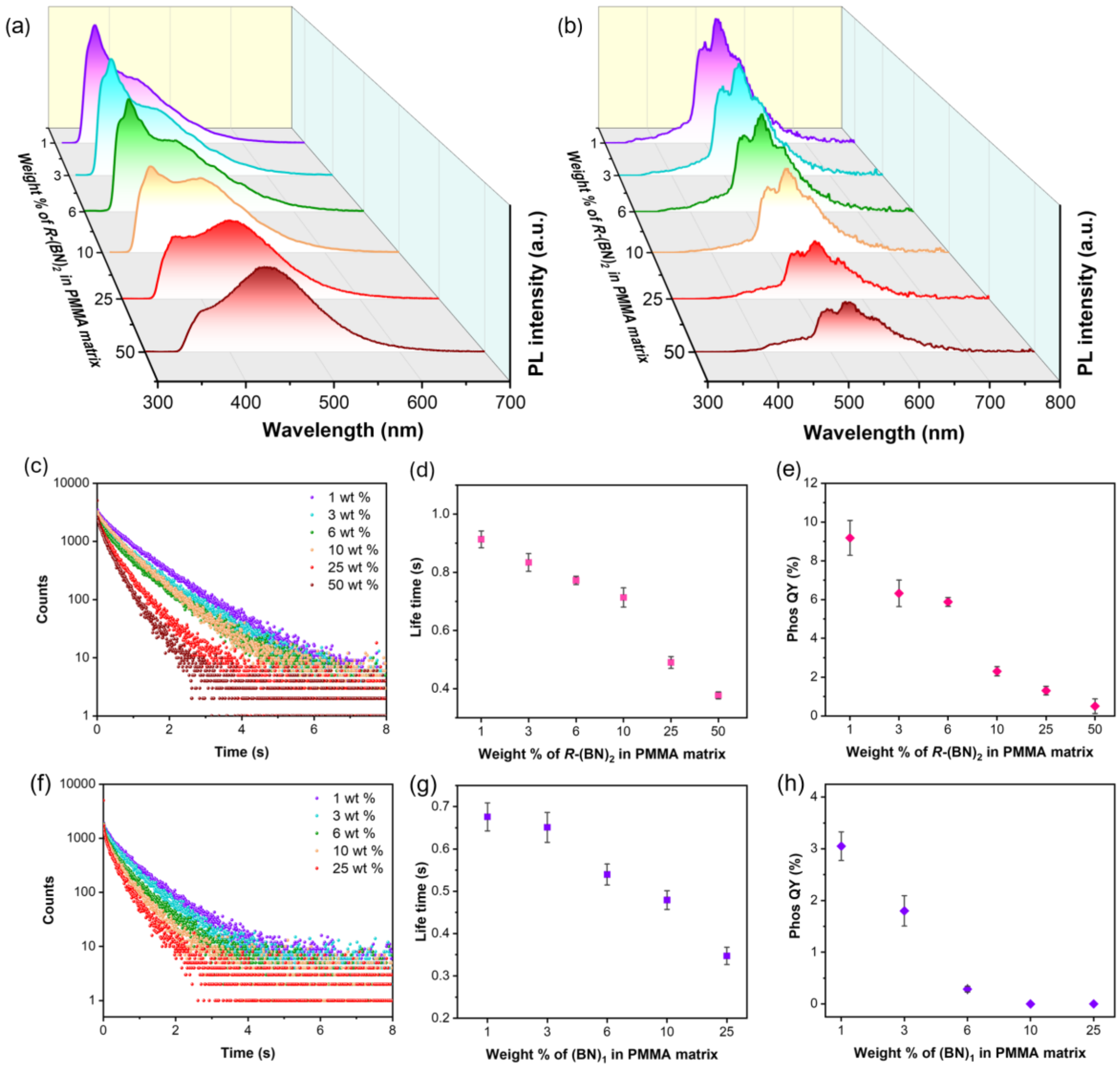

Figure 4. Optical properties of PMMA thin films with different phosphor concentrations. (a) PL spectra and (b) delayed PL spectra of ***R*-(BN)□** at varying phosphor concentrations. (c, f) Time-resolved decay profiles of ***R*-(BN)□** and **(BN)□** monitored at 530 nm and 525 nm respectively. (d, g) Phosphorescence lifetimes, and (e, h) phosphorescence quantum yields

