

Unravelling nonclassical beam damage mechanisms in metal-organic frameworks by low-dose electron microscopy

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

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Reviewer #2

(Remarks to the Author)

Overall:

In this manuscript Xu et al, are discussing electron beam induced structural modifications in UiO-66(Hf) metal-organic framework (MOF). The experiments are conducted using TEM with spherical aberration correction in HRTEM images (with direct detection devices (DDD) for low-dose imaging) and diffraction modes. The manuscript also includes simulations to support experimental observations.

All major results reported in this manuscript, including (1) observation of lattice constant reduction with exponential rate at early stage of electron irradiation, (2) amorphization of the MOF at lower electron doses, and (3) breakdown of molecular linkers (referred here as disappears of linkers and discussed in Fig. 4) at higher electron doses, are all observed and reported in literature. See paper by Ghosh et al, Chemistry of Materials (2021), where similar results were reported on another MOF (ZIF-L).

However, observation of amorphous-to crystal transition appears as new result. Such phenomenon in MOFs hasn't been reported before, and it need to be discussed in more details and needs more emphasis. However, there are several observations on beam induced crystallization from amorphous due to electron beam radiation. For example: Jencic et al, J. Appl. Phys. 78, 974 (1995), or Lee et al. RSC Adv. 7, 40279 (2017).

The argument presented here about electron beam induced healing, including the results in SI Fig. S15, is not convincing. Can authors proof that what they see is not just MOF reaching higher density of packing, due to initial shrinking and partial amorphazation, that it can not shrink any further and therefore low-order diffraction spots stay intact? Without such proof, their argument of self-healing is not supported.

Since most of results presented in this manuscript are not novel, I cannot recommend publishing it in high-profile journal Nature Communications. Specialized journal will be more appropriate for this work. But, before submitting it in another journal, I would recommend authors to compare their observations with those report by Ghosh et al and discuss similarities and differences. Also, I would recommend authors to fix many technical deficiencies indicated below.

Technical Side:

Sentences and phases are a bit awkward. Page numbers are missing. Technical terminology is used loosely and, in many places, incorrectly. The figures and panels are not cited in chronological order. Captions are not complete/clear. I would recommend editorial overhaul of this manuscript and SI file.

The manuscript somewhat poorly organized. For example, the entire first paragraph in Results and discussion section,

which is two page long and need reorganization, clearly belongs to Introduction section. The Introduction section is unnecessarily long and missing citations to critical papers, particularly on radiolysis.

In the early part of the manuscript, pages (??), where authors are discussing results in Figure 2(e-h) and arguing based on GPA analysis that at lower electron doses amorphization occur, amorphization should be also visible in their experimental diffraction patterns (broad rings). Can they show that? It is much simpler and more direct way of proving it.

Authors state that “We have proved by ab initio molecular dynamics (AIMD) simulations that an equilibrated supercell UiO-66(Hf) model with massive broken bonds exhibits significant volumetric shrinkage and elevated density (from 1.62 to 2.09 g cm⁻³) due to the collapsed porous network (Fig. S7).” It is not clear how in these simulations the electron beam irradiation and its effects are incorporated. What are the input parameters?

The ref [59] in main manuscript is not original papers, where equation (9) is derived. Correction is in order here.

In SI file, Details and technical specifications of the TEM used in these experiments are not provide, besides saying that “operated at 300 kV”. Additionally, a citation is missing where contrast-transfer-function(CTF)-based image processing is discussed and justified. Stating “To simulate the projected electrostatic potentials, the QSTEM code [<http://qstem.org/>] was employed, ...” doesn’t have proper citations, just link to webpage.

In SI file, when authors discussing the Mott cross-section (σ_K), neither citation is accurate/complete nor the terms in the equations (S5-S7) are explained. Therefore, it can’t be used to evaluate the results discussed in main manuscript. It is true for eq. (9) in main manuscript.

Reviewer #3

(Remarks to the Author)

This manuscript reports calculations and experimental results relating to electron-beam damage to a MOF [crystalline UiO-66(Hf)] during examination in a TEM. It includes an extensive discussion and references to previous work by the authors and other researchers.

Damage is found to be inhomogeneous and dependent on dose rate and the explanation involves both radiolysis, knock-on displacement and reverse reactions (repair mechanisms). An interesting temperature dependence of damage is noted (hidden away in Supplementary Information) but not really explained.

The work is original and casts light on the beam damage mechanisms in metal-organic frameworks, with possible relevance to other systems. It is certainly worthy of publication and my only criticisms are technical matters:

1. The GPA, CG-SA, DFT and AIMD calculations are highly technical and are necessarily incompletely explained in a relatively brief article such as this. The section “Data and Code Availability” contains the statement “This study did not generate any datasets”. Can the authors not make some of the important details accessible to the scientific public?

2. The six Figures are very elaborate, to the extent that some of the details are unreadable. I recommend that each Figure be split into two so that it becomes clearer and more digestible.

Below are a few suggested minor changes to the English:

line 73: thresholds termed as => thresholds, termed

line 88: local Columb repulsion => local Coulomb repulsion

lines 142,195,382,394: positive dose rate effect presumably means direct dose-rate effect?

line 168 iften misaligned => often poorly defined

line 178: a complete physical picture of => different stages of

line 222: an immediate outcome upon the homogeneous illumination of electron beam is the

=> an immediate outcome of homogeneous illumination of the electron beam is a

line 391: and can be experimentally validated. => that can be experimentally validated.

line 570: Columb => Coulomb

Reviewer #4

(Remarks to the Author)

In this study, Xu and coauthors unravelling nonclassical beam damage mechanisms in metal-organic frameworks via low-dose TEM and ab initio simulations. Through the real-space visualization, they observed radiation-induced structure dynamics at morphological, lattice, and molecular levels. In addition to the classical beam damage mechanism, they propose reversible radiolysis and radiolysis-enhanced knock-on displacement mechanism. Overall, this work enriches the fundamental understanding of damage mechanism for TEM characterizations and potentially inspire the development of new methodologies and techniques in the fields of electron-beam lithography and electron microscopy. Several issues need to be addressed before publication, which are detailed below.

What concerns me most is that this article involves a great deal of professional knowledge of electron microscope, which makes it difficult for researchers in the non-TEM field to understand.

How to obtain Fig. 2b as well as the dose information?

How to identify the amorphized region in Fig. 2h? Since the crystalline-amorphous interconversion can be identified from Fig. 2h, please also provide the pristine HRTEM images, which can directly present the crystalline and amorphous region. In addition, how does Fig. 2h relate with Fig. 2g? As stated in the line 246, the GPA results suggest there is no remarkable crystal contraction at $64.7 \text{ e } \text{\AA}^{-2}$, however, ϵ_{xx} and ϵ_{yy} in Fig. 2g reached about $\sim 7\%$ at $45 \text{ e } \text{\AA}^{-2}$.

Time scales should be unified into picosecond for better comparison.

The maximum Dc is reached at -50°C , why does this value decrease with lower temperature. Will this behavior be influenced by the dose rate?

The authors are suggested to avoid the red and green colors in figures.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Reviewer #2

(Remarks to the Author)

This is my review of revised manuscript by Xu et al., on study of electron beam damage of UiO-66(Hf) MOF.

I appreciate that authors have taken time to respond to my comments. There are a few things I agree and there are a few things I disagree.

Good news. All technical deficiencies that I highlighted in original review have been addressed. I am satisfied with changes made in manuscript in this regard. Those changes significantly improved the readability of the manuscript.

Bad news. Authors responses to my concerns about novelty of this work is not satisfactory. Despite long arguments that authors have made in their responses, the main issue stays the same. Authors are arguing that they made the same observation of beam induced damage of MOF through high-resolution imaging, instead of diffraction... While imaging is nice, it is still another technique of electron microscopy, and nothing special about it. Imaging-based analysis is analysis in real space and diffraction is analysis in reciprocal space. The main results stays the same. And I argue that the materials science portion of these results are already published in scientific literature. Reaching same answer with different method is nice confirmation of earlier report, but it is not groundbreaking achievement.

The fact that authors can reach the same main conclusions using imaging, is reinforcing my argument that this manuscript is really achievement in low-dose electron microscopy technique development and, therefore, the results are more suitable in electron microscopy journal such as Ultramicroscopy or Microscopy and Microanalysis.

The only portion of this work that is new, is recrystallizations of MOF, which is only small portion of this manuscript, unfortunately. More expansion on this topic could have been nice and would definitely deserve to be published in Nature Communications.

I can not recommend this manuscript for publication in Nature Communications.

Reviewer #3

(Remarks to the Author)

As is clear from the four reviewer reports and from the authors' responses, there are many aspects of this work that will not satisfy everyone and others that will not be understood. But I believe it represents a useful body of evidence and a contribution to the field of beam damage mechanisms. Nature Communications is not an obvious choice for publication of this material but if its editors think that the subject matter is appropriate, I support publication in the journal.

Reviewer #4

(Remarks to the Author)

The authors have well solved my concerns. I recommend the acceptance of the manuscript.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Reviewer #2

(Remarks to the Author)

Dear authors, this is my review on your newly resubmitted manuscript with new round of changes. I wish you read my previous comments carefully and followed the recommendations provided. If you followed provided recommendation, I would recommend the manuscript for publication. Therefore, my recommendation for this version of the manuscript will stay the same - it does not deserve to be published in Nature Communication due to lack of novelty.

Here is why. I indicated in my previous round of review: "The only portion of this work that is new, is recrystallizations of MOF, which is only small portion of this manuscript, unfortunately. More expansion on this topic could have been nice and would definitely deserve to be published in Nature Communications."

At first glance, reading authors response file, it appears that authors have added new content to the manuscript, in response to my comments, on topic of "recrystallizations of MOF". Actually they did not. What authors added is additional experiment where they show that radiolytic damage of the MOF can be enhanced in H₂ environment. Let me be clear, this new addition does not have any new insight on "recrystallizations of MOF". It is new experimental validation of well-known radiolytic damage of any material including MOFs.

I wish, I could be positive in my review. I was hoping to learn some new insight into electron-beam-induced re-crystallization of MOFs. But, since it is not there, I am going to hold the same view as I had before - this manuscript does not deserve to be published in Nature Communication due to lack of novelty.

Version 3:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

As I mentioned in my previous review, I appreciate the large effort made by the authors addressing the questions previously proposed. However, I still believe that the work should be published in a more specific journal.

- Image simulations presented in figure R1 are now more convincing.

- Stain analysis presented in figure R2 is not convincing or not sufficiently described, the authors stated that changing the size of the "reference ROI would not considerably affect the GPA results as we demonstrated in Fig. R2c by employing a larger ROI". However, by looking at that the bottom right part, the strain changes from $\approx +5\%$ to $\approx -7\%$. This aspect should be discussed.

Reviewer #2

(Remarks to the Author)

In this round of revision the authors finally made substantial addition to "recrystallizations of the MOF under electron beam irradiation" section of the manuscript that I was recommending, as it is the main new observation reported here. Now I can recommend the manuscript for publication in Nature Communications.

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Point-to-Point Responses to Reviewers' Comments

Reviewer #1 (Remarks to the Author):

The work by Xu and colleagues focuses on analyzing the impact of the electron beam on metal-organic frameworks and the subsequent framework breakage, even under low-dose conditions. Working under these low-dose conditions allowed the authors to reveal and propose alternative beam damage mechanisms. I found the work engaging, and I believe that the scientific community would benefit from more studies of this nature, as electron microscopy can unveil structural details inaccessible by other means. I defer to the editor to determine if this article aligns with the journal's scope. Nonetheless, I recommend the work for publication in this or another journal following necessary revisions.

My primary concern with this work is that I do not find the conclusions regarding the nonclassical beam damage, despite the frequent repetition of this term throughout the manuscript, adequately experimentally supported. Therefore, I strongly recommend rephrasing it as a potential alternative mechanism with plausible alternative bond breakages. This recommendation is based on the following observations:

- Despite the possible relationship with electron beam lithography, regarding the electron beam interaction, I do not think it is necessary to mention and to mention it here. As it may result a bit confusing.

Response: We thank the reviewer for insightful comments. Following the reviewer's suggestion, we rephrased the term "nonclassical beam damage mechanisms" in most parts of the manuscript by the term "potential alternative mechanisms" followed by the specific description or conclusion of the mechanism.

Specifically, "Based on these observations, potential alternative mechanisms including reversible radiolysis and radiolysis-enhanced knock-on displacement are proposed, which account for their respective dynamic crystalline-to-amorphous interconversion and site-specific ligand knockout events occurring during continuous

beam radiation.” on page 2, and “We comprehensively investigate potential mechanisms occurring in MOFs upon beam radiation, examining morphological, lattice, and molecular levels.” on page 5.

In addition, we agree with the reviewer that to avoid potential confusion, the statement about electron beam lithography in the introduction part has been removed in this revision.

- Page 8, Fig. S3. Could the authors mention something about the strong contrast inside the white dashed rhomb? Can they add the scale bar? Can they describe if this image is raw data or if there is any image treatment? Can they indicate the color code used in the models?

Response: We thank the reviewer for the comments. Following the reviewer’s suggestion, we have added the description about the contrast in the caption of the figure as follows, “In the white dashed rhomb region, the dark rhombic contrast closely resemble the $[1\bar{1}0]$ structural projection of UiO-66(Hf). Specifically, the dark dots at the corners of the rhombus refer to $\text{Hf}_6\text{O}_4(\text{OH})_4$ nodes, while the dark edges and short diagonal of the rhombus refer to BDC linkers with different orientations.” Due to the distinct orientations for these two types of BDC linkers, the edge-on BDC linkers that locate at short diagonals of the rhombi exhibit darker contrast than those tilted ones at the edges. Moreover, based on the reviewer’s comments, we added the scale bar and corresponding labels for different types of atoms, mentioned the denoising method and the color code used in Fig. S3 as follows, “The HRTEM images after correcting the CTF effects are denoised using a Wiener filter and rendered in black-body color code”.

- Page 8, Fig. S4. I have no doubts about the contraction as the structure may somehow collapse due to the framework disruption, but the two images do not necessarily imply a real contraction; a partial rotation could also occur. Could the authors provide a video of this shrinkage? Or a video using an SEM, that would verify

the real contraction?

Response: We thank the reviewer for good suggestion. Following the suggestion, we record the full dynamic process of crystal shrinkage and have provided a video collected over a randomly chosen UiO-66(Hf) crystal as shown in *Attachment 1*. From the video, the dynamic anisotropic crystal contraction without considerable rotation can be clearly monitored.

- Page 9, GPA data. Could the authors further explain how they calculated the strain? For GPA, a reference area must be selected, typically a region free of strain.

Response: We thank the reviewer for the comments. For the quantitative strain evaluation within crystal structures of UiO-66(Hf), the geometric phase analysis (GPA) method has been employed based on a reference area of a perfect region free of strain. This is achieved by montaging dose series HRTEM images and measuring the relative geometric phase shifts of two sets of lattice fringes that attain non-linear related reciprocal lattice vectors $\vec{x} = [110]$ and $\vec{y} = [001]$ respectively, which is referred to a pristine crystalline region under zero dose. Following the reviewer's comments, we clearly marked the reference area in the dose series HRTEM images for GPA analysis and mentioned in the captions as: "The reference region for GPA analysis is marked by a white dashed square." in Fig. 3d, S5 and S6.

- In figure S7b. It seems that the authors have maintained all bonds connected, however, this may not be the case, how are they sure?

Response: We thank the reviewer for the comments. We apologize for the confusion that all bonds remain connected in the collapsed model of UiO-66(Hf) used for simulation. This arises from the large supercell size of the collapsed model, which results in superimposition and indistinguishability of both connected and broken bonds surrounding $\text{Hf}_6\text{O}_4(\text{OH})_4$ nodes, as illustrated in Fig. R1a and Fig. S7b. We totally agree with the reviewer that the dynamic process of lattice collapse and contraction arise from the bond breakage of the structure. Actually, multiple Hf-O

broken bonds in $\text{Hf}_6\text{O}_4(\text{OH})_4$ nodes are involved in the AIMD simulation (i.e. 37/48 broken/overall BDC linkers), depicting the disconnection of BDC linkers. These BDC linkers with multiple Hf-O bonds disconnected from the network result in significant structural distortions and anisotropic lattice contractions as observed experimentally. To better visualize these broken bonds and disconnected BDC linkers while maintaining the overall clarity of the collapsed model, we select those disconnected BDC linkers with broken bonds and render them in the polyhedral style as shown in Fig. R1b. Additionally, we have replaced Fig. R1b to Fig. S7b in this revision.

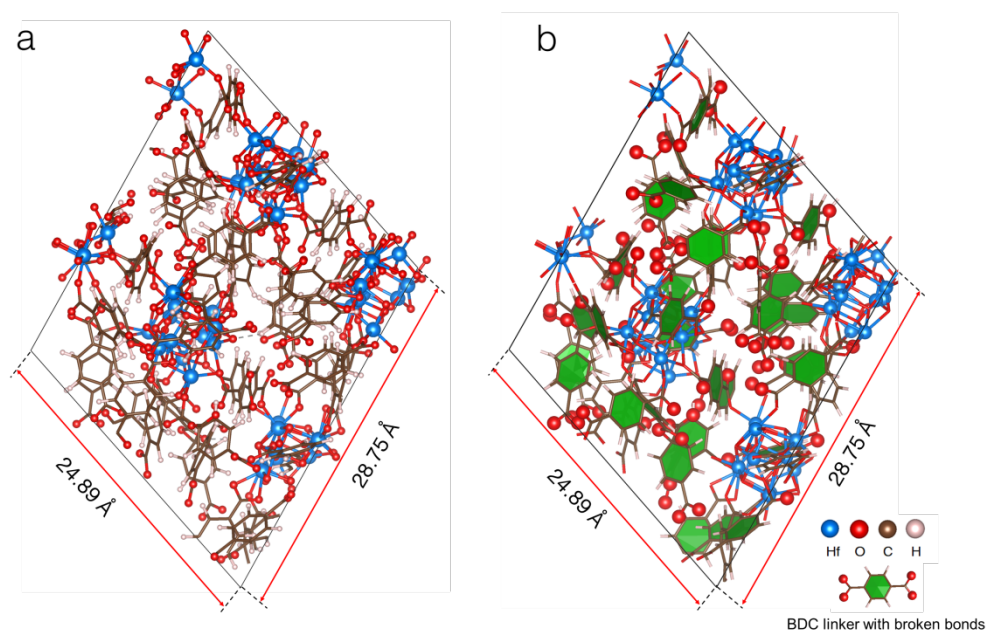


Fig. R1. (a-b) Schematic of disconnected BDC linkers from collapsed porous network within the UiO-66(Hf) crystal.

- In page 12, line 342, what is “e” in $1/e$?

Response: We thank the reviewer for the comments. The “e” is the electronic charge in $1/e$. To avoid potential confusion with “e” of eq. (7), we have replaced the “e” by “ e^- ” to refer to electronic charge. Additionally, we have added the notation “ e^- is the electronic charge” on page 13 and “where e is a natural logarithm ($e \approx 2.718$)” on page 14 in the revised manuscript.

- Figure S15. I have some concerns about the analysis presented in this figure. It would be better to start with an ED pattern without beam damage to prove that crystals are similar in terms of crystallinity. It seems that in figure S15b, the analysis already started from a damaged material. Additionally, how the thickness of the sample can affect the beam stability. By looking at the spot from the direct beam, the crystals and/or conditions seem different.

Response: We thank the reviewer for the comments. Following the reviewer's suggestion, to demonstrate similar crystallinity in the absence of radiation damage, we have added the initial state ED patterns as shown in Fig. R2 and Fig. S15 in the revised Supporting Information (SI). These ED patterns collected before structural damage exhibit well-defined high order diffraction spots and confirm the structural integrity of the UiO-66(Hf) crystals. Moreover, the size and shape of UiO-66 (Hf) crystals are relatively uniform as shown in Fig. R3, and should therefore exhibit very similar crystallinity and radiation damage behavior.

Furthermore, we totally agree that thickness effects on radiation damage should be investigated. Accordingly, we investigate two different UiO-66(Hf) crystals with similar octahedral crystal shape but distinct crystal sizes as shown in Fig. R4 (i.e. the long axes of octahedral crystals are 771.0 and 363.8 nm respectively), to examine the thickness effect on radiation damage and critical dose (D_c). By conducting the ED dose series experiments along $[1\bar{1}0]$ zone axis, the fading of high order diffraction spots similarly follows the first-order kinetics under the same dose rate of $1.0 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ (Fig. R4a-d). By fitting the fading curves, it is clear that two types of UiO-66(Hf) crystals with different sizes exhibit similar critical dose values (D_c) of $31 \text{ e}^- \text{ \AA}^{-2}$ and $35 \text{ e}^- \text{ \AA}^{-2}$ respectively, as shown in Fig. R4e. Accordingly, we prove here that the crystal thickness has minor effects on radiation damage kinetics and critical doses.

Regarding the comments from the reviewer about the difference in central spots from the direct beam under two dose rate conditions, the origin arises from the different degrees of intensity saturations in these two sets of ED dose series. It is because that under a higher dose rate of $1.5 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$, an equilibrium state with smaller quantity of

remnant crystalline domains is reached based on our proposed kinetic model dictated by reversible radiolysis mechanism. As a result of increasing the dose rate, the intensities of medium-order diffraction spots in the steady-state ED pattern become more diminished. This reduction in intensity requires enhanced visualization and clearer observation of these spots by adjusting the degree of intensity saturation in the ED patterns, which at the same time introduces of alterations in the central direct beam. Under a consistent degree of intensity saturation and a cumulative dose of 100 $\text{e}^- \text{\AA}^{-2}$ as shown in Fig. R5, the central beams in ED patterns look similar under different dose rate conditions.

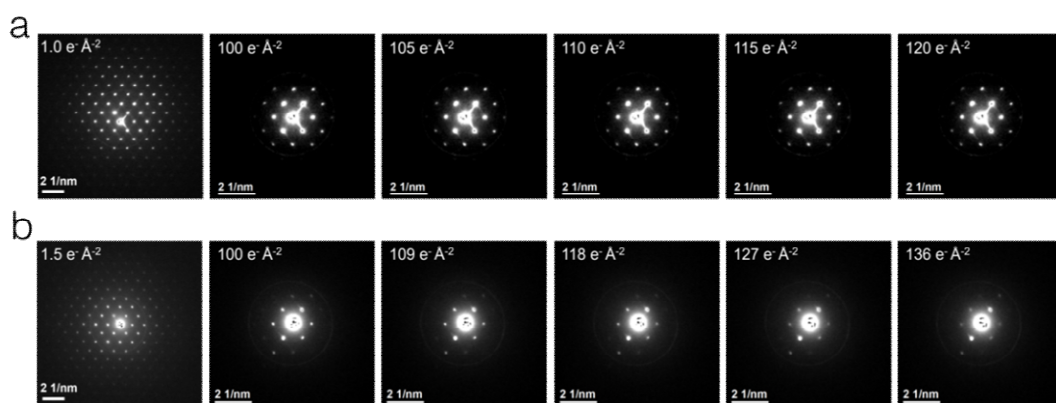


Fig. R2. ED patterns of UiO-66(Hf) crystals at an equilibrium state exposed to a dose rate of (a) $1.0 \text{ e}^- \text{\AA}^{-2} \text{ s}^{-1}$ and (b) $1.5 \text{ e}^- \text{\AA}^{-2} \text{ s}^{-1}$.

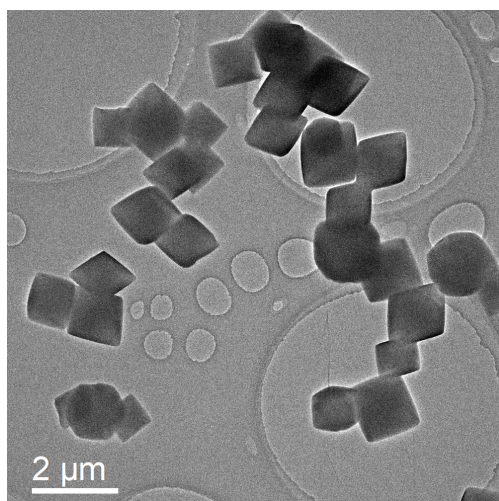


Fig. R3. The TEM image of the synthesized UiO-66(Hf) crystal.

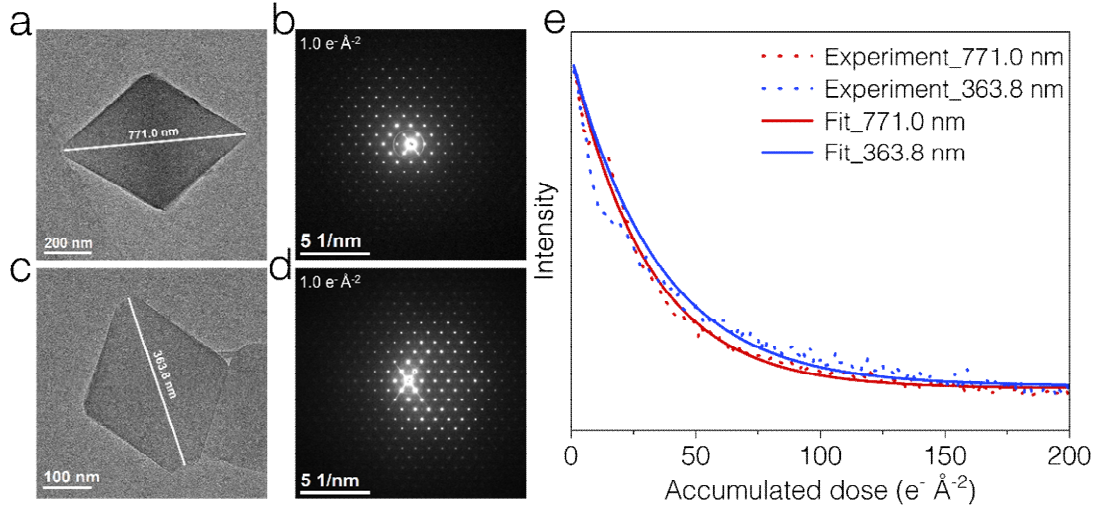


Fig. R4. (a), (c) TEM images of UiO-66(Hf) crystals in different sizes. (b), (d) The ED pattern of UiO-66(Hf) crystals at the initial state exposed to an identical dose rate of 1.0 e⁻ Å⁻² s⁻¹. (e) The exponential fitting of diffraction intensity decay curves as a function of accumulated dose for different sizes with a dose rate of 1.0 e⁻ Å⁻² s⁻¹.

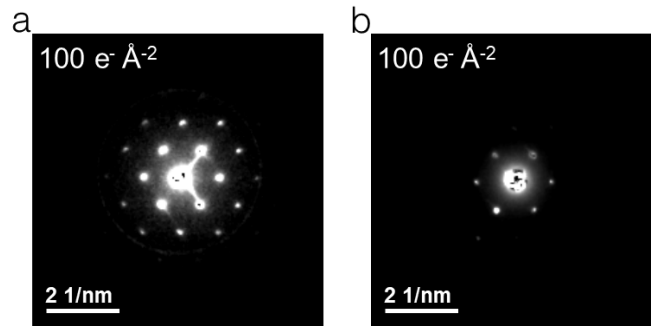


Fig. R5. (a-b) ED patterns of UiO-66(Hf) crystals at an accumulated dose of 100 e⁻ Å⁻² exposed to a dose rate of (a) 1.0 e⁻ Å⁻² s⁻¹ and (b) 1.5 e⁻ Å⁻² s⁻¹.

- In Fig. 4a and 4c. Why there is such a big contrast difference between the experimental and simulated data in the region marked by a dashed green ellipse. See below.

Response: We thank the reviewer for raising this question. In the revised main text, Fig. 4a and 4c correspond to Fig. 5a and 5c, respectively. The origin of contrast difference between the experimental and simulated data in the region of bridging linker arises from two aspects, i) The contrast of the ultralow electron dose HRTEM

image is inevitably interfered by the high level of shot noise and thus deviates from the noise-free simulated projected potential. ii) In order to avoid the strong noise interference in the vicinity the CTF crossovers, the CTF contrast inversion effects have been corrected by flipping the phase instead of amplitude in the frequency domain. As a result, the CTF corrected contrast usually closely resembles the simulated projected potentials of the crystal structure, but the correlation is not quantitative and the disparity could be notable especially in the presence of high-level shot noise.

- Additionally, Why there is such a big difference in the ligand signal between the initial and the beam damage?

Response: The variation in contrast of BDC linkers during the beam damage process originates from two reasons, i) The static structural distortions arising from the radiolytic bond breakage. In Fig. R1, we have demonstrated that extensive bond breakage results in notable local structural distortion. These distortions, when present along the projection, can significantly broaden the dark edges of the rhombi, thereby influencing the contrast of BDC linkers during the beam damage process. This effect could be more remarkable at increased framework flexibility when some critical BDC linkers at certain lattice sites are disconnected or knocked out at an elevated cumulative dose (e.g. the binding BDC linker at the bridge site). ii) The dynamic structural vibrations arising from the electron beam bombardment. As structural damage becomes more prominent and framework flexibility increases, the vibration effect becomes more pronounced. This vibration effect contributes to the overall broadening of dark edge contrast for BDC linkers.

- Line 513, along instead of long.

Response: We have corrected “long” to “along” on page 19 in this revision.

- Figure 6e, low temperature experiments. How many crystals are tested for these experiments?

Response: We thank the reviewer for raising this question. Fig. 6e corresponds to Fig.

7e in the revised main text. Despite of the limited time window that a cryo-transfer hold can offer for collecting high quality HRTEM images, we managed to acquire high-resolution low-dose images over multiple crystals in order to fully validate our conclusion in this work. Fig. R6 presents HRTEM images captured under identical imaging conditions from two additional crystals, which exhibit similar lattice contrast with site-specific missing linker defects that unequivocally support and validate the conclusions drawn in this study.

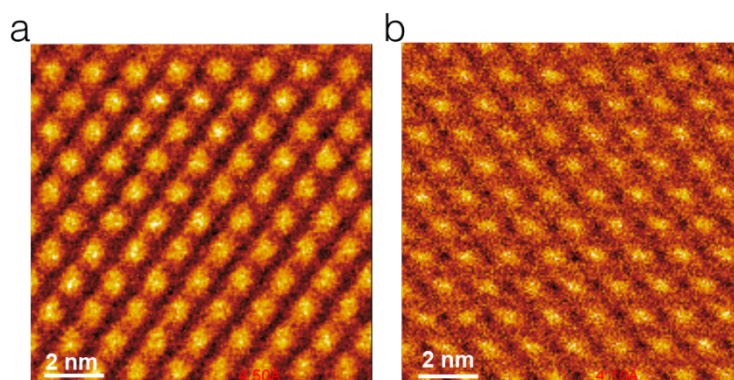


Fig. R6. (a-b) The CTF-corrected HRTEM images at low temperatures along the $[1\bar{1}0]$ projection for various UiO-66(Hf) crystals.

Finally, I would like to congratulate the authors for their extensive and cutting-edge work. However, I believe that the conclusions may not be fully supported by experimental evidence. Nevertheless, the study certainly opens up possible alternative routes to explain the low stability of these materials under the electron beam and deserves publication in a high-impact journal once these aspects are clarified.

Response: We sincerely appreciate the reviewer's commendation and constructive suggestions, which greatly improve the quality of our manuscript.

Reviewer #2 (Remarks to the Author):

Overall:

In this manuscript Xu et al, are discussing electron beam induced structural modifications in UiO-66(Hf) metal-organic framework (MOF). The experiments are

conducted using TEM with spherical aberration correction in HRTEM images (with direct detection devices (DDD) for low-dose imaging) and diffraction modes. The manuscript also includes simulations to support experimental observations.

All major results reported in this manuscript, including (1) observation of lattice constant reduction with exponential rate at early stage of electron irradiation, (2) amorphization of the MOF at lower electron doses, and (3) breakdown of molecular linkers (referred here as disappears of linkers and discussed in Fig. 4) at higher electron doses, are all observed and reported in literature. See paper by Ghosh et al, Chemistry of Materials (2021), where similar results were reported on another MOF (ZIF-L). However, observation of amorphous-to-crystal transition appears as new result. Such phenomenon in MOFs hasn't been reported before, and it need to be discussed in more details and needs more emphasis. However, there are several observations on beam induced crystallization from amorphous due to electron beam radiation. For example: Jencic et al, J. Appl. Phys. 78, 974 (1995), or Lee et al. RSC Adv. 7, 40279 (2017).

Response: We thank the reviewer for raising these concerns. The paper published in Chemistry of Materials (2021) as recommended by the reviewer conducted an excellent and detailed study on beam-induced structural degradation of another MOF (ZIF-L), mainly based on combined electron diffraction (ED) and electron energy loss spectroscopy (EELS). This study provides some interesting results and we have cited this paper in the revision of this manuscript. On Page 6 “In light of the disparity in evaluating the level of radiation damage of MOFs in relation to the electron dose, quantitative structural damage measurement can be achieved by ED dose series based on the fading of diffraction spots, which arises from the loss of different degrees of structural order^{48,49} (*Nanomaterials*. **2023**, 13, 1742; *Chem. Mater.* **2021**, 33, 5681–5689). The radiolytic damage basically follows first-order kinetics, and similar to the half-life of radioactive decay, a critical dose (D_c) that dictates the vulnerability of the materials can be derived by fitting the exponential decay of ED intensities^{3,49-51} (*Micron*. **2019**, 119, 72-87; *Chem. Mater.* **2021**, 33, 5681–5689; *Proc. Nat. Acad. Sci.*

2022, 119, e2200290119; *Microsc. Microanal.* **2018**, 24, 1988-1989).” and on page 9, “Actually, it has been widely observed that the radiation damage cause crystal contraction in open framework materials^{49,57,58} (*Chem. Mater.* **2021**, 33, 5681–5689; *CrystEngComm.* **2016**, 18, 4359-4368; *Phys. Chem. Chem. Phys.* **2019**, 21, 12389-12395).”.

Actually, the classical theoretical framework of radiation damage mechanisms has been built upon a wealth of exceptional pioneer works conducted by leading scientists such as R. Egerton (*Micron.* **2004**, 35, 6, 399-409; *Ultramicroscopy.* **2013**, 127, 100-108; *Microsc Res Tech.* **2012**, 75, 11, 1550-6). These works, which specifically delve into radiation damage and mainly based on diffraction and/or spectroscopy techniques, contribute significantly to our understanding of this field. An inherent limitation of either diffraction or spectroscopy characterization techniques lies in the indirect structural information retrieval from transformed spaces. This results in inevitable loss of structural information or ambiguities in structural determination. Most spectroscopy techniques, for example, have limited spatial resolution and utilize descriptive models to establish a connection between transformed information and structural characteristics. On the other hand, diffraction techniques often encounter challenges in preserving local structural information and necessitate the solution of the “inversion problem” to retrieve crystallographic structural details. Real space visualization through imaging represents a revolutionary technological advance, providing direct and high-resolution structural information. This not only grants unprecedented insights into the fundamental physical origins of reported phenomena but also enables the discovery of previously unreported events at the nanoscale. However, imaging beam-sensitive materials has long been challenging until the introduction of low-dose imaging techniques (*Science.* **2018**, 359, 675-679; *Nat. Mater.* **2017**, 16, 532; *Adv. Mater.* **2020**, 32, 1907619) and successful applications in MOFs (*Nat. Chem.* **2019**, 11, 622; *J. Am. Chem. Soc.* **2019**, 141, 12021; *J. Am. Chem. Soc.* **2021**, 143, 6681), COFs (*Angew. Chem. Int. Ed.* **2022**, 61, 04899; *J. Am. Chem. Soc.* **2022**, 144, 6475; *J. Am. Chem. Soc.* **2020**, 142, 13162; *J. Am. Chem. Soc.* **2017**, 139, 8698) and organic polymers (*Sci. Adv.* **2023**, 9, 1169, *J. Am. Chem. Soc.* **2024**,

DOI: 10.1021/jacs.4c01104) as pioneered in our series of reported works. By unraveling the real space radiation damage of a beam-sensitive MOF material, particularly through the dynamic process monitored in this study, we are presented with an unparalleled opportunity to comprehend the nanoscale structural evolutions induced by radiation and their underlying mechanisms. This expands the theoretical framework of radiation damage beyond classical mechanisms, paving the way for new insights and advances in the field.

Specifically, in response to the reviewer's comments, the findings in this work are highlighted as follows, (1) We agree with the reviewer that radiation induced crystal contraction of MOFs is widely acknowledged, and can be observed at morphological level and probed within averaged crystalline domains by diffraction. *However, the physical origin of such huge crystal contraction upon radiation remains elusive.* We pioneer the unraveling of the dynamic structural evolutions through real space visualization, shedding light on the primary cause of contraction originating from the collapsed porous framework, while also observing a minor contribution from lattice contraction within crystalline domains. (2) The amorphization of the MOFs under irradiation is reported and easily measurable by electron diffraction. *However, the spatially resolved amorphization behavior and dynamics remain unknown without the real space visualization.* We directly observed the dynamics of amorphous domains in MOFs including their emergence-disappearance-reemergence events and shape evolutions by low-dose imaging. Remarkably, this investigation represents one of the pioneering attempts to integrate real-space experimental observations with AIMD simulations, enabling a combined experimental and theoretical exploration of radiation damage mechanisms at the nanoscale. These findings entail the discovery of dynamic crystalline-to-amorphous interconversion and associated self-repairing events, which can be attributed to a nonclassical reversible radiolysis mechanism. (3) The intuitive consequence of radiation-induced structural damage and amorphization is the breakdown of molecular linkers. *However, unraveling the unconventional breakage events of metal-ligand linkages that go beyond those associated with framework collapse poses a significant challenge.* We managed to observe at

molecular-level the site-specific ligand knockout events that present in crystalline domains at elevated dose. By delving into these events, we are able to uncover a nonclassical radiolysis-enhanced knock-on displacement mechanism.

Generally, these new findings revealed through low-dose imaging not only enrich the theoretical framework of beam damage mechanisms but also transcend conventional phenomenological investigations. We propose nonclassical beam damage mechanisms and develop corresponding kinetic models, enabling accurate identification and prediction of nonclassical beam damage events and phenomena. These mechanisms and models have been unequivocally validated through comprehensive investigations of dose-rate and temperature effects on beam damage behaviors. We believe that these compelling points will convince reviewer to consider the publication of this work in esteemed journals such as Nature Communications.

The argument presented here about electron beam induced healing, including the results in SI Fig. S15, is not convincing. Can authors proof that what they see is not just MOF reaching higher density of packing, due to initial shrinking and partial amorphization, that it cannot shrink any further and therefore low-order diffraction spots stay intact? Without such proof, their argument of self-healing is not supported.

Response: We thank the reviewer for raising this point. *Firstly*, the self-healing process is validated by combined real space low-dose imaging and AIMD simulations. For clarity, we show here magnified local regions as depicted in Fig. R7-9, that the dynamic processes involving emergence-disappearance-reemergence of amorphous domain and their shape evolutions (i.e. from broad band-like to intermittent stripe-like domains) upon accumulated doses of $16.1 \text{ e}^- \text{ \AA}^{-2}$, $81.0 \text{ e}^- \text{ \AA}^{-2}$, and $121.5 \text{ e}^- \text{ \AA}^{-2}$ respectively. These dynamic self-repairing processes are now explicitly and directly visualized in the dose series of low-dose HRTEM images and dictated by the alternating presence and absence of crystal lattice contrast. We provide a movie for the dynamic crystalline-to-amorphous interconversion dictated for the self-repairing events as *Attachment 2*. Additionally, we utilized AIMD to successfully reproduce the cascade self-repairing events on picosecond time scale, presenting it as a competitive

process against the well-acknowledged radiolytic damage events that also manifest within a comparable time frame. **Secondly**, following the reviewer's suggestion, we provide experimental evidence demonstrating that the steady-state degraded structure of MOFs that adopts low-order diffraction spots is not the final structure upon irradiation. Specifically, as shown in Fig. R10, in contrast to the ED pattern obtained from a low dose rate applied to a steady-state MOF structure, an increased dose rate leads to a reduced fraction of remaining crystalline domains at steady-state and a weaker preservation of Bragg spots in the ED pattern. These observations align perfectly with our proposed reversible first-order kinetic model, which governs the nonclassical reversible radiolysis mechanism. Simultaneously, they unequivocally demonstrate that the degraded MOF structure at steady-state is not the final form after irradiation and can undergo further damage, resulting in a more extensively degraded steady-state structure that corresponds to a further reduction in low-order diffraction spots under an elevated dose rate. Furthermore, we include an ED dose series programmed illumination and acquisition conditions in Fig. R11 to enhance this point. By scripting control of the electron microscope, it enables the automated and programmable acquisition of ED dose series with flexible beam shuttering and beam current densities. Based on the acquired ED dose series, it is clear that an elevation of dose rate from $1.0 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ or $1.5 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ to $20 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ at the steady-state further damage the structure and finally lead to the completely diminished diffraction spots and amorphized structure.

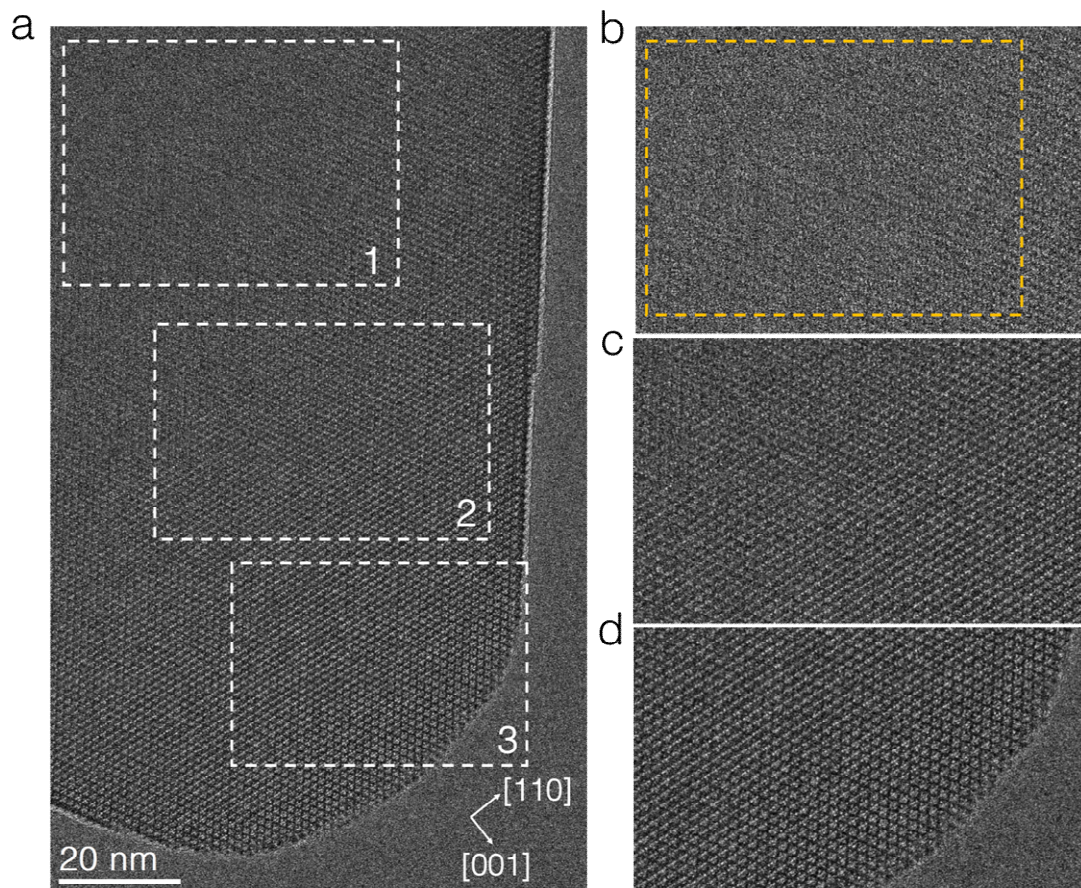


Fig. R7. (a) Low-dose HRTEM image of the UiO-66 crystal under an accumulated dose of $16.1 \text{ e}^- \text{ \AA}^{-2}$. (b) Local HRTEM image of area 1 in a, the yellow box area represent amorphous region. (c) Local HRTEM image of area 2 in a. (d) Local HRTEM image of area 3 in a.