of ***R*-(BN)$_2$** and **(BN)$_2$** at different concentrations in PMMA. All the measurements taken under vacuum at 298 K (Delay = 50 µs, λ_{ex} = 280 nm).

Comment 2:

2. *The impact of temperature on material performance is covered in the article, but other environmental parameters that are important in practical applications—like humidity and oxygen concentration—are not thoroughly examined. It would be beneficial to investigate the material's performance under different circumstances, particularly those that are pertinent to device functioning.*

Author Reply 2 (2):

We thank the reviewer for this valuable comment. In response, we have investigated the pRTP performance of the thin films under various environmental conditions, including vacuum, N_2, O_2, and ambient atmospheres, for all samples. As expected, the phosphorescence band was completely quenched in ambient or O_2 environments. However, under an N_2 atmosphere, the phosphorescence signal was retained, though the lifetime was slightly reduced compared to vacuum conditions. [Although we conducted an experiment with controlled O_2 purging to PMMA thin film, we observed a sudden quenching of the RTP emission even with the introduction of a small volume of O_2. This rapid quenching effect made it challenging to obtain consistent data and analyzing the results. Thus, we decided not to incorporate this data into the manuscript].

Regarding the impact of humidity, we regret to inform the reviewer that we could not perform this experiment due to our experimental limitations. (Creating a humid atmosphere inside the cryostat can potentially damage the setup by causing condensation, which may affect the optical components and electronic circuits, leading to measurement inaccuracies or equipment malfunction). However, we acknowledge the importance of such studies for practical applications and will address this aspect in our future works.

Change in manuscript:

Results section: Furthermore, the emission features of the samples were examined under ambient, N_2, and O_2 conditions. Under ambient and O_2 conditions, the delayed PL band completely disappears and is restored when the sample is placed under vacuum. Although the emission intensity was unaffected for the 530 nm band, there was a reduction in average lifetime of the emitter under an N_2 atmosphere (τ = 510 ms) compared to vacuum conditions (τ =930 ms) (Fig. 5e, Table S8). These observed variations in the phosphorescence features could be due to the trace amount of O_2 impurities in the N_2 (Fig. 5d). The pronounced susceptibility of the delayed PL bands to oxygen further supports the involvement of the triplet excited state in the radiative processes of these compounds.

Comment 3: *The article uses TD-DFT calculations to support experimental findings and analyze molecular orbitals and electronic transitions. However, the depth and connection of the theoretical analysis could be enhanced.*

1. *While the paper uses TD-DFT to explain the improved luminescence performance, the theoretical analysis is somewhat complex, especially regarding higher-order transition states. Simplifying and presenting the interaction between energy levels more intuitively, perhaps through diagrams or tables, would make it easier to follow.*

Author Reply 3 (1):

We sincerely thank the reviewer for their valuable comment. We have made efforts to simplify certain sections of the manuscript. However, we would like to highlight that terms such as LE, CT, and HLCT are essential for accurately explaining the mechanism and, therefore, could not be entirely avoided. To ensure clarity, we have provided explanation of these terms in detail in ESI.