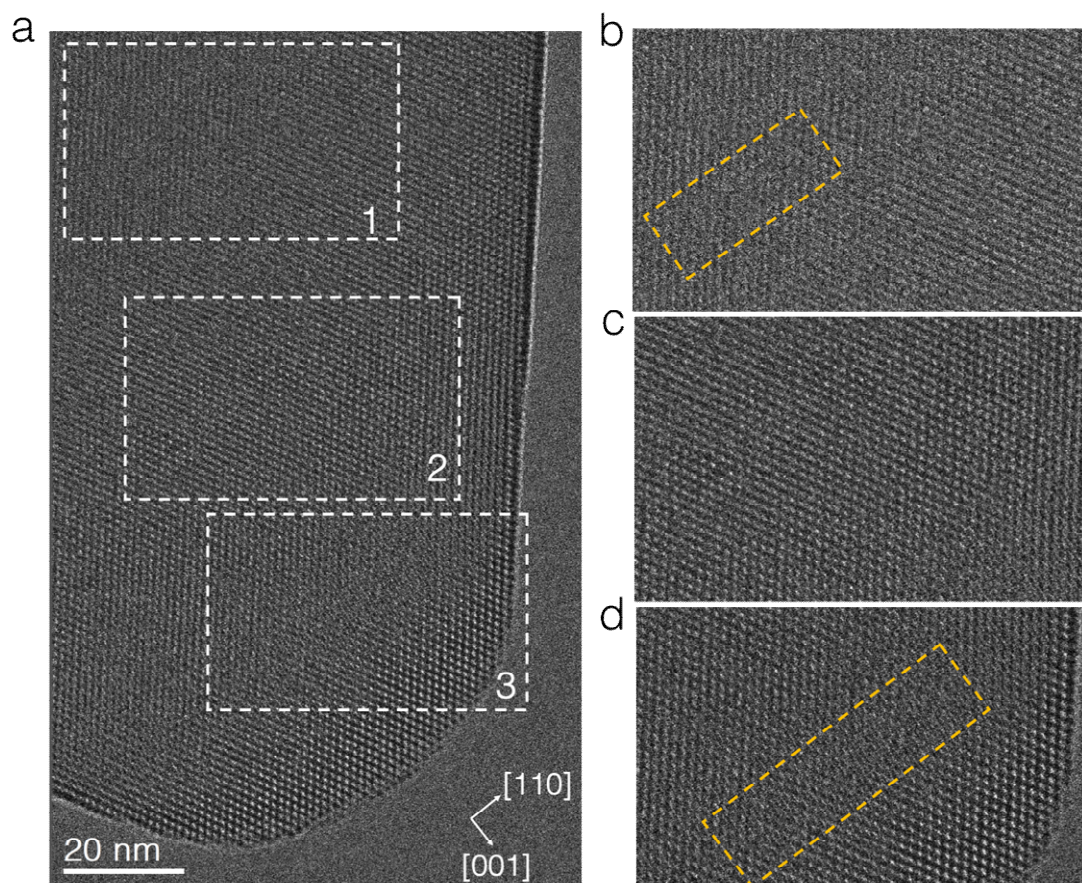


Fig. R8. (a) Low-dose HRTEM image of the UiO-66 crystal under an accumulated dose of $81.0 \text{ e}^- \text{ \AA}^{-2}$. (b) Local HRTEM image of area 1 in a. (c) Local HRTEM image of area 2 in a. (d) Local HRTEM image of area 3 in a. The yellow box area represent amorphous region.

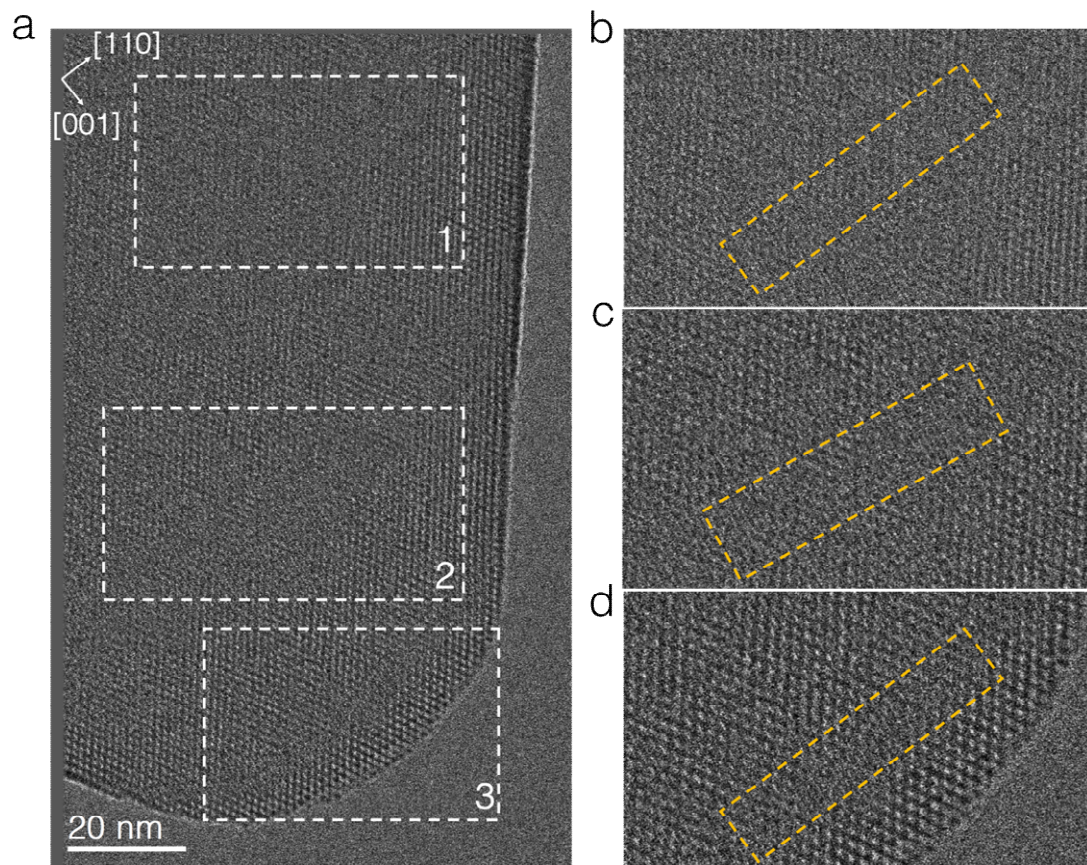


Fig. R9. (a) Low-dose HRTEM image of the UiO-66 crystal under an accumulated dose of $121.5 \text{ e}^- \text{ \AA}^{-2}$. (b) Local HRTEM image of area 1 in a. (c) Local HRTEM image of area 2 in a. (d) Local HRTEM image of area 3 in a. The yellow box area represent amorphous region.

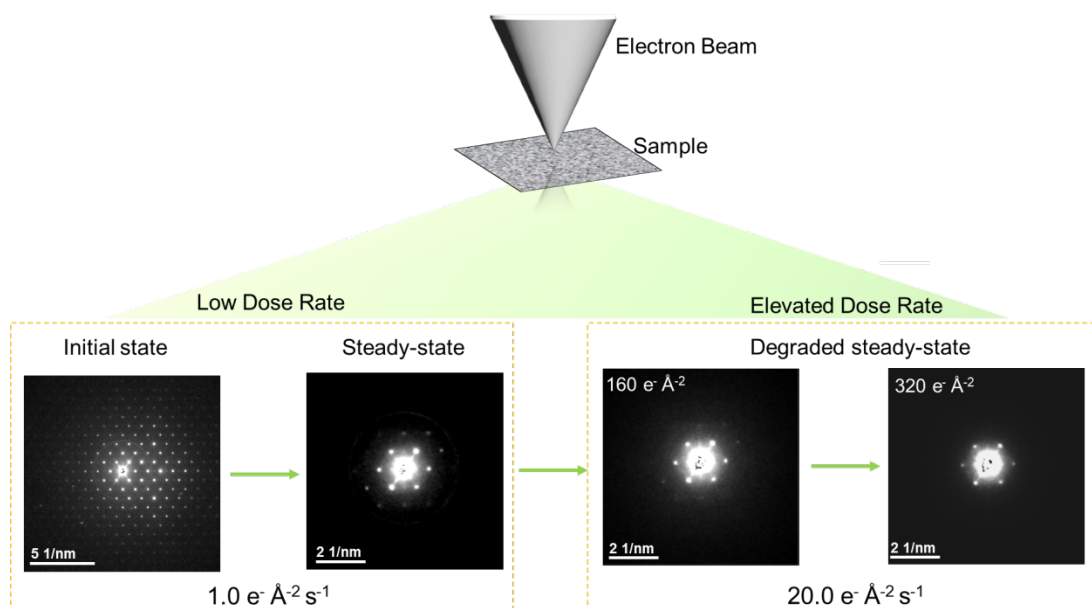


Fig. R10. ED patterns of the elevated dose rate after reaching steady-state at low dose rate for UiO-66(Hf) crystals.

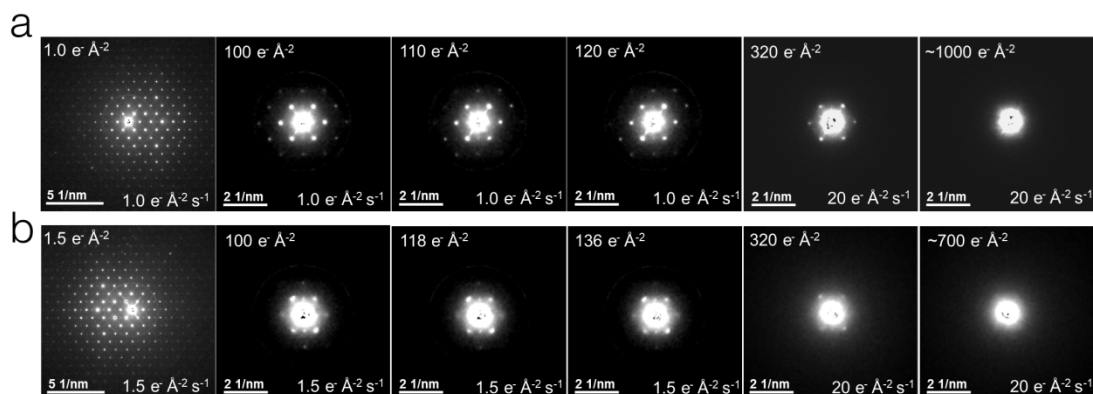


Fig. R11. (a-b) ED patterns of UiO-66(Hf) crystals exposed to an elevated dose rate of $20 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ after reaching steady-state.

Since most of results presented in this manuscript are not novel, I cannot recommend publishing it in high-profile journal Nature Communications. Specialized journal will be more appropriate for this work. But, before submitting it in another journal, I would recommend authors to compare their observations with those report by Ghosh et al and discuss similarities and differences. Also, I would recommend authors to fix many technical deficiencies indicated below.

Response: We thank the reviewer for these comments. In our previous response to the reviewer's question, we fully addressed concerns regarding the novelty of this work. The novelty primarily stems from our original findings, which were obtained through the state-of-the-art low-dose imaging technique and involved the visualization of structural dynamics under electron beam radiation. In this question, based on the reviewer's comments regarding the paper by Ghosh *et al* (*Chem. Mater.* **2021**, 33, 5681–5689), our response aims to address these concerns from a technical perspective.

Research Findings

(1) On the quantitative correlation between crystal contraction of MOFs and evolution of structural parameters. The crystal contraction of MOFs under electron

beam radiation is usually and intuitively related with the shrinkage of crystal lattice. While traditional structural characterization tools are limited to diffraction technique that measures the evolution of average lattice parameters upon radiation, such as conducted in the work by Ghosh *et al* (*Chem. Mater.* **2021**, 33, 5681–5689). However, in reality, as one can measure by morphological evolutions in TEM, the crystal contraction ratio of MOF crystals easily exceeds 10% upon beam radiation (Fig. S4). In this revision, we provide a movie that continuously tracked the shape evolution of a $[1\bar{1}0]$ projected UiO-66(Hf) crystal upon radiation as *Attachment 1*. It shows that after prolonged electron beam radiation, the anisotropic crystal contraction even exceeds 16% and 11% along long and short axes of the octahedral crystal respectively in Fig. R12. Apparently, such a huge crystal contraction cannot arise from the shrinkage of crystal lattice alone, as the range for stretching or compressing chemical bonds is significantly limited. Consequently, the exact physical origin of this substantial crystal contraction remains enigmatic without the valuable insights gained from real space visualization approaches. We unravel by integrating low-dose real space imaging that the overall crystal contraction is contributed by the concurrent intragranular and intergranular contractions. We hereby develop a coarse-grained strain analysis (CG-SA) method and integrate the geometric phase analysis (GPA) method, to simultaneously quantify the dose-dependent intergranular and intragranular deformations of the crystal. The results indicate that the crystal contraction is predominantly contributed by the intergranular deformation arising from volumetric shrinkage through amorphization. Only at an elevated cumulative dose, intragranular deformation (i.e. lattice contraction) occurs and arises from the knockout of bridging BDC linkers in the UiO-66(Hf) framework.

(2) On the spatial distribution and dynamics of amorphized domains. The radiation damage of crystalline matters is usually quantitatively measured by ED dose series through the fading of high-order *Bragg* spots. Nevertheless, this approach falls short in providing real space structural information that encompasses the dose-dependent spatial distribution and dynamics of amorphized domains resulting from radiation exposure. Intuitively, one would expect the emergence and continuous

growth of amorphous domains under radiation. However, in reality, the observed phenomenon reveals the repeated emergence and disappearance of these domains, governed by a nonclassical reversible radiolysis mechanism. This mechanism is characterized by self-repairing events and is quantitatively described by a first-order kinetic model. The validity of these findings is further confirmed through a combination of AIMD simulations and measurements of the dose-rate effect on steady-state structures. Moreover, this provides insights into materials that exhibit a dose rate threshold, offering a plausible interpretation for their behavior.

(3) On the behavior and mechanism of non-specific and site-specific metal-linker bond breakage upon radiation. The radiation-induced structural damage of MOFs is commonly attributed to a radiolysis mechanism, where in the metal-linker bonds of the same type are non-selectively broken through ionization. The corresponding long-lived excitations subsequently drive atomic displacements towards permanent structural damage through energy-momentum conversion *via* thermal vibration, local Coulomb repulsion, or in most cases the combination of both. This results in the collapse of porous crystalline framework and amorphization of illuminated domains. The lack of insights into specific types of metal-linker breakage events, which go beyond the radiolysis mechanism, stems from the challenge of accurately identifying structural evolutions at the molecular level in real space. By low-dose imaging to monitor the dynamic radiation damage process, we observe a brand-new type of damage event dictated by the site-specific removal of bridging BDC linkers in crystalline UiO-66(Hf) domains before amorphization occurs. This is attributed to presence of a nonclassical radiolysis-enhanced knock-on displacement mechanism, which arises from the site-selective alteration of metal-linker binding energies caused by anisotropic lattice deformation of UiO-66(Hf). These findings are also cross-validated by combined DFT simulations and low-dose cryo-TEM imaging.

Contributions

Taken together, this study has made groundbreaking contributions that significantly impact research fields from multiple aspects. *1) Research Paradigm.* This work has

established a new research paradigm and serves as an exemplary model for investigating dynamic structural changes in beam-sensitive materials. By utilizing in-situ low-dose electron microscopy, the study has achieved the long-standing and elusive goal of visualizing dynamic processes in real space with high spatial resolution for materials such as zeolites, MOFs, and COFs. This achievement carries profound significance across diverse fields in chemistry and materials sciences. **II) Fundamental Physics.** The study has revealed nonclassical mechanisms, expanding the theoretical framework of radiation damage beyond classical mechanisms. These findings provide vital physical insights into electron-matter interactions, serving as the cornerstone for advancements in modern electron-beam lithography and electron microscopy. **III) Technical Innovations.** Within this work, the introduction of the coarse-grained strain analysis (CG-SA) method, coupled with the integration of the geometric phase analysis (GPA) method, presents a comprehensive solution for the quantitative and collaborative analysis of intricate hybrid materials. These materials encompass both crystalline and amorphous domains, enabling the examination of dynamic structural deformations at both intra- and intergranular levels. The profound insights gained into nonclassical mechanisms, and their associated events serve as a catalyst, inspiring the development of mechanism-specific techniques to circumvent damage in electron microscopy. Furthermore, this achievement imparts us with the remarkable capability to discern between pristine and artificially induced structural features visualized through electron microscopy.

The current study, in essence, transcends the realm of routine research within a specific topic. It represents a synergistic amalgamation of new techniques, new observations, and new mechanisms. We believe that the exceptional attributes of our work merit its publication in prestigious journals, such as Nature Communications.

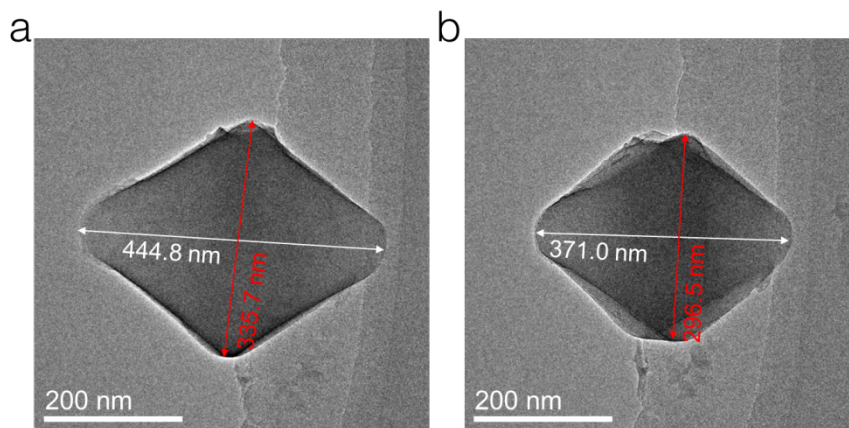


Fig. R12. (a-b) TEM images of the UiO-66(Hf) crystal in the initial state (a) and in the final state (b).

Technical Side:

Sentences and phrases are a bit awkward. Page numbers are missing. Technical terminology is used loosely and, in many places, incorrectly. The figures and panels are not cited in chronological order. Captions are not complete/clear. I would recommend editorial overhaul of this manuscript and SI file.

Response: We sincerely appreciate the valuable suggestion provided by the reviewer. In response, we have implemented the recommended changes to enhance the overall clarity and conciseness of the main text and Supplementary Information (SI). This includes adding detailed technical information reorganizing the SI file, and rectifying any improper sentences and phrases identified in the main text and figure captions. Furthermore, we have incorporated page numbers into the main text for improved accessibility and referencing. In addition, we have taken care to provide detailed descriptions of technical terms used in the formulas, ensuring clarity and understanding for readers in both the main text and the SI file. According to the reviewer's suggestion, we have also reordered some of the figures and panels, included subheadings and descriptions in the caption section to improve overall readability and facilitate better understanding of the research findings.

Specifically, we have provided explanations for the terms in equation (9), such as “ e^- is the electronic charge” and “ v is the velocity of the electron, c is the speed of light”

on page 17. Additionally, supplementary explanations for the terms used in each equation have been added on page 7 of the SI file.

Moreover, we have divided Fig. 2 into two separate Fig. 3 and Fig. 4 to improve the readability, while rearranging and formatting sub-panels c, d, e, and f in Fig. 6 to ensure the order of references to the figures. Additionally, we have added labels in Fig. S3, S5 and S6, and included supplementary explanations in the captions to enhance clarity.

The manuscript somewhat poorly organized. For example, the entire first paragraph in Results and discussion section, which is two page long and need reorganization, clearly belongs to Introduction section. The Introduction section is unnecessarily long and missing citations to critical papers, particularly on radiolysis.

Response: We thank the reviewer for the comments. In response, we have restructured the results and discussion section to improve coherence of the manuscript. Specifically, we have relocated the following paragraph to the introduction section on page 5:

“As a unique class of crystalline porous materials featuring tunable topologies, large specific surface areas, and adjustable chemical compositions, MOFs are promising candidates for catalysis^{37,38}, gas storage and separation³⁹, energy storage and conversion⁴⁰, chemical sensing⁴¹, water adsorption^{42,43}, and lithium-ion storage⁴⁴. The precise structural elucidation of MOFs by traditional EM is however challenging because they are extremely beam-sensitive and predominantly subjected to radiolytic damage^{27,29,45}. For instance, MIL-101(Cr) was reported to withstand an electron dose of approximately $16 \text{ e}^- \text{ \AA}^{-2}$ ⁴⁶. The high order reflection of UiO-66(Zr) starts to fade when the cumulative dose reaches about $17 \text{ e}^- \text{ \AA}^{-2}$ ¹⁹, while the crystallinity of ZIF-8(Zn) quickly lost at a dose as low as $25 \text{ e}^- \text{ \AA}^{-2}$ ⁴⁷.”.

Furthermore, we have relocated the short paragraph beginning with “Integrating both classical and nonclassical damage events occurring in UiO-66(Hf), a complete physical picture of different stages of radiation damage mechanisms and their logical relations are summarized in Fig. 1.” to the beginning of the second paragraph on page

7, as highlighted.

Moreover, we have incorporated key citations in the radiolysis section of the manuscript, such as: “These mechanisms encompass knock-on displacement and radiolysis (ionization) as the primary damage mechanisms. Additionally, electrostatic charging, electron-beam heating, and other secondary or ternary events such as diffusion, contamination, and segregation further contribute to the overall understanding of radiation-induced phenomena¹ (*Micron*. **2004**, *35*, 399-409).” on page 3.

“In contrast to knock-on displacement that dominates radiation damage in conducting materials, radiolysis usually dominates in non-conducting materials and arises from inelastic scattering of primary and secondary electrons that creates long-lived electronic excitations ($\tau > 1$ ps) to drive atomic displacements towards permanent breakage and reformation of chemical bonds^{3,9,10} (*Micron*. **2019**, *119*, 72-87; *Dertinger, H. et al*, ISBN: 978-0-387-90013-1, **1970**; *J. Phys.: Condens. Matter*. **1993**, *5*, 995). Such energy-momentum conversion can be readily achieved by thermal vibration, local Coulomb repulsion, or in most cases the combination of both, which leads to temperature-dependent radiolytic structural damage⁸ (*Rep. Prog. Phys.* **2016**, *79*, 016501). The radiolysis cross section can be approximately estimated based on the Bethe ionization cross section model¹¹ (*Rev. Mod. Phys.* **1971**, *43*, 297-347) by summing up corresponding terms for individual electron shells considering the efficiency of radiolytic damage transferred from ionization events^{12,13} (*Phys. Rev. A*. **1994**, *50*, 3954-3967; *J. Phys. Chem. Ref. Data*, **2014**, *43*, 013102).” on pages 3 and 4.