Additionally, we have simplified energy level diagrams to illustrate a plausible phosphorescence pathway. The spin-orbit coupling (SOC) values for higher-order transitions are also presented in the form of energy level diagrams to further support our discussion (Figure 8)

Change in manuscript:

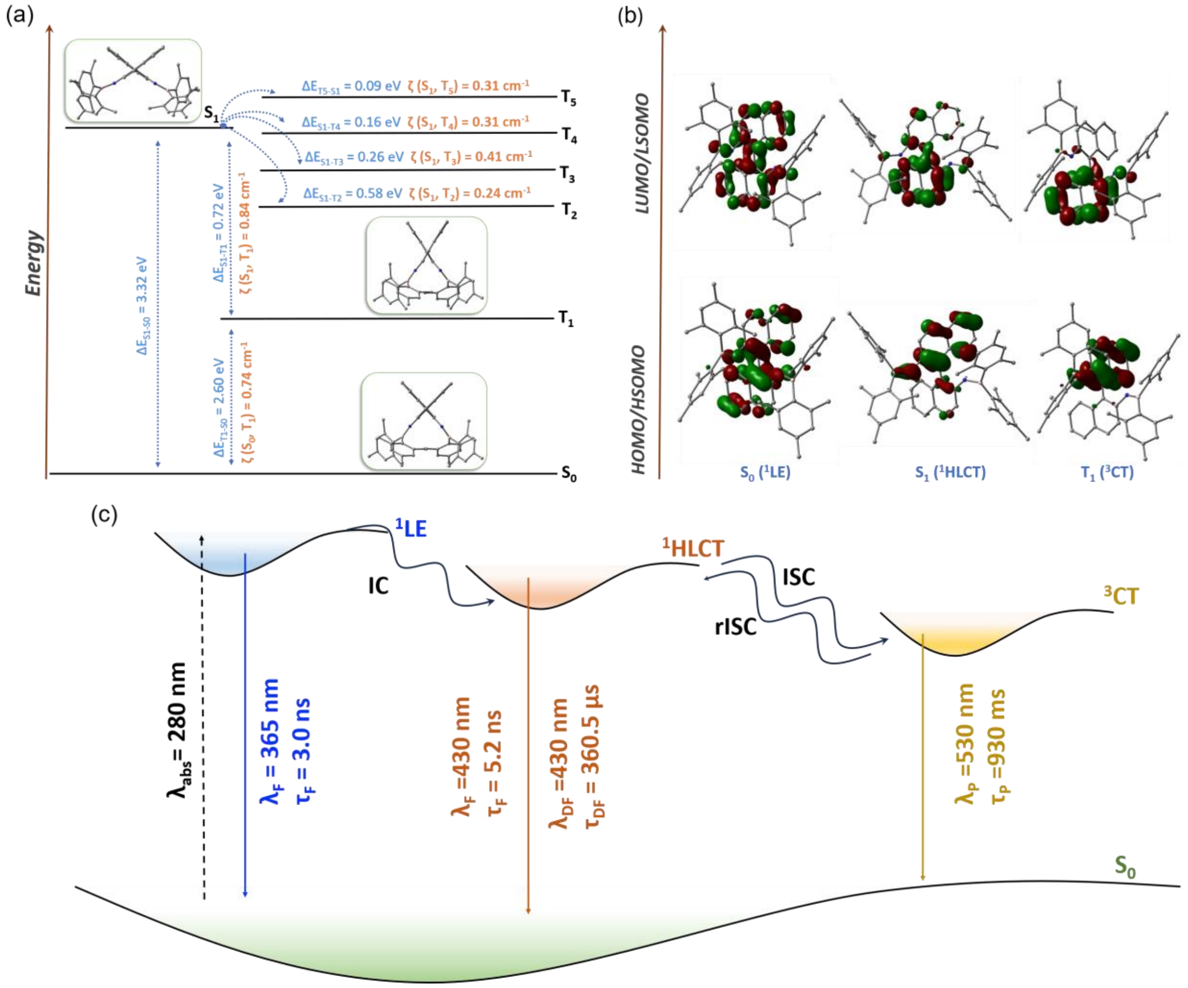

Figure 6. Theoretical analysis of phosphorescence process (a) Schematic representation of the TD-DFT calculated energy gaps of ***R*-(BN)$_2$**; optimised geometries of S_0, S_1, T_1 and significant SOC constant values are also included.(b) Frontier molecular orbitals of ***R*-(BN)$_2$** in S_0, $S_1$and T_1 state obtained from DFT and TD-DFT calculations using Gaussian 16 software with B3LYP functional and 631G-(d,p) basis set (|isovalue| = 0.04). (c) potential energy diagram depicting one of the plausible photophysical pathway occurring at 298 K in the 1 wt % ***R*-(BN)$_2$** doped PMMA matrix. [F: Fluorescence, DF: Delayed fluorescence, P: Phosphorescence],

Comment 3:

2. *Though the theoretical results align well with experimental data, further emphasizing the assumptions of the theoretical models and how they match real experimental conditions would enhance understanding of model applicability. For example, more discussion on how the solvent models in TD-DFT relate to actual experimental environments could be helpful.*

Author Reply 3 (2):

We thank the reviewer for this valuable comment. In the revised manuscript/ESI, we have provided a discussion on the assumptions made in our theoretical models and their relevance to the experimental conditions. Specifically, in the manuscript we have elaborated on the choice of solvent model used in TD-DFT calculations and how they correlate with the actual experimental environments.

Change in manuscript:

Results: Photophysical properties section : TD-DFT calculations were modelled by the polarizable continuum model (PCM), using the integral equation formalism variant (IEFPCM) which simulates the solvent as a continuous polarizable medium. This approach approximates the experimental environment by accounting for solute-solvent interactions, particularly dielectric polarization effects. These findings results closely align with the experimental plot, confirming the suitability of the selected computational methods.

ESI: Materials and methods section/ theoretical calculations section

Comment 4: *The article cites a wide range of relevant literature, particularly in the areas of metal-free phosphorescent materials, triplet states, and organic light-emitting devices. However, citations on recent developments are somewhat limited, especially those published in the last two years.*

1. *The most cited references in the paper are classic. It would be beneficial to include more recent studies from the past two years, particularly the latest advancements related to axial-chirality-based organic luminescent materials. This would make the literature review more up-to-date and forward-looking.*

Author Reply 4 (1):

We thank the reviewer for this valuable comment. In response, we have reviewed recent literature and added citations to include more up-to-date studies, particularly focusing on axial-chirality-based organic luminescent materials and metal-free phosphorescent materials.

Change in manuscript:

Introduction section citations are revised

Comment 4:

2. *While the paper provides a detailed background in organic luminescent materials, discussions on cross-disciplinary fields, such as phosphorescence applications in biomaterials or gamma-ray detectors, are relatively lacking. Broadening the discussion into these areas would further enrich the potential application scope of the materials.*

Author Reply 4 (2):

We thank the reviewer for this valuable comment. In response, to the reviewer's suggestion, we revised the manuscript's discussion section.

Change in manuscript:

Discussion: Beyond their fundamental significance, these non-toxic and cost-effective materials can be particularly important for high-resolution bioimaging, as they enable time-gated imaging independent of autofluorescence and excitation light scattering, as well as for organic scintillation for gamma-ray detection methodologies. The bright and prolonged afterglow observed in these samples were utilized in demonstrating anti-counterfeiting applications, further highlighting their potential in multilevel security applications, especially when combined with their chiroptical properties.

Comment 5: *The paper is well-structured, and the language is fluent, but certain sections, such as theoretical calculations and complex spectroscopic analysis, seem slightly lengthy and too technical, which may affect the understanding of the results by some readers.*

1. *To make the theoretical analysis portion more comprehensible to a wider audience, it is advised to simplify the language and use less scientific jargon.*

Author Reply 5 (1):

We have addressed this important comment by simplifying the language in the theoretical analysis section while retaining the scientific rigor. We also detailed terms used in the theoretical section in ESI for ensuring clarity to the readers.