“The radiolytic damage basically follows first-order kinetics, and similar to the half-life of radioactive decay, a critical dose (D_c) that dictates the vulnerability of the materials can be derived by fitting the exponential decay of ED intensities^{3,49-51} (*Micron*. **2019**, *119*, 72-87; *Chem. Mater.* **2021**, *33*, 5681–5689; *Proc. Nat. Acad. Sci.* **2022**, *119*, e2200290119; *Microsc. Microanal.* **2018**, *24*, 1988-1989).” on page 6.

“Primary radiolysis originates from electronic excitations at a very short time scale (~ 0.1 fs) followed by immediate bond dissociation ($\sim$ fs) but requires momentum

transfer and long-lived core-hole excitation states (> 1 ps) to drive mechanical displacement of molecular ligand groups and structural damage of MOFs through coupling with vibrations (~ 0.1 to ~ 1 ps) and/or Coulomb Coulomb interactions (~ 0.01 ps)^{8,52,54,55} (*Rep. Prog. Phys.* **2016**, 79, 016501; *Prog. Surf. Sci.* **1989**, 32, 211-332; *Phys. Rev. Lett.* **2021**, 126, 117403; *Phys. Rev. B.* **2020**, 101, 235310).” on page 7.”

In the early part of the manuscript, pages (??), where authors are discussing results in Figure 2(e-h) and arguing based on GPA analysis that at lower electron doses amorphization occur, amorphization should be also visible in their experimental diffraction patterns (broad rings). Can they show that? It is much simpler and more direct way of proving it.

Response: We thank the reviewer for the comments. While real space imaging offers an opportunity to directly visualize the amorphization process and distribution of amorphous domains, electron diffraction also allows the monitoring of amorphization process for a $[1\bar{1}0]$ oriented UiO-66(Hf) crystal through the continuous degradation of Bragg diffraction spots, as depicted in Fig. R13a. Sometimes, as mentioned by the reviewer, the beam damage creates randomly oriented and short-range ordered domains with different coherence lengths. These domains give rise to diffuse scattering rings with different intensities and band widths. In the case of domains that are nearly completely amorphized, the diffuse scattering rings often lack discernible clarity due to their weak and broad nature. However, upon meticulous examination of the ED pattern at an elevated electron dose of $100\text{ e}^- \text{ \AA}^{-2}$, as depicted in Fig. R13a, a weak and broad diffuse scattering ring is barely visible near the direct beam. Notably, this diffuse scattering ring disappears entirely when the cumulative electron dose reaches as high as $1000\text{ e}^- \text{ \AA}^{-2}$, signifying the complete amorphization of the MOF structure. Furthermore, we sought to replicate this phenomenon by creating supercell models that mimic pristine, partially damaged, and completely amorphized structures, as shown in Fig.13b. These models were meticulously constructed to represent three distinct structures: a perfect crystal structure, a structure with broken metal-linker

bonds, and a structure with randomly packed atoms. Notably, all three models maintain an identical stoichiometry. Dynamic electron diffraction simulations of these structures are conducted using multi-slice method and the results are shown in Fig. R13c-e. The presence of distinct and sharp Bragg spots characterizes the perfect lattice, while the high-distortion lattice with broken metal-linker bonds exhibits a degradation of these sharp spots, accompanied by the emergence of diffuse scattering arcs. As for the disordered structure, the diffuse scattering bands are nearly absent, coinciding well with experimental observations.

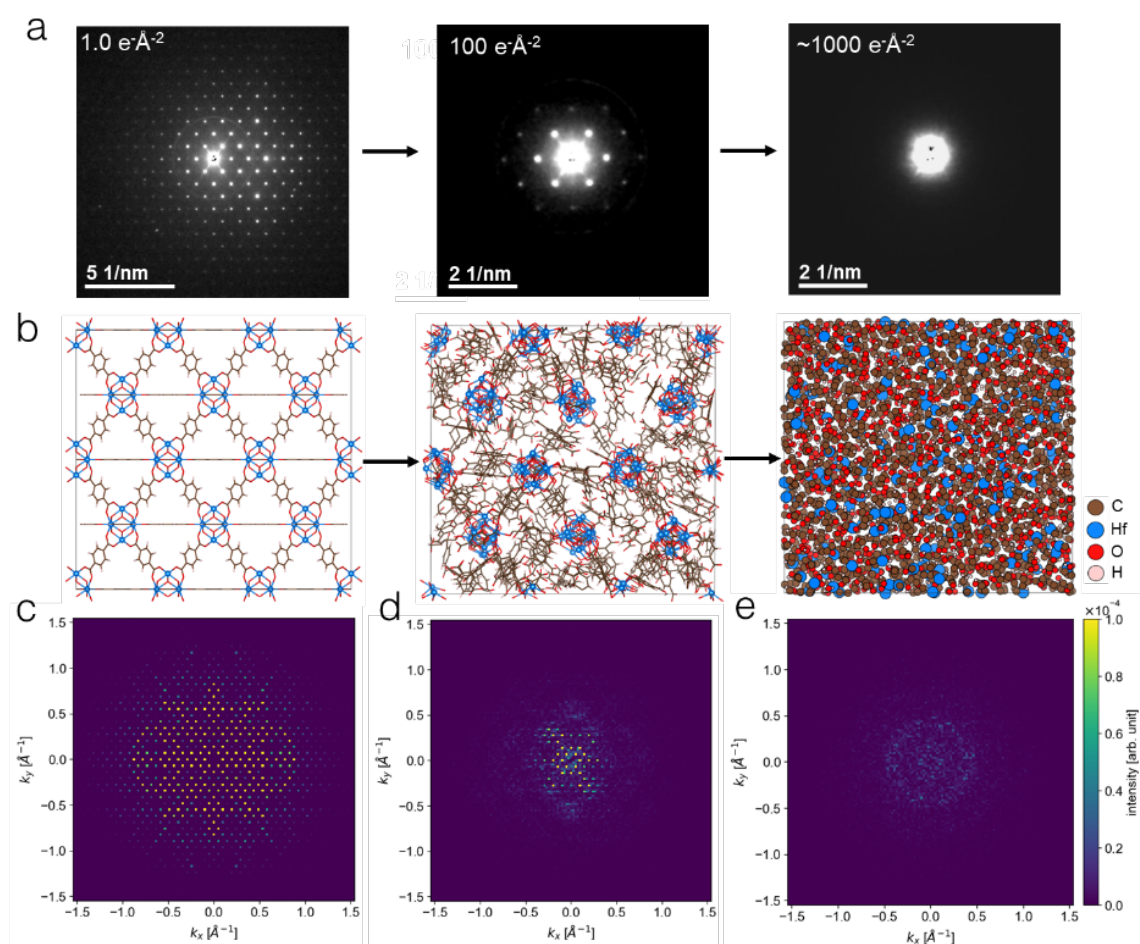


Fig. R13. (a) The ED pattern of UiO-66(Hf) crystals at various electron doses. (b) The structural models of pristine, partially damaged, and completely amorphized for ED simulation. (c-e) The ED simulations corresponding to structural models in (b), respectively. Here, “k_x” and “k_y” refer to inverse space distance along x and y directions. The direct beam is blocked as it typically has a much higher intensity than the scattered beams.

Authors state that “We have proved by ab initio molecular dynamics (AIMD) simulations that an equilibrated supercell UiO-66(Hf) model with massive broken bonds exhibits significant volumetric shrinkage and elevated density (from 1.62 to 2.09 g cm⁻³) due to the collapsed porous network (Fig. S7).” It is not clear how in these simulations the electron beam irradiation and its effects are incorporated. What are the input parameters?

Response: We thank the reviewer for the comments. We clarify that a complete radiolytic damage event encompasses two consecutive stages, i) bond ionization under illuminated condition, and ii) atomic displacement under dark condition. Radiolysis usually dominates in non-conductive materials and ionizes chemical bonds through inelastic scattering events by electron radiation, creating long-lived electron excitations ($\tau > 1$ ps). These excitations subsequently drive atomic displacements, leading to permanent structural damage through energy-momentum conversion based on thermal vibrations, local Coulomb repulsion, or a combination of both (*Micron.* **2019**, 120, 96-103; *Rep. Prog. Phys.* **2016**, 79, 016501). The structural relaxation process, arising from ionized intermediate structures featuring multiple dangling bonds, plays a crucial role in the dynamic relinkage and cross-linkage of metal-linker bonds. These relaxation events are paramount in understanding the overall structural damage induced by radiation and can occur independently of the illuminated condition. Importantly, they provide a fundamental basis for the experimentally observed phenomena of self-repairing, amorphization, structural collapse, and crystal contraction.

Accordingly, our ab initio molecular dynamics (AIMD) simulations focus on the dynamic structural relaxation of intermediate structures with dissociated metal-linker linkages and under dark conditions. On page 10 of the revised manuscript, we clarify that the AIMD simulation is based on spontaneous and post-ionization structural dynamics, which account for the amorphization induced volumetric contraction. The concurrent distortion of Hf₆O₄(OH)₄ nodes, misalignment and misconnection of metal-linker bonds enable us to visualize the structural relaxation and volumetric

contraction, resulting in a 22.3% reduction in volume. For clarity, specific parameters for both structural models (i.e. the intermediate and relaxed structures) and simulation process are added in the “**1.3.1 Models and visualization**” and “**1.3.3 Ab initio molecular dynamics (AIMD) simulations**” sections of the SI file as follows,

“1.3.1 Models and visualization

Models for the pristine and collapsed porous network structure

To better simulate the anisotropic contraction process of UiO-66(Hf), we chose the primitive cell with *P1* symmetry corresponding to the octahedron of UiO-66(Hf). We constructed a $2 \times 2 \times 2$ supercell, with lattice parameters $a_o = a_b = a_c = 29.10 \text{ \AA}$ and $\alpha = \beta = \gamma = 60.0^\circ$ based on an unstrained primitive cell as the pristine structure. Meanwhile, the supercell model incorporating multiple Hf-O broken bonds in $\text{Hf}_6\text{O}_4(\text{OH})_4$ nodes (i.e. 45/48 broken/overall BDC linkers) were constructed as the collapsed porous network structure.

All visualization of crystal structural models was conducted using the VESTA software (*J. Appl. Crystallogr.* **2011**, 44, 1272-1276).

1.3.3 Ab initio molecular dynamics (AIMD) simulations

For simulation of the pristine and collapsed porous network structures, the convergence criterion for the maximum and root-mean-square of atomic displacements was set to 0.005 and 0.0035 Bohr, respectively. The convergence criterion for the maximum and root-mean-square of atomic forces was set to 0.0045 and 0.003 Hartree/Bohr. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) quasi-Newton algorithm (*W.H. Press et al*, ISBN: 0-521-43064-X, **1992**) was used to optimize the geometry structure.”.

The ref [59] in main manuscript is not original papers, where equation (9) is derived. Correction is in order here.

Response: We thank the reviewer for the comments. We have made the necessary correction to reference [59] (*Scanning.* **1992**, 14, 86-90), updating it to [62-64] (*Proc. R. Soc. Lond. A.* **1932**, 135, 429-458; *Phys. Rev.* **1948**, 74, 1759-1763; *Bradley, C. R.* ANL-88-48, **1988**) on page 17.

In SI file, Details and technical specifications of the TEM used in these experiments are not provide, besides saying that “operated at 300 kV”. Additionally, a citation is missing where contrast-transfer-functon(CTF)-based image processing is discussed and justified. Stating “To simulate the projected electrostatic potentials, the QSTEM code [<http://qstem.org/>] was employed, ...” doesn’t have proper citations, just link to webpage.

Response: We thank the reviewer for the comments. In response, we have included detailed technical specifications of the TEM used in our experiments in section “**1.2 Structural Characterization**” in the SI file on page 3.

For instance: “**1.2.1 General Characterization**

Polycrystalline X-ray diffraction (PXRD, PANalytical X’Pert Powder diffractometer) was employed to validate the crystalline structures of the MOFs samples. Experimental transmission electron microscope (TEM) images of these samples were collected using an objective aberration corrected Thermo Fisher Scientific (TFS) Themis Environmental Transmission Electron Microscope (ETEM) equipped simultaneously with a Gatan OneView fiber coupled CMOS camera and a K3 electron counting direct detection camera, for conventional and low-dose high-resolution TEM imaging/diffraction applications respectively. The operating accelerating voltage was 300 kV, together with a beam convergence angle of 0.2 mrad and minimized aberrations using an image corrector. The microscope is also equipped with a high brightness electron gun (X-FEG) and a monochromator that was used to continuously control the beam current density and dose rate in this work.

1.2.2 Low-dose (cryogenic) TEM imaging and data processing.

The low-dose HRTEM image stacks were captured using an objective aberration corrected TFS Themis Environmental Transmission Electron Microscope (ETEM) equipped with Gatan K3 direct detection camera. The specific experimental setup is as follows: a Cs of about 1 μm , an acceleration voltage of 300 kV, and a maximum frame rate of 400 fps at an extremely low electron dose rate. Before acquisition, the specimens were searched, tilted to zone axis for optimal crystal structure information

retrieval using our reported low-dose imaging procedures (*Science*. **2018**, 359, 675-679) with a minimal dose consumption below $1 \text{ e}^- \text{ \AA}^{-2}$. Following the image stack acquisition, the dataset was subject to a motion correction procedure to fully restore high-frequency information. The motion-corrected image stack was then subject to a contrast-transfer-function (CTF) correction procedure to achieve chemically interpretable image. Low-dose cryogenic electron microscopy (cryo-EM) was conducted by a Gatan custom-designed double-tilt ultrastable cryo-transfer holder to investigate the low temperature effects on radiation damage behaviors.

1.2.3 Electron diffraction acquisition and data processing.

Electron diffraction patterns and dose series were acquired in diffraction mode by using Gatan OneView camera on a TFS ETEM. The acquisition parameters were adjusted upon required cumulative dose and dose rate.

The dataset of electron diffraction dose series can be transformed to visualize the fading dynamics of *Bragg* spots and mapped onto the axes for cumulative dose and reciprocal vector respectively through the following steps, i) The acquisition of the electron diffraction dose series; ii) The correction of drift in the stack; iii) The radial averaging of diffraction patterns within the stack, and iv) The creation of a 1D projection of the diffraction pattern, spanning along the stack direction to accumulate the electron dose. The fading dynamics of a specific *Bragg* spot can be profiled and then fitted by the exponential decay function to derive the D_c value.

Additionally, following the reviewer's suggestion, we have added citations about the image processing procedures and CTF correction in this revision, such "The motion-corrected image stack was then subject to a contrast-transfer-function (CTF) correction procedure¹ (*Science*. **2018**, 359, 675-679) to achieve chemically interpretable image." on page 4 of the SI file, as highlighted. Moreover, we have included citations and deleted the links for the QSTEM simulation code. For instance: "The QSTEM⁴ (*C. T. Koch*. ISBN: 9780493562612, **2002**) code was employed to simulate the projected electrostatic potentials, convoluted with a point-spread-function (PSF) of specific width ($2.1 \text{ \AA}$) corresponding to the crystalline structural information transfer of the low-dose HRTEM image." on page 6 of the SI

file.

In SI file, when authors discussing the Mott cross-section (σ_K), neither citation is accurate/complete nor the terms in the equations (S5-S7) are explained. Therefore, it can't be used to evaluate the results discussed in main manuscript. It is true for eq. (9) in main manuscript.

Response: We thank the reviewer for the comments. We have added references to “By evaluating analytically the McKinley-Feshbach asymptotic approximation of the Mott cross-section^{9,10} (*Proc. R. Soc. Lond. A.* **1932**, 135, 429-458; *Phys. Rev.* **1948**, 74, 1759-1763)” on page 7 of SI file and “The probabilities for knock-on damage arising from events such as generation of Frenkel pairs, vacancy-enhanced displacement and surface sputtering⁶²⁻⁶⁴ (*Proc. R. Soc. Lond. A.* **1932**, 135, 429-458; *Phys. Rev.* **1948**, 74, 1759-1763; *Bradley, C. R.* ANL-88-48, **1988**)” on page 17 of the manuscript. Additionally, explanations for the terms in equations (S5-S7) and eq. (9) have been respectively provided on page 7 of the SI file and on page 17 of the manuscript.

Reviewer #3 (Remarks to the Author):

This manuscript reports calculations and experimental results relating to electron-beam damage to a MOF [crystalline UiO-66(Hf)] during examination in a TEM. It includes an extensive discussion and references to previous work by the authors and other researchers.

Damage is found to be inhomogeneous and dependent on dose rate and the explanation involves both radiolysis, knock-on displacement and reverse reactions (repair mechanisms). An interesting temperature dependence of damage is noted (hidden away in Supplementary Information) but not really explained.

The work is original and casts light on the beam damage mechanisms in

metal-organic frameworks, with possible relevance to other systems. It is certainly worthy of publication and my only criticisms are technical matters:

Response: We thank the reviewer for commendation and the insightful comments. These suggestions are greatly helpful for improving the quality of our manuscript.

1. The GPA, CG-SA, DFT and AIMD calculations are highly technical and are necessarily incompletely explained in a relatively brief article such as this. The section “Data and Code Availability” contains the statement “This study did not generate any datasets”. Can the authors not make some of the important details accessible to the scientific public?

Response: We thank the reviewer for the suggestion. Details regarding the methodologies for GPA, CG-SA, DFT, and AIMD methods are provided in the “**1.2.4 Image analysis and simulation**” and “**1.3 Theoretical Calculations**” section of the SI file. Following the reviewer’s suggestion, we have deleted the statement “This study did not generate any datasets” on page 25 and have added the statement “The methods for Chemical Synthesis, Structural Characterization, and Theoretical Calculations are available in the supporting information. Additional data that support the findings of this study are available from the corresponding author upon request.” on page 20. Additionally, we have removed the section “Data and Code Availability” on page 25 to comply with the journal’s format requirements, changing it to the “Data availability” section on page 20.

2. The six Figures are very elaborate, to the extent that some of the details are unreadable. I recommend that each Figure be split into two so that it becomes clearer and more digestible.

Response: According to the reviewer’s advice and to maintain an acceptable length and number of items for the whole manuscript, we have split the most crowded Fig. 2 into two separated figures as the new Fig. 2 and Fig. 3 in the revision for clarity.

Below are a few suggested minor changes to the English:

Response: We thank the reviewer for pointing out these English issues.

line 73: thresholds termed as => thresholds, termed

Response: We have corrected “thresholds termed as” to “thresholds, termed” on page 3.

line 88: local Columb repulsion => local Coulomb repulsion

Response: We have corrected the term “local Columb repulsion” to “local Coulomb repulsion” on page 3. Additionally, we have rectified “Columb interactions” to “Coulomb interactions” on page 7, as well as “local Columb repulsion” to “local Coulomb repulsion” on page 26.

lines 142,195,382,394: positive dose rate effect presumably means direct dose-rate effect?

Response: We thank the reviewer for the comments. Indeed, in this work, we used “positive dose rate effect” term to describe the “direct dose-rate effect”. Specifically, this means that as the dose rate increases, the radiation damage per dose increases. To avoid potential confusion, we have replaced the “positive dose rate effect” by the more often used “direct dose-rate effect” in the revised manuscript.

line 168 often misaligned => often poorly defined

Response: We have corrected “often misaligned” to “often poorly defined” on page 7.

line 178: a complete physical picture of => different stages of

Response: We have corrected “a complete physical picture of” to “different stages of” on page 7.

line 222: an immediate outcome upon the homogeneous illumination of electron beam is the => an immediate outcome of homogeneous illumination of the electron beam is a

Response: We have corrected “an immediate outcome upon the homogeneous illumination of electron beam is the” to “an immediate outcome of homogeneous illumination of the electron beam is a” on page 8.

line 391: and can be experimentally validated. => that can be experimentally validated.

Response: We have corrected “and can be experimentally validated.” to “that can be experimentally validated.” on page 14.

line 570: Columb => Coulomb

Response: We have corrected “Columb” to “Coulomb” on page 26.

Reviewer #4 (Remarks to the Author):

In this study, Xu and coauthors unravelling nonclassical beam damage mechanisms in metal-organic frameworks via low-dose TEM and ab initio simulations. Through the real-space visualization, they observed radiation-induced structure dynamics at morphological, lattice, and molecular levels. In addition to the classical beam damage mechanism, they propose reversible radiolysis and radiolysis-enhanced knock-on displacement mechanism. Overall, this work enriches the fundamental understanding of damage mechanism for TEM characterizations and potentially inspire the development of new methodologies and techniques in the fields of electron-beam lithography and electron microscopy.

Several issues need to be addressed before publication, which are detailed below.

Response: We sincerely thank the reviewer’s insightful comments and suggestions, which greatly improve the overall quality of our manuscript.

What concerns me most is that this article involves a great deal of professional knowledge of electron microscope, which makes it difficult for researchers in the non-TEM field to understand.

How to obtain Fig. 2b as well as the dose information?

Response: We thank the reviewer for the comments. To clarify the processing workflow for obtaining the Fig. 2b from the electron diffraction dose series, the following steps were taken:

- i) The acquisition of the electron diffraction dose series.
- ii) The correction of drift in the stack.
- iii) The radial averaging of diffraction patterns within the stack.
- iv) The creation of a 1D projection of the diffraction pattern, spanning along the stack direction to accumulate the electron dose.

Accurate measurement of the dose and dose rate during the electron diffraction acquisition was accomplished through electron counting using a direct detection camera. In order to facilitate the understanding of technical parts to wider audience, we include these technical details in the “**1.2 Structural Characterization**” section of the Supporting Information (SI). Moreover, all technical specifications of both TEM imaging and diffraction experiments are more detailed described in “**Section 1.2.2 Low-dose (cryogenic) TEM imaging and data processing**” and “**Section 1.2.3 Electron diffraction acquisition and data processing**” of the SI file on page 4.

How to identify the amorphized region in Fig. 2h? Since the crystalline-amorphous interconversion can be identified from Fig. 2h, please also provide the pristine HRTEM images, which can directly present the crystalline and amorphous region. In addition, how does Fig. 2h relate with Fig. 2g? As stated in the line 246, the GPA results suggest there is no remarkable crystal contraction at $64.7 \text{ e } \text{\AA}^{-2}$, however, ϵ_{xx} and ϵ_{yy} in Fig. 2g reached about $\sim 7\%$ at $45 \text{ e } \text{\AA}^{-2}$.