Comment 5:

2. *Optimize the abstract: Although the abstract summarizes the study, it could more clearly highlight the innovations and application prospects, especially with quantified descriptions of key results (e.g., pRTP lifetime, quantum yield) to attract readers' attention.*

Author Reply 5 (2):

We thank the reviewer for these suggestions, we modified the abstract accordingly.

Change in manuscript:

Abstract: Long-lived triplet exciton harvesting materials are of immense interest for applications in bioimaging, optoelectronics, anticounterfeiting, and sensing. However, achieving persistent room-temperature phosphorescence (pRTP) in metal-free systems remains a significant challenge. Herein, we present purely organic axially chiral aminoboranes

(***R/S*-(BN)□**) with enhanced pRTP properties and circularly polarized luminescence (CPL). By introducing axial chirality, the dual-core (***R/S*-(BN)□**) system achieves steric-hindrance-caused rigidity, which restricts molecular motions leading to superior phosphorescence properties. Notably, ***R*-(BN)□** demonstrates a phosphorescence quantum yield (Φ_P) of 9.2 % (***S*-(BN)□** : Φ_P = 8.7 %) and an extended lifetime of 0.9 seconds at room temperature, significantly outperforming its mono-core counterpart **(BN)□** (Φ_P = 3.0 % and τ_P = 0.6 s). Theoretical analysis corroborates the observed improvements, revealing the synergistic role of borylation and axial chirality in stabilizing triplet states. Furthermore, the axially chiral aminoboranes exhibited CPL in dichloromethane solutions with a dissymmetry factor of ~10^{-3}. These findings highlight the potential of axially chiral frameworks in designing efficient metal-free pRTP materials, as demonstrated in the security writing application, further paving the way for their use in bioimaging, anti-counterfeiting technologies, and next-generation organic electronics.

General comment: *This paper has high academic value, particularly in its significant contribution to improving persistent room-temperature phosphorescence and circularly polarized luminescence performance through molecular design. However, the article could further expand on the discussion of application prospects, increase research on device performance and stability, and enhance the readability of the theoretical sections. Simplifying certain complex parts will make the article more understandable and accessible to a broader readership.*

Reply to the report of the Reviewer 2

General comment: *This manuscript reports on the room temperature phosphorescence (RTP) emission from naphthyl-incorporated aminoboranes. The synthesized chiral R/S-(BN)2 molecules exhibited a phosphorescence quantum yield of 2.5% and a long lifetime of 0.9 seconds at room temperature. The authors attribute this to the restricted molecular motion induced by the more rigid and bulky structure of the R/S-(BN)2 molecules. This conclusion is supported mainly by simulations and photophysical analysis. Therefore, I recommend the manuscript for publication after the authors address the following points:*

Comment 1: *The authors used the term “chirally-locked” to explain the origin of the enhanced RTP in R/S-(BN)2. However, the term seems inaccurate. While the restricted molecular motions of R/S-(BN)2 are an exact description, the chiral structure and its corresponding electronic configuration do not appear to directly contribute to the improvement in RTP.*

Additionally, circularly polarized luminescence (CPL) was not observed in the PMMA thin films, which actually exhibited the best RTP properties. The correlation between the "chirally-locked" structure and the RTP properties has not been fully substantiated.

Author Reply 1:

We appreciate the reviewer’s insightful comment regarding the term "chirally-locked" and its correlation to the enhanced RTP properties observed in ***R/S*-(BN)□.** We agree that the terminology could be refined to better describe the origin of the observed improvements in RTP properties.