Response: We thank the reviewer for the comments. In Fig. 2h (Fig. 3d in the revised main text), the amorphous domains can be explicitly visualized by negative masking of Bragg-filtered crystalline domains in the serial HRTEM images under different electron dose as shown in white stripe-like regions. To better visualize the crystalline and amorphous regions, the serial HRTEM images are rendered in a false-color code as shown in Fig. R14 (Fig. S13). The amorphous domains are rendered in green and

marked with red arrows, while the crystalline domains are rendered in blue. Following the reviewer's suggestion, we have provided the pristine HRTEM images as shown in *Attachment 3*. The discrimination between crystalline and amorphous domains is straightforward from the image based on both lattice contrast and diffraction contrast. Specifically, the crystalline domains exhibit both strong lattice contrast and diffraction contrast that degrades in amorphous domains. The white rectangles in the HRTEM images highlight the amorphous domains.

In addition, we hereby clarify that the overall crystal deformation is contributed by the concurrent intergranular and intragranular deformations as shown in Fig. 3a. These two types of deformations can be quantitatively evaluated by coarse-grained strain analysis (CG-SA) method and geometric phase analysis (GPA) method, as shown in Fig. 3b-c and Fig. 3d respectively. As mentioned by the reviewer, the intragranular deformation is negligible as evaluated by GPA method and shown in Fig. 3d at a cumulative dose below $64.7 \text{ e}^- \text{ \AA}^{-2}$. On the contrary, the intergranular deformation becomes already remarkable as measured by CG-SA method and shown in Fig. 2g (Fig. 3c in the revised main text). These results indicate that the crystal contraction is predominantly contributed by the intergranular deformation arising from volumetric shrinkage through amorphization. Only at an elevated cumulative dose, intragranular deformation (i.e. lattice contraction) occurs and arises from the knockout of bridging BDC linkers in the UiO-66(Hf) framework. In this revision, the methods have been described in more details in “**1.2.4 Image analysis and simulation**” Section on page 5 of the Supporting Information (SI).

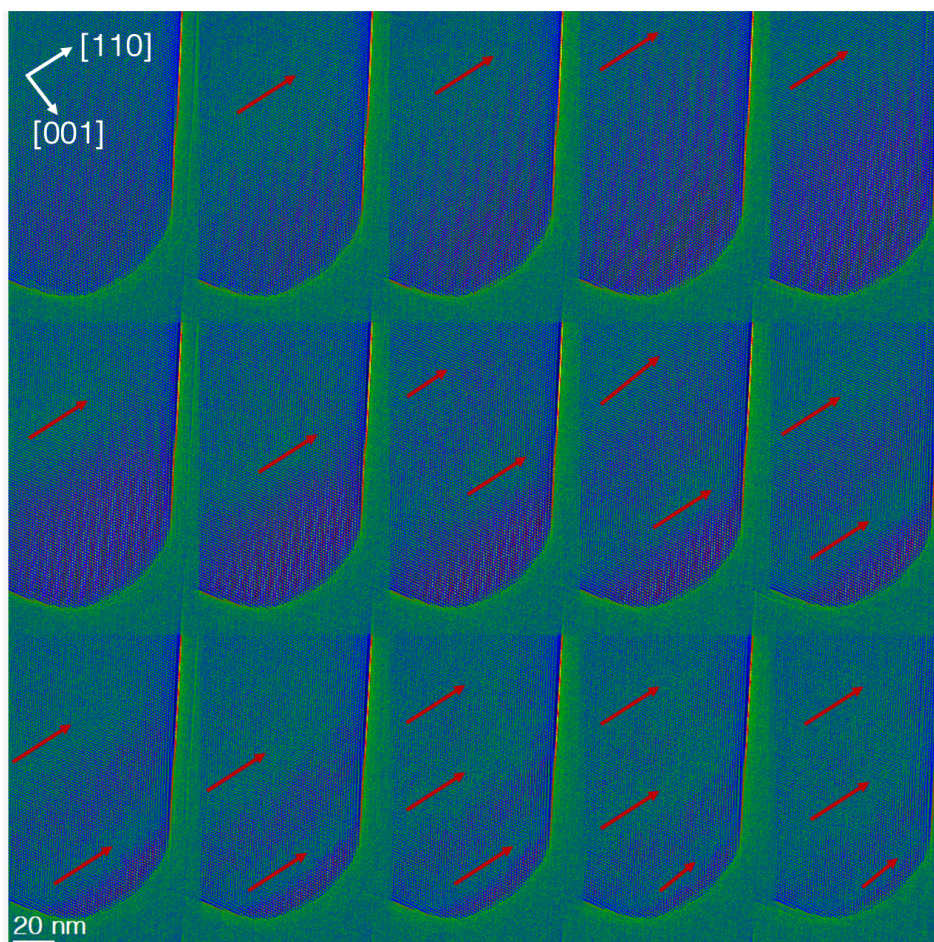


Fig. R14. Serial CTF-corrected HRTEM images for UiO-66(Hf) crystals along the $[1\bar{1}0]$ projection. These images were obtained under increasing accumulated electron doses ranging from $8.0 \text{ e}^- \text{ \AA}^{-2}$ to $121.5 \text{ e}^- \text{ \AA}^{-2}$.

Time scales should be unified into picosecond for better comparison.

Response: We thank the reviewer for the suggestion. We have revised the time on page 7 from “Coulomb interactions ($\sim 10 \text{ fs}$)” to “Coulomb interactions ($\sim 0.01 \text{ ps}$)”. Additionally, we have corrected “400 fs” and “595 fs” in Fig. 4d to “0.4 ps” and “0.6 ps”, respectively.

The maximum D_c is reached at $-50 \text{ }^\circ\text{C}$, why does this value decrease with lower temperature. Will this behavior be influenced by the dose rate?

Response: We thank the reviewer for the insightful comments. The temperature dependence of D_c on MOFs materials is indeed an intriguing phenomenon that

deserves in-depth study. We have accordingly conducted preliminary experiments and try to unravel the physical origin of non-monotonic temperature dependence of D_c value. Here we would like to share with the reviewer our interesting experimental observations. Firstly, following the reviewer's suggestion, we explore the influence of dose rate on this behavior by conducting low-temperature experiments on ED dose series and fitting results to achieve D_c at a dose rate of $1.0 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ and $3.0 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$, as shown in Fig. R15a. Despite the noticeable decrease in the D_c value at a higher dose rate of $3.0 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ as depicted to the direct dose rate effect, the overall temperature dependence of the system exhibits a similar behavior to that observed at a lower dose rate. This consistency is demonstrated in Fig. R15b, which provides a strong implication that the temperature dependence of D_c originates from intrinsic structural evolution in response to temperature variation. Through a synergistic integration of theoretical simulations and experimental data, we try to unravel the intricate factors contributing to this captivating phenomenon.

i) The temperature dependence of radiolysis. The radiolytic events stem from the chemical bond ionization followed by the formation long-lived excitations ($\tau > 1 \text{ ps}$). These excitations subsequently drive atomic displacements, leading to permanent structural damage through energy-momentum conversion based on thermal vibrations, local Coulomb repulsion, or a combination of both (*Micron.* **2019**, 120, 96-103; *Rep. Prog. Phys.* **2016**, 79, 016501). The damage probability attributed to thermal vibrations is weighted by the rate of individual atomic jumps. Usually, an Arrhenius law holds for the jump rate,

$$P = P_0 \exp\left(\frac{-\Delta G}{k_B T}\right)$$

in which k_B is the *Boltzmann* constant, ΔG is the Gibbs free energy of activation, T is the absolute temperature, and P_0 is the ‘attempt frequency’ proportional to the frequency of atomic vibrations. In this regard, lowering the temperature reduces the radiolytic damage.

ii) The temperature dependence of mechanical properties. The amorphization of MOFs is also closely related with the mechanical properties, and more specifically the

resistance against deformation that is attributed to the stiffness of the framework. To evaluate the temperature effects on mechanical properties of MOFs, we have conducted AIMD simulations of pristine and defective UiO-66(Hf) structures at different low temperatures and calculated the Young's modulus of these structures. Fig. R16a illustrates the construction of a model for the defective UiO-66(Hf) structure, where the bridging BDC linker within the framework is partially disconnected. This model is specifically designed to mimic the bond ionization that occurs due to partial radiolytic damage. Using the isothermal-isobaric (NPT) ensemble, we conducted simulations for 6 ps to relax the structural model to an equilibrium state at different temperatures. To further stabilize the structure, we performed canonical (NVT) ensemble simulations for an additional 2 ps, as shown in Fig. R16b and c, respectively. Each NPT and NVT simulation are initialized with a time of 300 fs. Consequently, we obtained structural models at different temperatures for further analysis. The inherent mechanical properties of pristine and defective UiO-66(Hf) structures can be compared by evaluating their respective Young's modulus at 0 K. The result is quite intuitive and shows that the pristine UiO-66(Hf) has a stiffer framework than defective UiO-66(Hf) structure ($E = 50.6 \text{ and } 22.4 \text{ GPa}$). In addition, when the influence of temperature is taken into account, as illustrated in Fig. R16d, it becomes evident that the Young's modulus exhibits a decreasing trend with decreasing temperature. Notably, this variation is significantly more pronounced in defective structures. The above-mentioned results show that the UiO-66(Hf) structure, when subjected to partial bond ionization, experiences a significant reduction in stiffness, which has already been experimentally observed in a polymer system at an elevated electron dose (*Jpn. J. Appl. Phys.* **2007**, 46, L1225). More importantly, both the pristine and defective UiO-66(Hf) structures demonstrate reduced stiffness and an increased susceptibility to deformation and structural damage at lower temperatures.

iii) The low temperature phase transition. Belonging to a type of porous coordination polymers with crystalline framework, MOFs are also expected to exhibit unique low temperature physical properties similar to organic polymers. However,

low-temperature physical properties and structural evolutions of MOFs have rarely been studied. By investigating the low temperature differential scanning calorimetry (DSC) of UiO-66(Hf), a step shaped change in heat capacity characteristic for the presence of glass transition ($T_g = -120.5^\circ\text{C}$) as second-order phase transition can be observed in Fig. R17. Such a glass transition can usually be observed in polymers that are not fully crystallized (i.e. semi-crystalline) and the transition from glassy to rubbery state takes place in the amorphous domains (*Colloid. Polym. Sci.* **2007**, 285, 575–580). Slowly heating the semi-crystalline polymer above the T_g entails the exothermic cold crystallization at a temperature of T_{cc} . Indeed, we did observe the exothermic peak in the DSC profile of UiO-66(Hf) that can be possibly attributed to the cold crystallization ($T_{cc} = -4.5^\circ\text{C}$). Diverging from the typical behavior exhibited by most polymers, which experience positive thermal expansion and increased heat capacity at the glass transition temperature (T_g) due to enhanced chain mobility for heat distribution, UiO-66(Hf) showcases a unique attribute. It demonstrates negative thermal expansion (NTE) (*Phys. Chem. Chem. Phys.* **2015**, 17, 11586-11592) and reduced heat capacity in its DSC profile at T_g . The presence of these unique features in DSC profile implies that the fast-cooling process of the cryogenic holder most likely introduce amorphous domains in the crystalline framework of UiO-66(Hf) within the low-temperature regime. As a result, both the temperature and radiation induced amorphization probably contribute to more rapid degradation of *Bragg* spots in ED pattern and thus a reduced D_c value.

In combination, these aforementioned effects, along with potentially other factors, collectively contribute to radiation damage within the low-temperature regime of MOFs. By conducting quantitative comparisons of these effects and incorporating a wider range of MOF materials, we aim to offer a more comprehensive and profound comprehension of the first-order and second-order phase transition events occurring at low temperatures, as well as their impact on the radiation damage mechanism. We intend to publish a separate study on this subject in the near future.

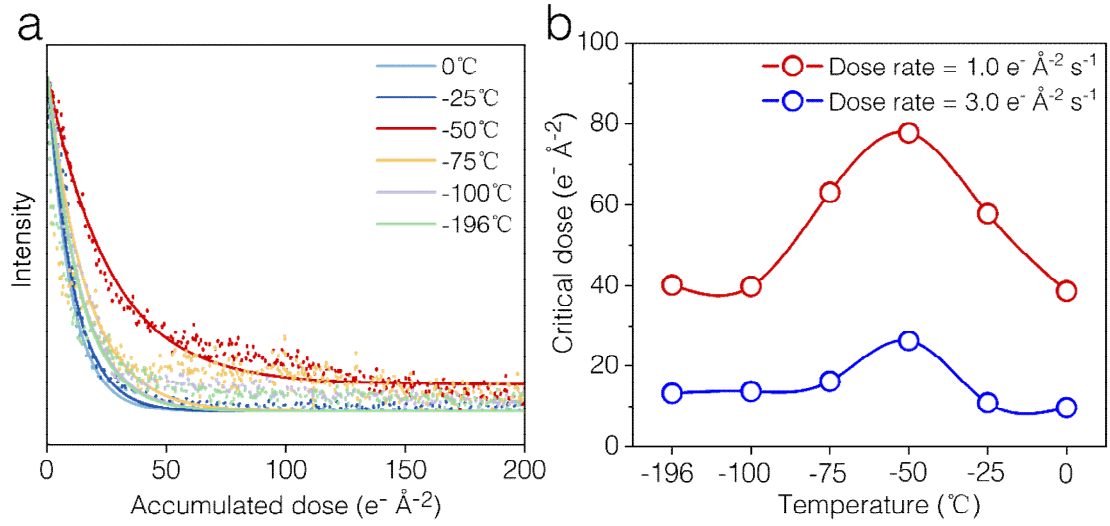


Fig. R15. (a) The exponential fitting of diffraction intensity decay curves as a function of accumulated electron dose for different temperatures with a dose rate of 3.0 $e^- \text{Å}^{-2} \text{s}^{-1}$. (b) The evolution of critical dose (D_c) with different doses rate at low temperature.

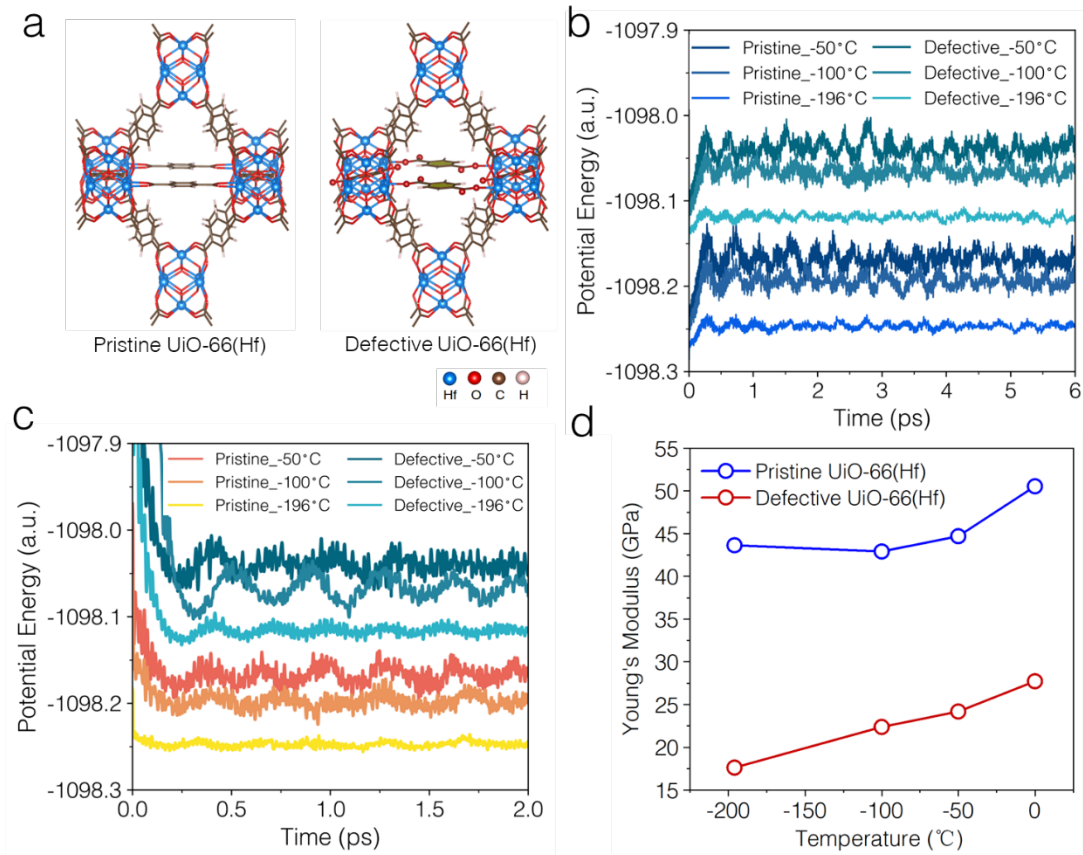


Fig. R16. (a) The corresponding structural model of pristine and defective UiO-66(Hf)

crystals. (b) The potential energy as a function of time for the AIMD simulation of UiO-66(Hf) in the NPT ensemble. (c) The potential energy as a function of time for the AIMD simulation of UiO-66(Hf) in the NVT ensemble. (d) The Young's modulus evolution of pristine and defective UiO-66(Hf) at various temperatures.

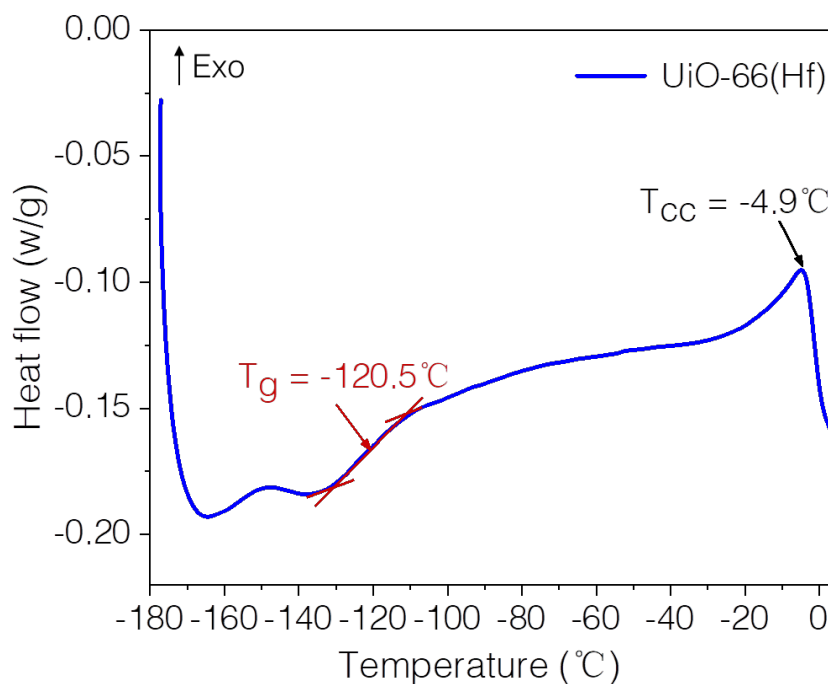


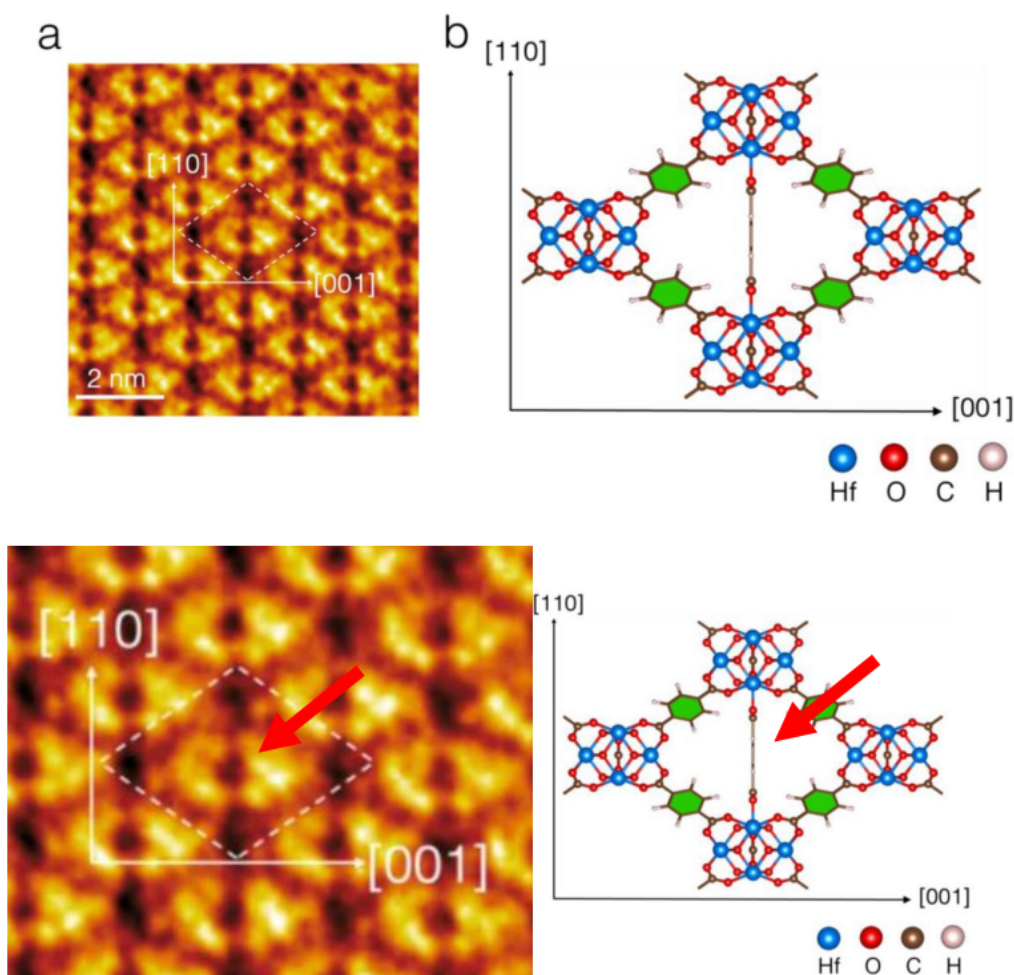
Fig. R17. The DSC curve of the UiO-66(Hf). The “ T_g ” represents the glass transition temperature, while “ T_{cc} ” refers to the cold crystallization temperature.

The authors are suggested to avoid the red and green colors in figures.

Response: We thank the reviewer’s suggestion. To avoid the use of red and green colors in the figures, we replaced the green color with yellow for the cascade self-repairing process in Fig. 4a and d on page 29. Additionally, we substituted the colors for 0°C and 25°C in the temperature scale of Fig. 7b, as well as in Fig. 7f for 0°C and 25°C, on page 32.

Reviewer #1 (Remarks to the Author):

The authors have made an extraordinary effort to response most of the concerns raised. The writing and manuscript organization has been improved which helps for a better understanding. Still there are a couple of points that I believe should be corrected.



I would ask the authors make an effort to explain the contrast indicated by the arrow. When I see the simulation in figure 5, that contrast is very different in the simulated image, the green dash oval is very weak in signal, while in the experimental image is very strong, equivalent to the metal node and it should be very weak as in theory that contrast is owed to C and O only. In the simulated data, aberrations or distortions or electron dose can be added, could they try to find a better fit between experimental and simulation?

Response: We thank the reviewer for raising this question. The discrepancy in contrast between the experimental and simulated data in the area of the bridging BDC

linkers originates from two primary factors. First, the spatial frequency dependent contrast reversals arising from the contrast transfer function (CTF) effects of objective lens need to be corrected in order to achieve image contrast closely resembles the projected electrostatic potentials and chemical structures. However, for low-dose imaging, to mitigate the interference of high-level shot noise near the CTF crossovers, a widely accepted correction approach only flips the signs of CTF profiles without correcting their amplitudes in the frequency domain. This results in interpretable image contrast approximately resembles the projected chemical structures, despite that the correlation between image contrast and projected electrostatic potential is not quantitative. Accordingly, as mentioned by the reviewer, the contrast of bridging BDC linker may deviate from that obtained by simulation under certain circumstances. Second, as a minor contribution, the shot noise directly impose contrast modulations under limited electron dose. These two factors collectively contribute to the observed discrepancy between experimental and simulated image contrast.

Following the reviewer's suggestions, we reproduced the contrast discrepancy of bridging BDC linkers between simulated CTF corrected HRTEM images under a defocus condition and projected electrostatic potential. A slight defocus condition, such as $\Delta f = -45$ nm used here, is usually employed to image MOFs in order to enhance the contrast. As shown in Fig. R1, the bridging BDC linker in the UiO-66(Hf) MOF structure exhibits much darker contrast (Fig. R1b) comparing with that of the simulated projected potential (Fig. R1a), as similarly observed experimentally after correcting the CTF effects of a slightly defocused HRTEM image.

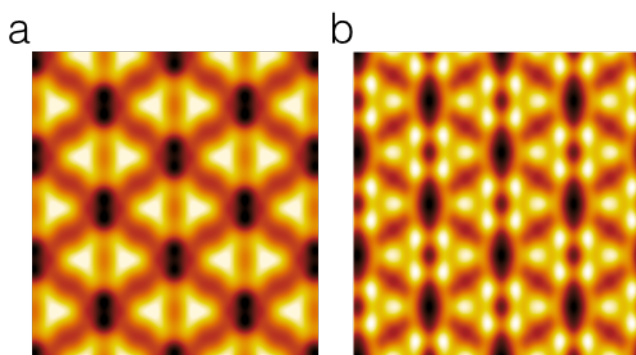


Fig. R1. (a) The simulated projected electrostatic potential of pristine UiO-66(Hf) structures with a point-spread-function (PSF) width of 2.5 Å. (b) Simulated HRTEM

image after conducting a CTF correction procedure. The simulation parameters used include a convergence angle of 1 mrad, $\Delta f = -45$ nm, $C_s = 10$ μ m, a focal spread of 5 nm and an objective aperture of 6 mrad.

Regarding the GPA analysis, I cannot find the white dashed square.

Response: We thank the reviewer for the comments. Following the reviewer's comments, we have used the white square as the reference area in the dose series HRTEM images for GPA analysis and mentioned in the captions as: "The reference region for GPA analysis is marked by a white square." in Fig. 3d, S5 and S6.

Reviewer #2 (Remarks to the Author):

This is my review of revised manuscript by Xu et al., on study of electron beam damage of UiO-66(Hf) MOF.

I appreciate that authors have taken time to respond to my comments. There are a few thing I agree and there are a few things I disagree.

Good news. All technical deficiencies that I highlighted in original review have been addressed. I am satisfied with changes made in manuscript in this regard. Those changes significantly improved the readability of the manuscript.

Response: We sincerely appreciate the reviewer's constructive suggestions, which greatly improve the quality of our manuscript. We thank the reviewer for the acknowledgment of our technical revisions.

Bad news. Authors responses to my concerns about novelty of this work is not satisfactory. Despite long arguments that authors have made in their responses, the main issue stays the same. Authors are arguing that they made the same observation of beam induced damage of MOF through high-resolution imaging, instead of

diffraction... While imaging is nice, it is still another technique of electron microscopy, and nothing special about it. Imaging-based analysis is analysis in real space and diffraction is analysis in reciprocal space. The main results stays the same. And I argue that the materials science portion of these results are already published in scientific literature. Reaching same answer with different method is nice confirmation of earlier report, but it is not groundbreaking achievement.

The fact that authors can reach the same main conclusions using imaging, is reinforcing my argument that this manuscript is really achievement in low-dose electron microscopy technique development and, therefore, the results are more suitable in electron microscopy journal such as Ultramicroscopy or Microscopy and Microanalysis.

The only portion of this work that is new, is recrystallizations of MOF, which is only small portion of this manuscript, unfortunately. More expansion on this topic could have been nice and would definitely deserve to be published in Nature Communications.

I can not recommend this manuscript for publication in Nature Communications.

Response: We regret that the reviewer does not appreciate the novelty of this work. However, we greatly thank reviewer's suggestion to expand on the recrystallization part of MOF and we totally agree that exploration in this part would further enhance this work. As mentioned by the reviewer: "The only portion of this work that is new is the recrystallizations of MOF, which is only a small portion of this manuscript, unfortunately. More expansion on this topic could have been nice and would definitely deserve to be published in Nature Communications." Following the reviewer's advice, we include in this revision exciting new observations after conducting extensive imaging work that integrated two cutting-edge imaging techniques together, namely environmental transmission electron microscopy (ETEM) and low-dose electron microscopy (LD-EM). Fig. R2 illustrate the schematic of a dedicated ETEM equipped with a differential pumping vacuum system. The integration of ETEM and LD-EM introduces a gas atmosphere as a new degree of freedom to modulate the beam-induced structural dynamics in electron

microscopy, which has not been reported before. This allows the dramatic alteration of the beam damage behaviors and kinetics of MOFs. The observation not only validates the proposed nonclassical mechanism but also provides a novel regulation strategy based on a previously unexplored physical parameter! These intriguing observations are achieved by simultaneously combining aberration-corrected ETEM, direct-detection electron detector (DDEC) and low-dose electron microscopy (LD-EM) methods developed by our group (*Science*. **2018**, 359, 675-679; *Nat. Mater.* **2017**, 16, 532; *Adv. Mater.* **2020**, 32, 1907619). The novelty of this work is ensured by the uniting of these leading tools and techniques.

Specifically, the new findings in this revised manuscript on the recrystallizations of MOFs (i.e., self-repairing events) are highlighted as follows:

i) Novel strategy for regulating beam damage mechanisms. Beam damage behaviors have traditionally been limited to strategies associated with illumination conditions (e.g. acceleration voltage or beam current density) and specimen treatment (e.g. coating or cooling). For the first time, we introduce a gas atmosphere (specifically, an H₂ atmosphere) as a strategy to regulate the beam damage behavior and mechanism, while simultaneously monitoring the structural dynamics with high spatial resolution and maintaining structural integrity. During the process of radiolytic damage, the ionization of chemical bonds generates radicals and subsequent atomic displacements that lead to the structural damage. The dynamic interplay between crystalline and amorphous domains originates from the inherent competition between structural damage and self-repair processes. This competition, at its core, arises from the breaking and reformation of bonds. As a new beam damage mechanism regulation strategy, the introduction of molecular hydrogen as a widely-known radical scavenger effectively terminates the broken bonds arising from the radiolytic damage and significantly inhibits the bond reformation and self-repairing processes as schematically illustrated in Fig. R3. The inhibited self-repairing processes of the reversible radiolysis mechanism would lead to more rapid structural damage of UiO-66(Hf) crystals under hydrogen atmosphere. Comparing with the measured critical dose ($D_c = 30.3 \text{ e}^- \text{ \AA}^{-2}$) of UiO-66(Hf) crystals under vacuum condition, the D_c

values significantly decrease to $19.8 \text{ e}^- \text{ \AA}^{-2}$ and $16.4 \text{ e}^- \text{ \AA}^{-2}$ for UiO-66(Hf) crystals under hydrogen atmosphere with a pressure of 5 mbar and 10 mbar respectively (Fig. R4). These observations unambiguously confirm the significantly diminished rate of self-repairing process in contrast to that of structural damage process. This arises from the inhibition of bond reformation after ionization, a direct result of hydrogen termination of the broken bonds.

ii) New observations for real-time responsive structural dynamics. We conducted *in-situ* low-dose HRTEM imaging of structural dynamics of MOF crystals in response to the hydrogen atmosphere. This approach allows us to observe, in real-time, the diminished crystalline-to-amorphous interconversion in real space. This diminished interconversion is a result of the inhibited self-repair processes, which occur under a hydrogen atmosphere rather than in a vacuum. From the serial HRTEM images, it is observed that the beam damage behaviors under hydrogen atmosphere are dramatically altered comparing with that in vacuum. Firstly, under a hydrogen atmosphere, the rate of beam-induced structural damage in UiO-66(Hf) crystals is significantly accelerated compared to a vacuum environment. This phenomenon can be clearly visualized through the use of lattice contrast enhanced by *Bragg* filtering in serial HRTEM images. These images, collected under hydrogen atmospheres of 5 mbar and 10 mbar, are rendered in a purple-blue-green false-color code as shown in Fig. R5 and R6. Only a relatively small portion of the crystal lattice is amorphized under vacuum conditions, as shown in Fig. S13. In contrast, under a hydrogen environment and a similar electron dose, most of the crystal becomes amorphous. Secondly, under vacuum conditions, the material exhibited a dynamic crystalline-to-amorphous interconversion, characterized by intermittent and mobile stripe-like domains. However, this behavior is significantly diminished in a hydrogen environment. Instead, the hydrogen atmosphere promotes a continuous growth and interconnection of amorphous domains, resulting in a scattered distribution across the material. These real-space, time-resolved observations provide important insights into the regulated beam damage behavior and underlying mechanisms. The molecular hydrogen acts as a radical scavenger, terminating the broken bonds generated by

ionization. This inhibits the self-repairing events and promotes irreversible radiolytic structural damage. As a result, the rate of amorphization is significantly accelerated, and the dynamic crystalline-to-amorphous interconversion is no longer available. Accordingly, the intermittent and mobile stripe-like amorphous domains, which arise from anisotropic structural recovery rates under vacuum, are replaced by widespread, localized growing domains in the hydrogen atmosphere, as observed in the serial HRTEM images. This stark contrast in the material's response to the different environmental conditions highlights the profound influence that the surrounding medium can exert on the beam damage behavior.

iii) Validation of nonclassical beam damage mechanism and kinetic model. The introduction of a hydrogen environment during beam illumination has significantly accelerated beam-induced structural damage, clearly validating the nonclassical reversible radiolysis mechanism. This effect is attributed to the inhibited self-repairing processes, which are hindered by the presence of hydrogen as a radical scavenger. In this work, we have demonstrated that nonclassical radiolysis follows a reversible first-order kinetic model, resulting in a steady-state structure characterized by mixed crystalline and amorphous domains during continuous beam illumination. This steady state emerges from the equilibrium between structural damage and self-repairing processes, influenced by the damage-to-repair ratio dictated by the kinetic model. A higher damage-to-repair ratio arises from inhibited structural recovery in hydrogen environment, resulting in a diminished quantity of remnant crystalline domains at steady state. To verify this, we conducted electron diffraction (ED) dose series on UiO-66(Hf) MOF crystals in a hydrogen atmosphere (5 mbar and 10 mbar), as illustrated in Fig. R7. A significantly lower fraction of remnant crystalline material at steady state, along with fewer Bragg spots in the equilibrium ED patterns, is observed for MOF crystals illuminated in a hydrogen atmosphere compared to those subjected to vacuum conditions. These findings further substantiate the proposed reversible radiolysis mechanism and its associated kinetic model.

Building on these new insights, we have enhanced the novelty of our work by thoroughly demonstrating the recrystallization of MOFs, encompassing **phenomena**

such as crystalline-to-amorphous interconversion, **dynamics** involving self-repairing molecular processes, **kinetics** described by a steady-state kinetic model, and **regulations** including dose rate effects and gas atmosphere during reversible radiolysis. These comprehensive observations and strategies provide unprecedented insights into the nonclassical beam damage mechanism, aided by low-dose imaging techniques. We believe that this revision fully addresses the reviewer's request to expand on the recrystallization of MOFs, particularly by integrating multiple cutting-edge imaging methodologies. These exciting new results are included in the main text as Fig. 5 and in the supporting information as Fig. S16, S17 and S18. Based on these contributions, we hope that the highlights presented in this work would convince the reviewer to consider its publication in Nature Communications.

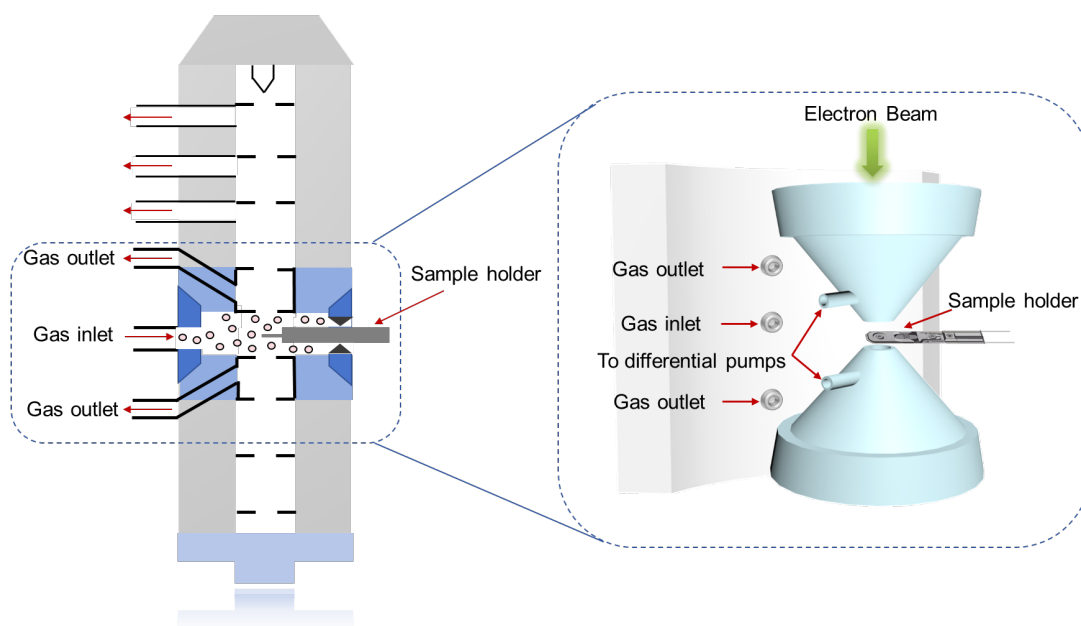


Fig. R2. The schematic of a dedicated ETEM equipped with a differential pumping vacuum system

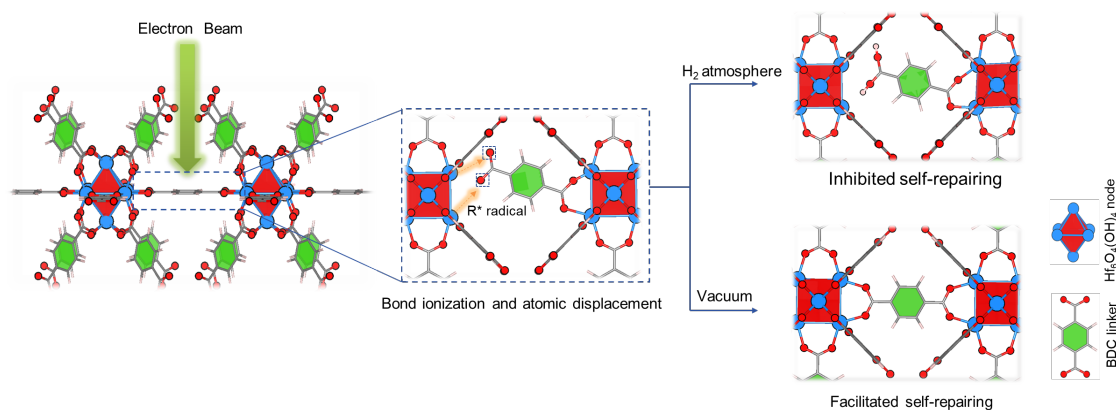


Fig. R3. The schematic illustration of bond ionization followed by either inhibited or facilitated self-repairing events in hydrogen environment and vacuum respectively. The R^* radical refers to O (red color) radical.

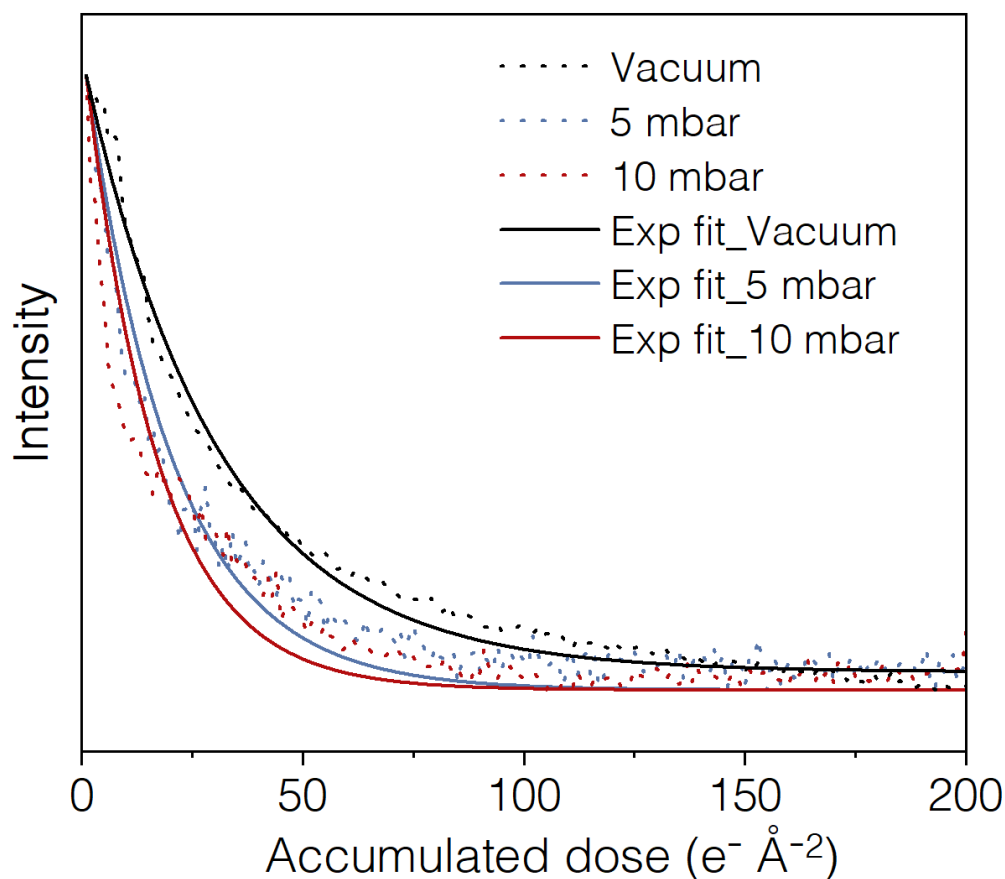


Fig. R4. The exponential fitting of diffraction intensity decay curves as a function of accumulated dose in vacuum and hydrogen atmosphere with a pressure of 5 mbar and 10 mbar, respectively.

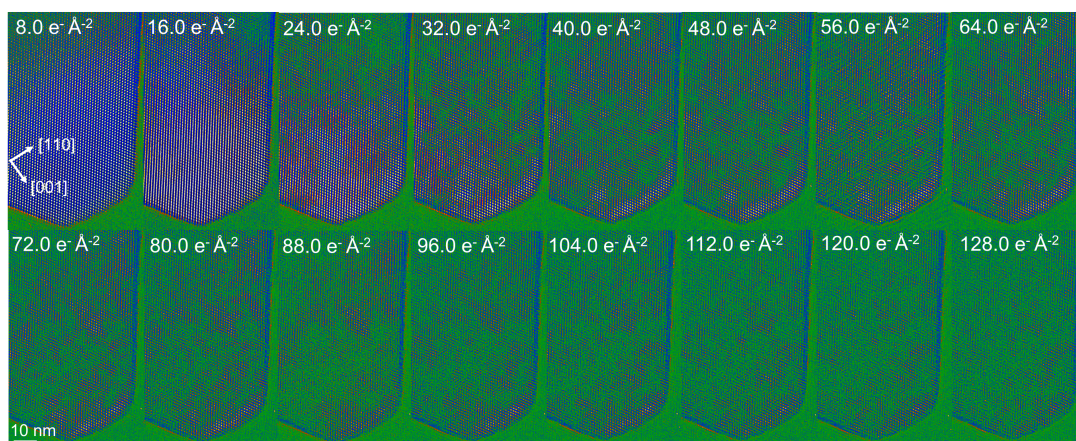


Fig. R5. The dose series HRTEM images of the UiO-66(Hf) crystal in hydrogen atmosphere with a pressure of 5 mbar. The lattice contrast is enhanced by Bragg filtering. The crystalline-to-amorphous domains are rendered in a purple-blue-green false-color code.

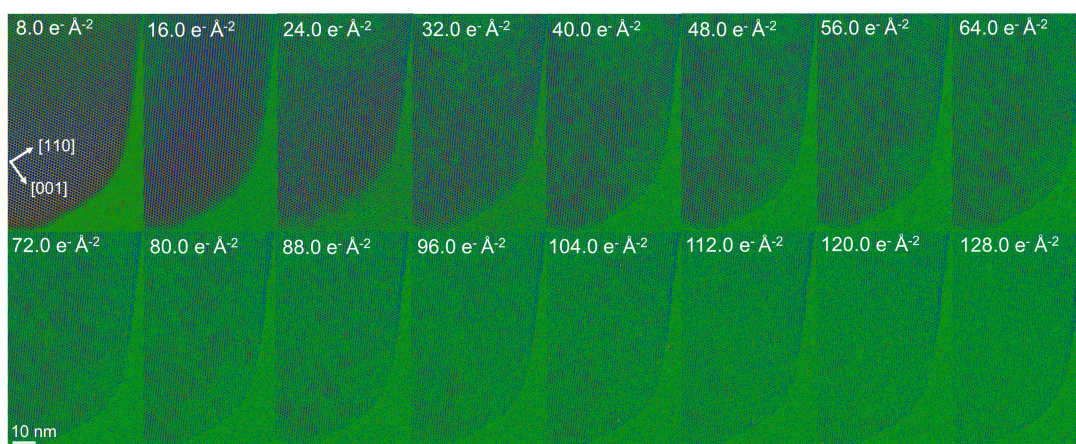


Fig. R6. The dose series HRTEM images of the UiO-66(Hf) crystal in hydrogen atmosphere with a pressure of 10 mbar. The lattice contrast is enhanced by Bragg filtering. The crystalline-to-amorphous domains are rendered in a purple-blue-green false-color code.