The restricted bond rotation around the chiral axis in ***R/S*-(BN)□** plays an essential role in introducing structural rigidity into the aminoborane system. This rigidification effectively restricts intramolecular motions such as vibrations and rotations, reducing non-radiative decay pathways and enhancing triplet exciton stability. The steric hindrance imparted by the axially chiral framework is key to the restricted molecular dynamics that enable persistent room-temperature phosphorescence (pRTP) and CPL. We revisited the title and changed the “chirally-locked” to **“Axial Chirality-Induced Rigidification”.** We hope this terminology more precisely conveys the role of the axial chirality in restricting molecular motion and aligns with the evidence presented

While it is true that CPL could not be detected in the PMMA thin films due to the weak signals, the solution-phase CPL measurements of the ***R/S*-(BN)□** molecules demonstrated luminescence dissymmetry factors on the order of $\sim 10^{-3}$, underscoring their inherent chiroptical activity. However, the PMMA matrix at a low doping level disrupts the uniform orientations required for detectable chiroptical properties.

Furthermore, we have included a discussion in the manuscript to substantiate the correlation between the chiral framework, restricted motion, and enhanced RTP properties. We emphasize that while chirality alone may not directly improve RTP, the structural rigidity it induces synergizes with the BN moiety to significantly enhance spin-orbit coupling (SOC) and reduce non-radiative losses.

We hope these revisions adequately address the reviewer’s concerns.

Comment 2: In Figure 2c, the absorption intensity of R-(BN)2 in different solvents varies, despite the concentrations being the same. What is the reason for this discrepancy? Regarding the chiroptical properties, the dissymmetry factor (g-value) for absorption needs further explanation. Additionally, it would be helpful to discuss why CPL was not observed in the R-(BN)2 doped PMMA thin films.

Author Reply:

Part 1: Regarding the absorption intensity variations in ***R*-(BN)$_2$**: This experiment was repeated multiple times for confirming the observation. The observed discrepancy in the absorption intensity of ***R*-(BN)$_2$** across different solvents, can be primarily attributed to slight solubility differences. As a non-polar molecule, ***R*-(BN)$_2$** exhibits higher solubility in non-polar solvents (like cyclohexane) or medium polar solvent (like DCM) than polar solvents (like ACN). To verify this, we performed a solvent titration study using a dichloromethane (DCM)-acetonitrile (ACN) mixture (as they are miscible), and we observed a gradual decrease in absorption intensity as the ACN fraction increased (Figure R1).

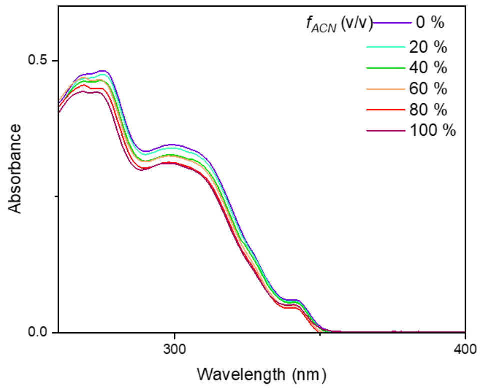

Figure R1: The absorption spectra of R-(BN)2 in DCM with varying solvent fractions of ACN (conc. = 10 μM)

Part 2: Regarding the absorption dissymmetry values: The explanation related to gabs value is added in the chiroptical properties section. The g-value reflects the intrinsic chiral nature of the molecule, in the ground state and is expected to be higher than that of glum values as we observed.

Part 3: Regarding the CPL of ***R/S*-(BN)$_2$** doped PMMA thin films: We repeated the CPL measurements multiple times, and found that the signals are undetectable (noisy spectra). Additionally, we observed that the CD signals of the 1 wt% ***R/S*-(BN)$_2$** doped PMMA thin films were of very low intensity. This suggests that the weak or undetectable chiroptical signals may be attributed to the lower doping concentration and the inhomogeneous alignment of the binaphthyl units within the rigid polymer matrices.

3) Was there any difference in the photophysical and RTP properties between the R- and S-(BN)2 enantiomers? It is recommended to include data for the S-(BN)2 enantiomer in the manuscript for comparison.

Author Reply:

As expected, there are no significant differences in the photophysical and RTP properties between the **R-** and **S-(BN)**□ enantiomers. We have included some of the photophysical properties in the manuscript, while all other relevant data for this enantiomer are provided in the ESI.