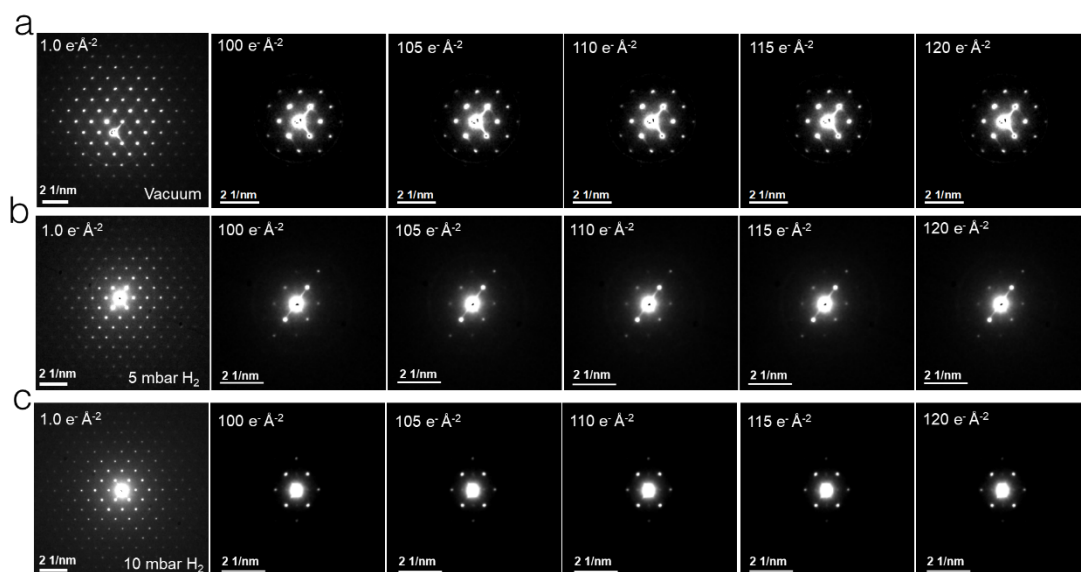


Fig. R7. (a-c) Patterns of ED dose series for UiO-66(Hf) MOF crystals under (a) vacuum and hydrogen atmosphere with a pressure of (b) 5 mbar and (c) 10 mbar, respectively.

Reviewer #3 (Remarks to the Author):

As is clear from the four reviewer reports and from the authors' responses, there are many aspects of this work that will not satisfy everyone and others that will not be understood. But I believe it represents a useful body of evidence and a contribution to the field of beam damage mechanisms. Nature Communications is not an obvious choice for publication of this material but if its editors think that the subject matter is appropriate, I support publication in the journal.

Response: We sincerely thank the reviewer for the insightful comments and suggestion for this work. These comments from the reviewer indeed help us to improve the quality of this manuscript.

Reviewer #4 (Remarks to the Author):

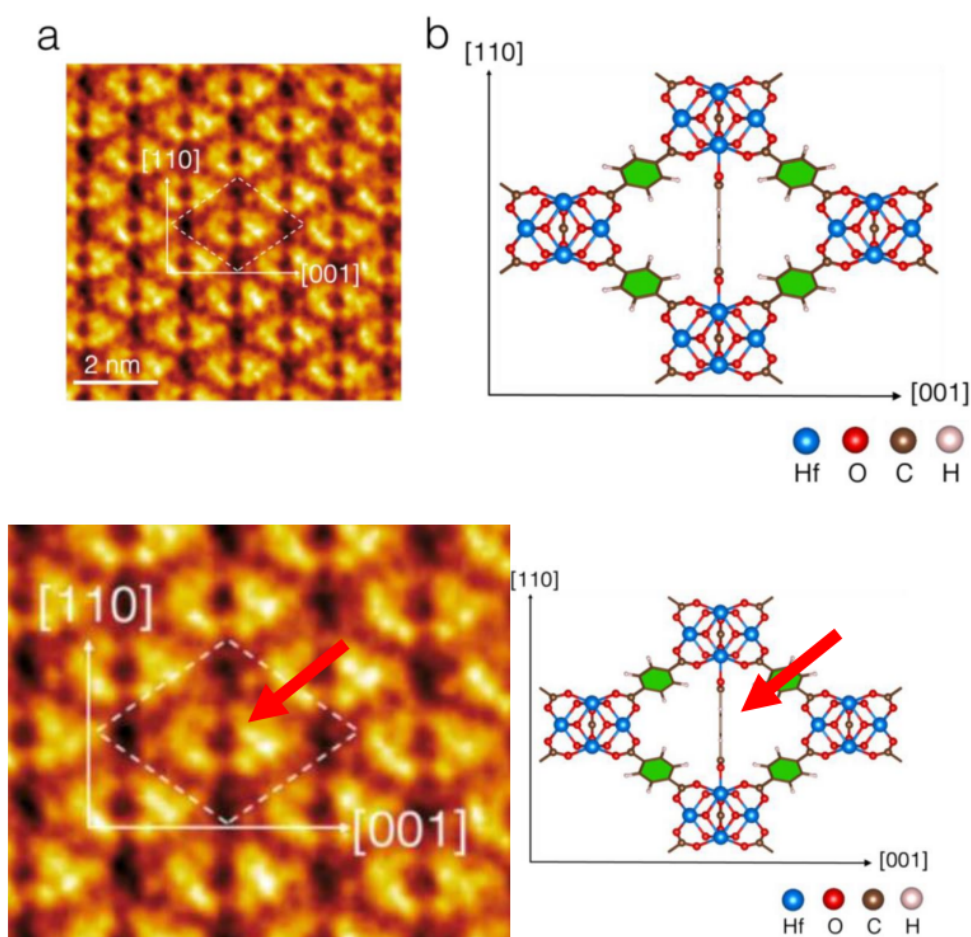
The authors have well solved my concerns. I recommend the acceptance of the manuscript.

Response: We appreciate the reviewer's recommendation of this work and the valuable insights provided.

Point-to-Point Responses to Reviewers' Comments

Reviewer #1 (Remarks to the Author):

The authors have made an extraordinary effort to response most of the concerns raised. The writing and manuscript organization has been improved which helps for a better understanding. After, reading the responses provided from the authors, I believe that the work should be published, but in a more specific journal. Furthermore, there are still there are a couple of points that I believe should be corrected.



I would ask the authors make an effort to explain the contrast indicated by the arrow. When I see the simulation in figure 5, that contrast is very different in the simulated image, the green dash oval is very weak in signal, while in the experimental image is very strong, equivalent to the metal node and it should be very weak as in theory that

contrast is owed to C and O only. In the simulated data, aberrations or distortions or electron dose can be added, could they try to find a better fit between experimental and simulation?

Response: We thank the reviewer for the insightful comments. In response to the suggestions, we have clarified the origin of the contrast discrepancy observed between the simulated and high-resolution transmission electron microscopy (HRTEM) images of bridging BDC linkers. A slight defocus condition, specifically $\Delta f = -45$ nm, was utilized to enhance the contrast of MOFs for low-dose imaging. It is important to note that correcting for contrast inversion effects associated with aberrations only alters the signs, not the amplitude, of the contrast-transfer-function (CTF) profile. This adjustment aims to mitigate noise effects near the CTF crossovers. Consequently, while the contrast in the HRTEM image qualitatively resembles the simulated projected electrostatic potential and becomes chemically interpretable, a contrast discrepancy for the bridging BDC linkers remains. In this revision, we reproduced the ligand contrast by addressing the contrast inversion effects in a defocused simulated HRTEM image. As illustrated in Fig. R1b, the bridging BDC linker in the UiO-66(Hf) MOF structure displays a significantly darker contrast compared to the simulated projected potential (Fig. R1c), aligning closely with the experimental HRTEM image (Fig. R1a). Thus, we have achieved a strong correspondence between the simulation and the experimental HRTEM image, in line with the reviewer's suggestion.

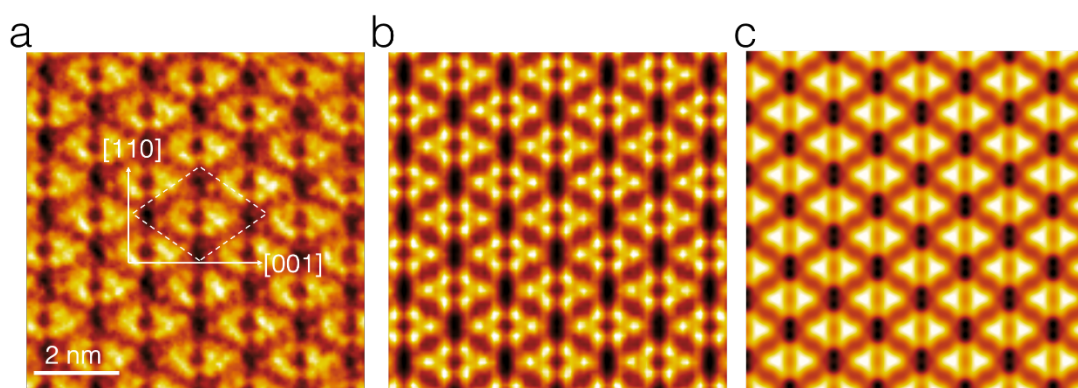


Fig. R1. (a) HRTEM images of pristine UiO-66(Hf) structures after CTF correction. (b) Simulated HRTEM image after a CTF correction procedure. The simulation parameters include a convergence angle of 1 mrad, $\Delta f = -45$ nm, $C_s = 10$ μm , a focal spread of 5

nm, and an objective aperture of 6 mrad. (c) The simulated projected electrostatic potential of pristine UiO-66(Hf) structures with a point-spread-function (PSF) width of 2.5 Å.

Regarding the GPA analysis, after finding the small white square, I still have the concern if that can be considered as an areas of reference due to its small size. Even, in that a small region different strain is considered as reference.

Response: We thank the reviewer for the comments and apologize for any confusion caused by the small size of rectangular region of interests (ROIs) annotation due to the limited size of HRTEM images in Fig. 3d. To improve clarity, we have enlarged the HRTEM image at an accumulated dose of $8 \text{ e}^- \text{ \AA}^{-2}$ and corresponding geometric phase analysis (GPA) map with a reference ROI region marked, as shown in Fig. R2a and b. Notably, the beam radiation cause negligible structural damage at early stage and thus minimal strain fluctuations across the whole crystal. Accordingly, the size of the reference ROI would not considerably affect the GPA results as we demonstrated in Fig. R2c by employing a larger ROI. This rectangular ROI in the first frame is used as a common reference region for GPA strain analysis in the whole image dose series. As a result, the size of the ROI region generally would not affect the GPA analysis of the HRTEM image dose series.

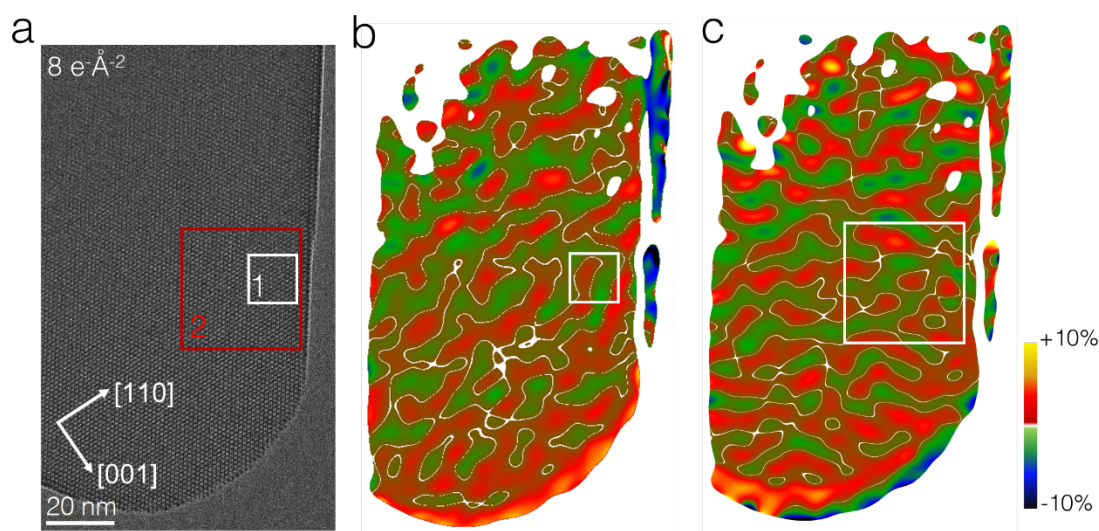


Fig. R2. (a) The HRTEM image in an accumulated dose of $8 \text{ e}^- \text{ \AA}^{-2}$. (b) The GPA image

of the ε_{yy} [001] strain component corresponding to (a), using white square (1) as the reference region. (c) The GPA image of the ε_{yy} [001] strain component corresponding to (a), using red square (2) as the reference region.

Reviewer #2 (Remarks to the Author):

Dear authors, this is my review on your newly resubmitted manuscript with new round of changes. I wish you read my previous comments carefully and followed the recommendations provided. If you followed provided recommendation, I would recommend the manuscript for publication. Therefore, my recommendation for this version of the manuscript will stay the same - it does not deserve to be published in Nature Communication due to lack of novelty.

Here is why. I indicated in my previous round of review: “The only portion of this work that is new, is recrystallizations of MOF, which is only small portion of this manuscript, unfortunately. More expansion on this topic could have been nice and would definitely deserve to be published in Nature Communications.”

At first glance, reading authors response file, it appears that authors have added new content to the manuscript, in response to my comments, on topic of “recrystallizations of MOF”. Actually they did not. What authors added is additional experiment where they show that radiolytic damage of the MOF can be enhanced in H_2 environment. Let me be clear, this new addition does not have any new insight on “recrystallizations of MOF”. It is new experimental validation of well-known radiolytic damage of any material including MOFs.

I wish, I could be positive in my review. I was hoping to learn some new insight into electron-beam-induced re-crystallization of MOFs. But, since it is not there, I am going to hold the same view as I had before - this manuscript does not deserve to be published in Nature Communication due to lack of novelty.

Response: We sincerely apologize for any confusion or inconvenience caused in our previous response. We indeed carefully read the comments from the reviewer and

follow the suggestions to expand the part of MOF recrystallization. We regret that our presentation of the new results was not sufficiently clear in previous round of revision, which may have created a misleading impression that these results were related to radiolytic damage rather than recrystallization of MOFs. In this revision, we have significantly improved several key aspects and incorporated exciting new experimental findings, particularly emphasizing the recrystallization of MOFs, in response to the reviewer's feedback. These results are summarized as follows:

i) Direct observation of molecular-level recrystallization process. In this revision, we successfully acquired a molecular-resolution HRTEM image dose series of a crystalline domain in a UiO-66(Hf) MOF crystal along the [110] projection and near Scherzer defocus, utilizing an *in-situ* low-dose HRTEM imaging technique. This approach enables us to directly observe the molecular-level structural dynamics associated with the recrystallization of UiO-66(Hf) MOFs while approximately preserving the ordered framework. These exciting findings are summarized in Fig. R3. The serial imaging results allow us to visualize the radiolytic bond breaking and relinkage within the UiO-66(Hf) framework, as indicated by the appearance and disappearance of dark rod-like contrasts between the dark metal nodes. Magnified views of the regions of interest (ROIs) marked by white, yellow, blue, and green dashed rectangles in Fig. R3a are presented in Fig. R3b-e, accompanied by schematic illustrations of the structural models. Overall, the crystal lattice of UiO-66(Hf) MOFs displays rhombic-shaped dark contrasts, characterized by dark dot-like contrasts at the corners of the rhombi corresponding to $\text{Hf}_6\text{O}_4(\text{OH})_4$ nodes, and dark rod-like contrasts along the edges and short diagonals for the BDC linkers. The molecular-level recrystallization process governs the sequential appearance, disappearance, and reappearance of BDC linkers under beam radiation, as observed in a specific region. This phenomenon results from the partial dissociation of metal-linker bonds and the detachment of BDC linkers from one end to the metal nodes. Although the partially detached and displaced BDC linkers exhibit negligible contrast, they become visible again when they approach and reconnect to the metal nodes. Above an accumulated electron dose of $48 \text{ e}^- \text{ \AA}^{-2}$, by carefully inspecting these image contrasts, the bridging

BDC linkers at the short diagonals of the rhombi are more frequently subject to radiolytic damage and most of them are knocked out when the cumulative dose approaching $64 \text{ e}^- \text{ \AA}^{-2}$, which coincides well with our previous observations associated with the radiolysis-enhanced knock-on displacement. These molecular-level experimental insights perfectly align with *ab initio* molecular dynamics (AIMD) simulations, where the partially detached and displaced BDC linkers would spontaneously and sequentially subject to self-repairing events. These phenomena further corroborate the nonclassical reversible radiolysis mechanism, driven by simultaneous structural damage and self-repairing events, which accounts for the observed dynamic recrystallization process of MOFs.

The molecular-resolution observations presented in this revision offer valuable insights that extend beyond the crystal lattice-level observations related to the recrystallization of MOFs, specifically regarding the dynamic interplay between crystalline and amorphous domains. The recrystallization process follows a reversible first-order kinetic model, accommodating the direct dose-rate effect. In this revision, we further conducted *in-situ* low-dose HRTEM imaging to investigate the structural dynamics associated with recrystallization under a programmed dose rate. A UiO-66(Hf) MOF crystal was initially irradiated with a high-energy electron beam at a dose rate of $3 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ for 20 seconds, followed by a lower dose rate of $1 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ for 32 seconds. Serial *Bragg*-filtered HRTEM images, as shown in Fig. R4, reveal that a local crystalline domain becomes fractionally amorphized once the accumulated electron dose exceeds the critical dose (D_c) of $30.3 \text{ e}^- \text{ \AA}^{-2}$. The size, shape, and spatial distribution of the amorphous domains vary with radiation, indicating an ongoing dynamic recrystallization process. Notably, we observed a significant acceleration in the recrystallization rate immediately after switching the dose rate from $3 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ to $1 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$. This acceleration results from the marked reduction in damage rate corresponding to the decreased dose rate, facilitating a more rapid structural recovery of the amorphized domains alongside the reemergence of crystalline regions. After an accumulated dose of $92 \text{ e}^- \text{ \AA}^{-2}$ under continuous low-dose-rate beam radiation, a substantial fraction of the amorphized domains fully recrystallized, as illustrated in Fig.

R4.

Collectively, this revision provides compelling experimental evidence for the recrystallization process of MOFs, spanning from molecular to lattice scales, thereby significantly enhancing and expanding this aspect of our work as requested by the reviewer.

ii) The recrystallization of MOFs in response to the gas atmosphere. We have demonstrated that the recrystallization process can be modulated by introducing gas atmosphere as a new physical parameter. This is characterized by distinct radiation-induced crystalline-to-amorphous interconversion behavior in MOF crystals within a hydrogen atmosphere compared to that in a vacuum (Fig. 8c, S13, and S18). The dynamic interplay between crystalline and amorphous phases arises from the inherent competition between structural damage and self-repairing processes, linked to bond breaking and reformation, respectively. The introduction of molecular hydrogen as a radical scavenger effectively terminates broken bonds resulting from radiolytic damage, significantly inhibiting bond reformation and, consequently, the recrystallization process of the MOF. This leads to accelerated structural damage and altered amorphization behavior. This observation is further supported by the electron diffraction dose series (Fig. S18).

In this revision, we enhance our discussion by providing mechanistic insights into the recrystallization of MOFs in response to a hydrogen atmosphere. During radiation damage, the ionization of chemical bonds generates radicals, leading to atomic displacements due to Coulomb repulsion or vibrations, resulting in structural damage. Our previous AIMD simulations have illustrated the cascade of self-repairing steps involved in the recrystallization process under vacuum conditions.

To further assess the effects of hydrogen environments on MOF recrystallization, we conducted AIMD simulations of UiO-66(Hf) structures with a 4% molar ratio of hydrogen molecules per unit cell. We identified the preferential adsorption sites for hydrogen molecules using Monte Carlo (MC) simulations with a universal forcefield (UFF) (Fig. R5a). The density distribution map of these adsorption sites is clearly visualized as red dots, representing the probability distribution for molecular hydrogen

adsorption. Among ten generated configurations, we selected the most stable hydrogen-containing configuration with the lowest energy (Fig. R5b). This configuration was then used to construct and optimize a structural model with broken Hf-O bonds and detached BDC linkers (Fig. R5c and d). This hybrid structural model facilitates the reproduction of the recrystallization process under a hydrogen atmosphere. The hybrid model was equilibrated over a timescale of 200 fs, followed by AIMD simulations using a canonical (NVT) ensemble for 11 ps. The dynamic process reached equilibrium, as indicated by the evolution of the time-dependent overall potential energy profile shown in Fig. R6a. Serial snapshots of the geometries during the molecular dynamics simulations at 298.15 K reveal that the introduction of hydrogen molecules as radical scavengers significantly retards the recrystallization processes of UiO-66(Hf) by terminating broken bonds before they can reform. The trajectories involving geometries with hydrogen-terminated and detached BDC linkers are clearly visualized in Fig. R6d. The dynamic structural evolution can be quantitatively described by the partial pair distribution functions (PDFs) of O-H and Hf-O pairs among the trajectories collected during the recrystallization process (Fig. R6b and c). Comparing snapshots at 0 ps and 11 ps, we observe the emergence of a correlation peak centered at approximately 1.0 Å for H-O pairs, indicating the formation of H-O bonds, while the weakened correlation peak at around 2.2 Å for Hf-O pairs suggests inhibited formation of Hf-O bonds and decreased structural order. These observations stem from the hydrogen termination of partially detached BDC linkers and the enhanced structural distortion due to inhibited reformation of metal-linker bonds. In summary, the combined experimental observations and theoretical simulations elucidate the behaviors and mechanisms of the recrystallization process in response to the gas atmosphere.