Reply to Reviewers' Comments for Manuscript COMMSCHEM-24-0535A for Communications Chemistry

Reply to the report of the Reviewer 1

General comment: *The manuscript entitled ' Axial Chirality-Induced Rigidification in Aminoboranes: Molecular Persistent Room-Temperature Phosphorescence and Circularly Polarized Luminescence ' describes a unique method for borylating and axially chirally locking aminoborane molecules to enhance the performance of persistent room-temperature phosphorescence (pRTP). Additionally, it shows for the first time that these compounds can simultaneously display both pRTP and CPL characteristics. However, some issues still need to be addressed before publication.*

Author Reply: We sincerely thank the reviewer for their thoughtful evaluation and for recognizing the significance of our work. We appreciate the constructive feedback, which has greatly helped in refining and improving the manuscript. Below, we provide a detailed point-by-point response to the reviewer's comments.

Comment 1: *The introduction offers a solid background on room-temperature phosphorescence (RTP), but the transition to your specific research approach can be made smoother. The discussion of the limitations of current systems, especially those relying on heavy metals or crystalline environments, can be emphasized earlier. This would give a clearer lead-in to the significance of your work in developing metal-free organic systems using axial chirality.*

Author Reply 1

We appreciate the reviewer's suggestion to improve the flow and clarity of the introduction. In response, we have carefully restructured the introduction to create a more seamless transition into our research approach. The revised introduction is now structured as follows:

Change in manuscript:

- **Paragraph 1:** Provides a foundational background on room-temperature phosphorescence (RTP), emphasizing its fundamental principles and significance in various applications.
- **Paragraph 2:** Discusses the most widely explored strategy—heavy metal incorporation—for achieving RTP, highlighting its drawbacks and the growing need for environmentally friendly organic alternatives.

- **Paragraph 3:** Introduces the concept of persistent RTP (pRTP) with lifetimes exceeding 0.1 seconds, explaining the most common strategies such as halogen bonding, hydrogen bonding, and crystallization. It also addresses the limitations of these approaches, particularly regarding processability, and how amorphous polymer matrices offer a viable alternative with added advantages.
- **Paragraph 4**: Discusses the suitability of PMMA as a polymer matrix for developing amorphous thin-film emitters. It also acknowledges that ambient conditions may introduce vibrational and diffusion-based quenching effects, even in such rigid matrices. This underscores the need for improved phosphor design strategies with enhanced structural rigidity to increase triplet harvesting efficiency.

- **Paragraph 5:** Discusses the role of BN incorporation in RTP materials, citing previous studies that demonstrate its effectiveness in facilitating triplet harvesting through the promotion of the otherwise forbidden ISC process. Additionally, it highlights our group’s prior research on aminoboranes for pRTP and chiral aminoboranes for CPL

- **Paragraph 6**: Discusses the effectiveness of BN incorporation and axial chirality in achieving enhanced pRTP and chiroptical properties. This section also briefly summarizes the key findings of our study and their potential applications, emphasizing the broader significance of our approach.

Comment 2: *The following concerns should be addressed by the authors' revision and improvement of Figure 5's arrangement:*

(1)Figure 5 is now arranged in an unclear and inconsistent manner, especially with regard to the images' alignment, spacing, and dimensions. Both the figure's legibility and overall visual impact are diminished by these problems.

Author Reply 2(1):

We sincerely apologize for the unclear arrangement of Figure 5. The misalignment was primarily due to the inclusion of a stacked plot depicting the photophysical properties of the thin films at different temperatures (298 K and 77 K), which affected the overall figure layout.

To improve clarity and visual consistency, we have now reorganized Figure 5 as follows:

- The single-molecular properties of **R-(BN)**□ in viscous media and dilute cyclohexane solution are now distinctly separated from the photophysical properties in PMMA (1 wt% dispersion) using a divider.

- Alignment, spacing, and dimensions have been carefully adjusted to enhance legibility and overall visual impact.

Change in manuscript:

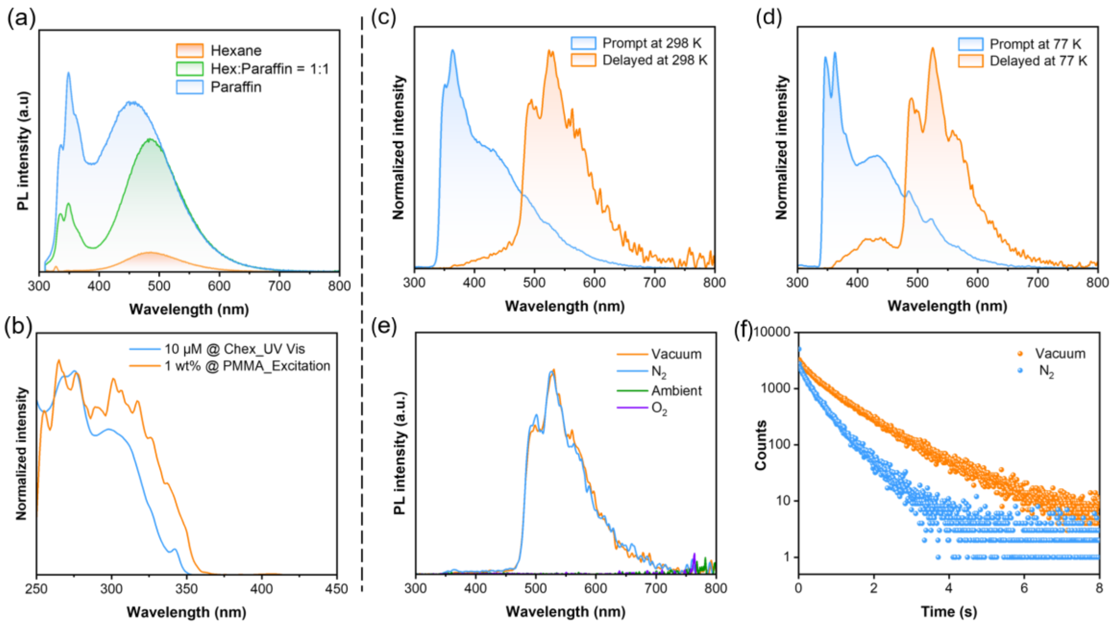

Figure 5. Molecular optical properties of *R*-(BN)□ in viscous and rigid media. (a) Fluorescence spectra in hexane, paraffin, and a hexane/paraffin mixture (1:1) (concentration = 10 μM). (b) Absorbance spectrum (in cyclohexane solution) and excitation spectrum (1 wt% in PMMA), monitored at λ_{em} = 530 nm. Prompt and delayed emission spectra (1 wt% in PMMA matrix) under vacuum conditions (c) at 298 K and (d) at 77 K. (e) Delayed emission spectra (1 wt% in PMMA matrix) under different environments. (f) Time-resolved decay kinetic profiles measured at 530 nm under vacuum and N□ atmospheres (delay = 50 μs, λ_{ex} = 280 nm).

Comment 2:

(2)There are inconsistencies between the description of the figure notes and the content of the pictures in Figure 5, which may lead to readers' misunderstanding of the data.

Author Reply 2(2):

We sincerely apologize for this oversight. We have carefully revised the arrangement of the plots in Figure 5 to ensure consistency between the figure description and the corresponding images.

We hope these changes ensures better clarity of the data.

Reply to the report of the Reviewer 2

General comment: *The manuscript has been revised according to the reviewer's comments, and most of major concerns have been properly addressed. So, it is recommended for publication in Communications Chemistry.*

Author Reply 1:

We sincerely appreciate the reviewer’s positive feedback and recommendation for publication. Thank you for recognizing our efforts in addressing the concerns and improving the manuscript.