Building on these new observations and insights, we have significantly expanded the discussion of recrystallization, enhancing the novelty of our work by thoroughly demonstrating the phenomena and underlying mechanisms associated with this process. This includes robust experimental evidence for the recrystallization of MOFs, spanning from molecular to lattice scales, as well as insights into the recrystallization behaviors and mechanisms in response to the gas atmosphere.

These comprehensive results collectively provide unprecedented insights into the nonclassical beam damage mechanism, utilizing low-dose imaging techniques. The new findings have been incorporated into the main text and supporting information. We believe that our discoveries in this revision fully address the reviewer's request regarding recrystallization and merit publication in Nature Communications.

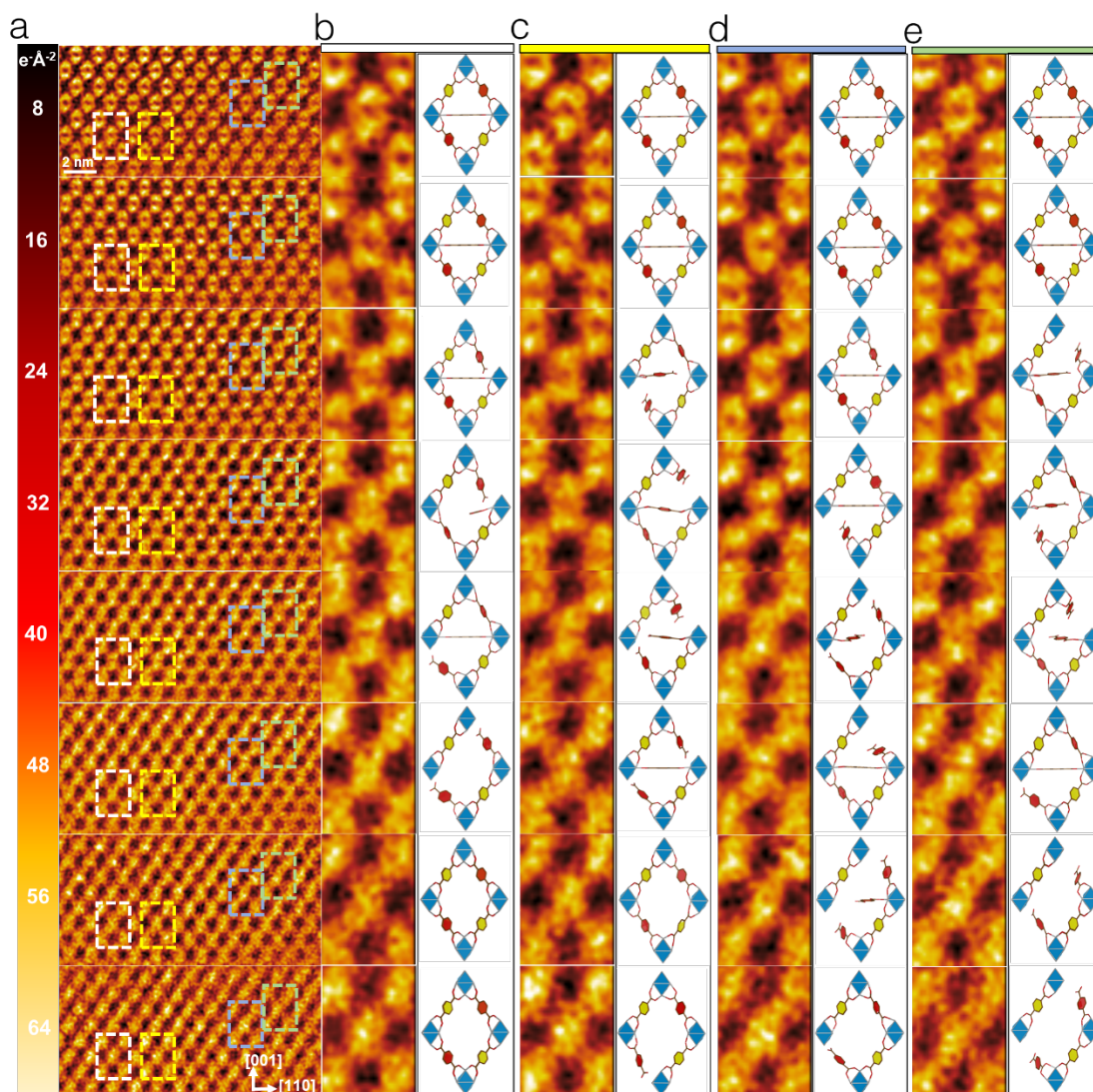


Fig. R3. (a) Serial HRTEM images of UiO-66(Hf) crystals along the $[1\bar{1}0]$ projection, after correcting CTF effects, under increasing accumulated electron dose in vacuum. (b-e) Magnified views of ROIs marked by white, yellow, blue, and green dashed rectangles in (a), accompanied by schematic illustrations of the structural models. The HRTEM images are rendered in a black-body false-color code. Blue represents the $\text{Hf}_6\text{O}_4(\text{OH})_4$ nodes, red indicates BDC linkers with broken bonds, and yellow indicates pristine BDC linkers.

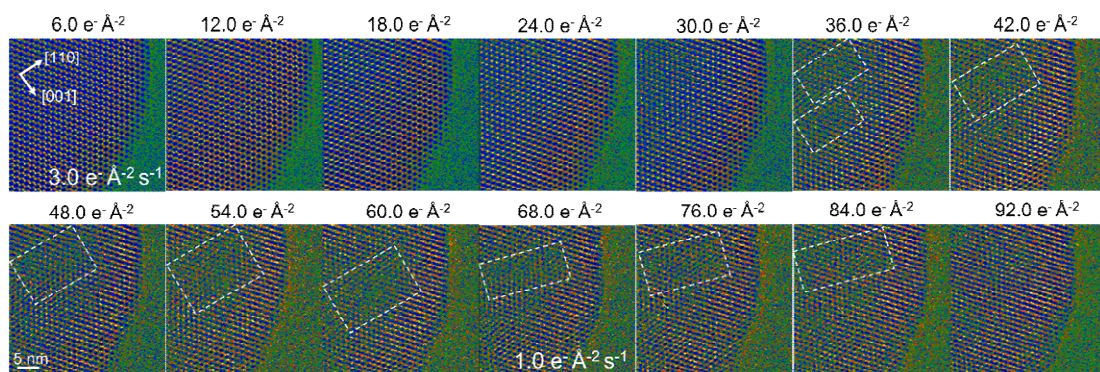


Fig. R4. The dose series HRTEM images of the UiO-66(Hf) crystal in vacuum at a dose rate of $3.0 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$, followed by subsequent images at a dose rate of $1.0 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$. The distribution of crystalline domains can be visualized by enhancing the lattice contrast using a *Bragg* filter. The crystalline-to-amorphous domains are rendered in a purple-blue-green false-color code.

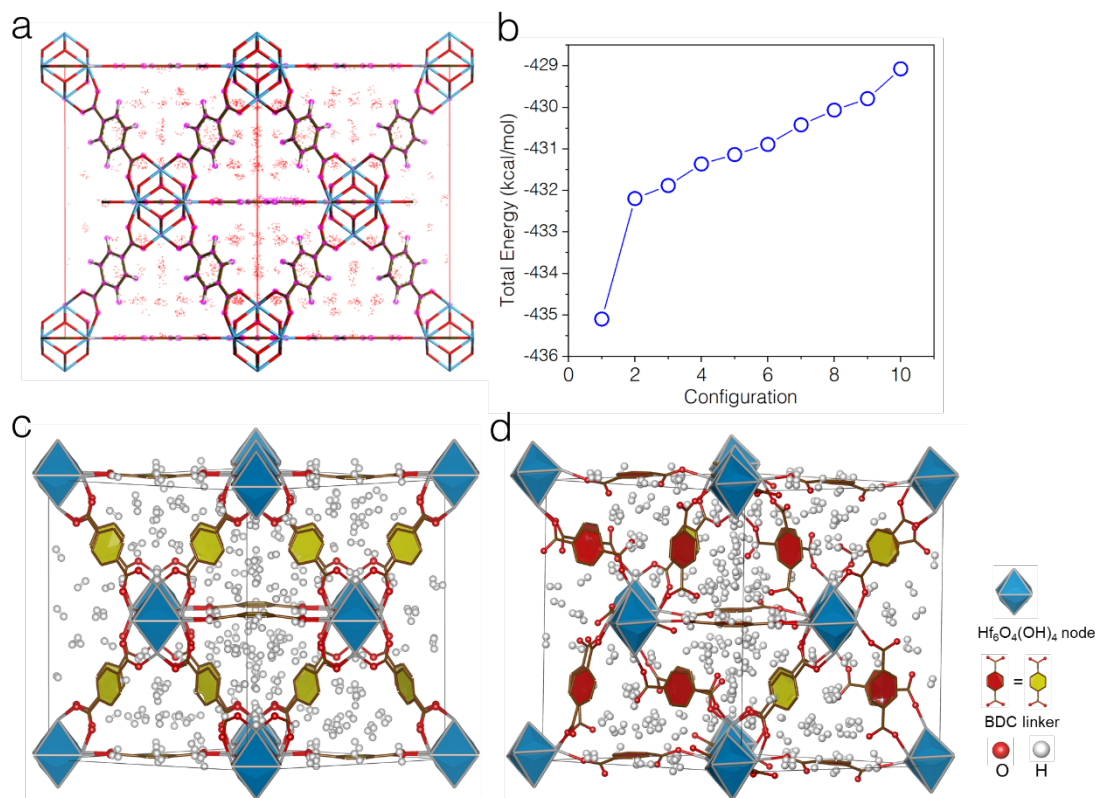


Fig. R5. (a) The structural model of pristine UiO-66(Hf) crystals. The red dots represent the probability distribution of hydrogen molecule adsorption sites, while the rose-red color indicates the target atoms. (b) The total energy of the 10 generated configurations

at the optimal adsorption sites for hydrogen molecules, determined using Monte Carlo simulations. (c) The structural model of the lowest energy configuration after the introduction of a hydrogen atmosphere in (b). The yellow regions represent the pristine BDC linker. (d) The structural model with broken Hf-O bonds (i.e., red BDC linker) and detached BDC linkers after geometric optimization. The number of hydrogen molecules is set to 200.

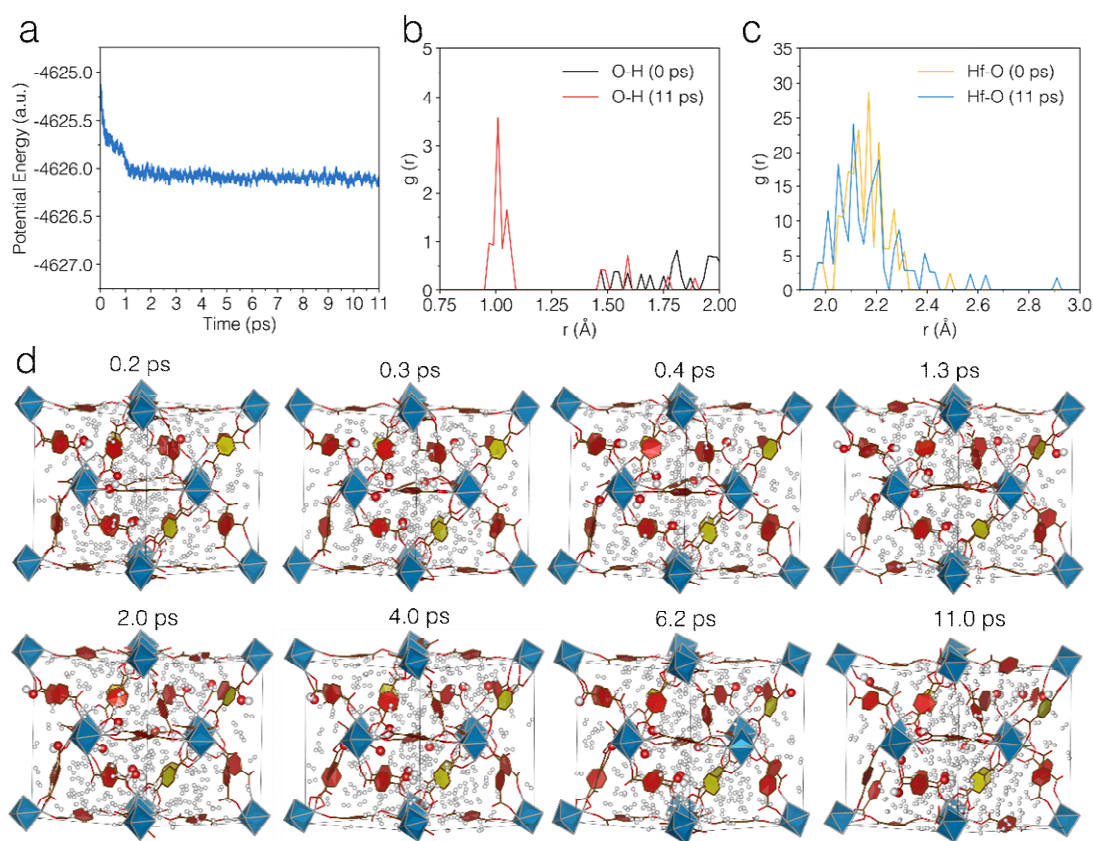


Fig. R6. (a) The potential energy as a function of time during the AIMD simulation of UiO-66(Hf) in a hydrogen atmosphere. (a) pPDF profiles of the total Hf-O bonds between O atoms in the BDC linkers and Hf atoms in the $\text{Hf}_6\text{O}_4(\text{OH})_4$ nodes of the UiO-66(Hf) crystal, obtained from the AIMD simulation over the time range of 0 to 11 ps. (b) pPDF profiles of the total O-H bonds between O atoms in the BDC linkers and H atoms from broken hydrogen molecules in the UiO-66(Hf) crystal during the AIMD simulation from 0 to 11 ps. (d) Trajectories of geometries with hydrogen-terminated and detached BDC linkers. The red BDC linkers indicate broken BDC linkers, with part of the O-H bonds recombined (highlighted by magnified O atoms in red and H atoms

in white). The rest BDC linkers are shown in yellow, and the $\text{Hf}_6\text{O}_4(\text{OH})_4$ nodes are represented by blue octahedra.

Point-to-Point Responses to Reviewers' Comments

Reviewer #1 (Remarks to the Author):

As I mentioned in my previous review, I appreciate the large effort made by the authors addressing the questions previously proposed. However, I still believe that the work should be published in a more specific journal.

- Image simulations presented in figure R1 are now more convincing.
- Stain analysis presented in figure R2 is not convincing or not sufficiently described, the authors stated that changing the size of the “reference ROI would not considerably affect the GPA results as we demonstrated in Fig. R2c by employing a larger ROI”. However, by looking at that the bottom right part, the strain changes from $\approx +5\%$ to $\approx -7\%$. This aspect should be discussed.

Response: We thank the reviewer for the comments. We would like to clarify that the geometric phase analysis (GPA) method is specifically designed for analyzing the strain distribution within the crystalline domains of a particle. However, it may produce random and meaningless contrast outside these domains. To enhance the visualization of strain distribution within the crystalline regions, an image mask is typically generated by thresholding the amplitude images of Bragg spots. This enhancement is illustrated by comparing the strain maps with and without the application of masks, as shown in Fig. R1a and b. The strain variation observed at the outer rim of the particle, generated by a larger reference regions of interest (ROI) and the original mask, clearly results from the random contrast beyond the particle's boundary. Applying thresholding to the mask derived from the amplitude image, in conjunction with the recalculated strain map from a larger reference ROI, facilitates better extraction of the particle boundary and provides a more reliable strain distribution near this boundary (see Fig. R1c). Overall, these minor features do not influence the conclusions drawn from the strain distribution across the main body of the particle.

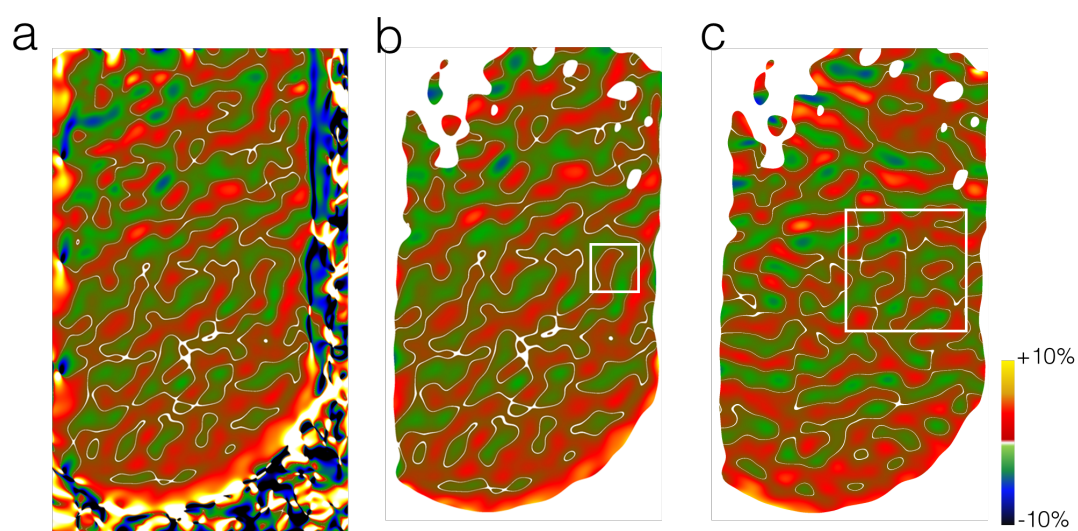


Fig. R1. (a-c) The GPA image of the ε_{yy} [001] strain component corresponding to the white square as the reference region: (a) without the mask, (b) with the mask and (c) with the mask and a larger reference region.

Reviewer #2 (Remarks to the Author):

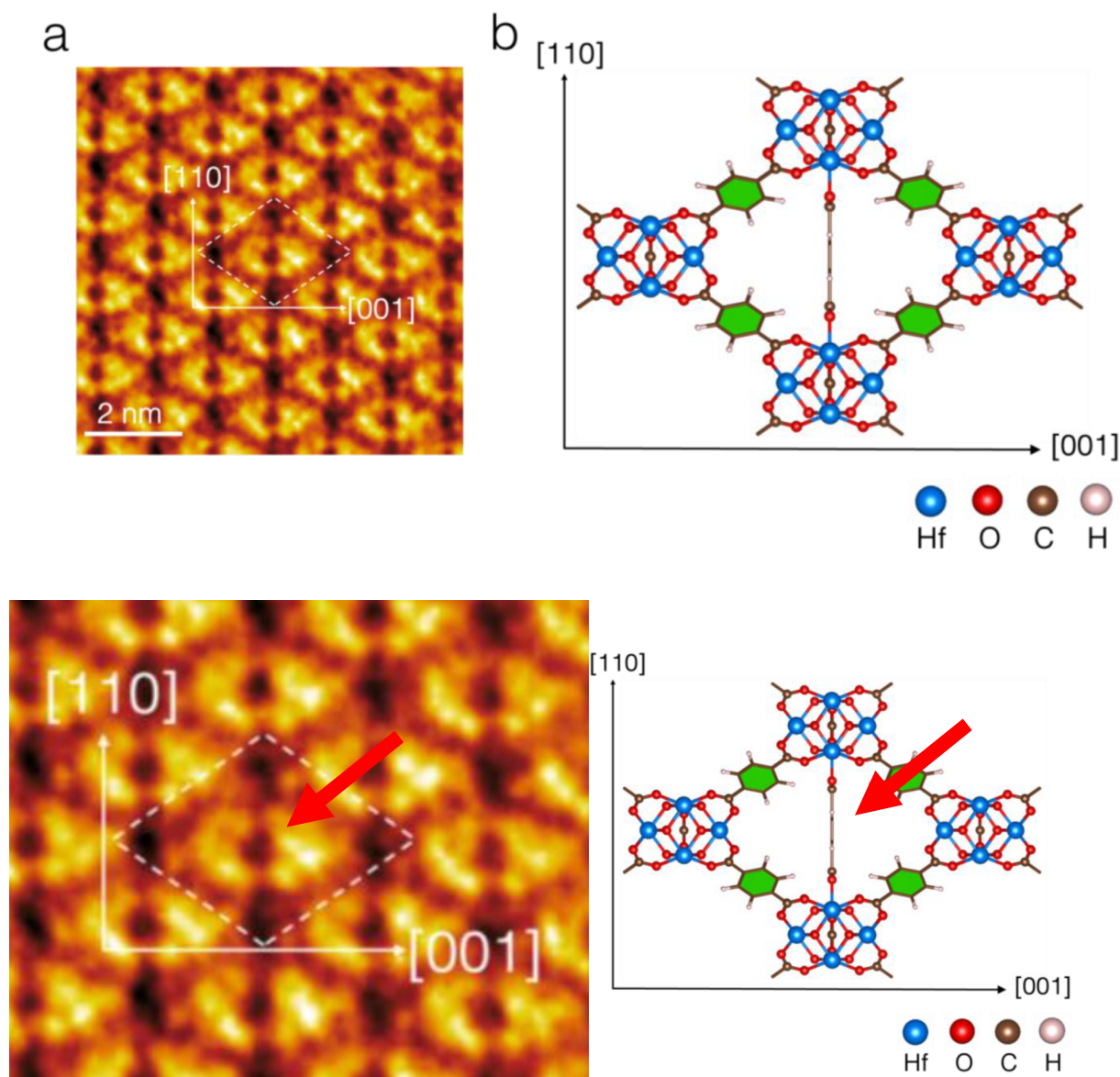
In this round of revision the authors finally made substantial addition to “recrystallizations of the MOF under electron beam irradiation” section of the manuscript that I was recommending, as it is the main new observation reported here. Now I can recommend the manuscript for publication in Nature Communications.

Response: We sincerely thank the reviewer for the insightful comments and suggestion for this work. These comments have greatly helped us improve the quality of the manuscript. We also deeply appreciate the reviewer’s recommendation and support for our work.

Reviewer attachment:

Reviewer #1 (Remarks to the Author):

The authors have made an extraordinary effort to response most of the concerns raised. The writing and manuscript organization has been improved which helps for a better understanding. After, reading the responses provided from the authors, I believe that the work should be published, but in a more specific journal. Furthermore, there are still there are a couple of points that I believe should be corrected.



I would ask the authors make an effort to explain the contrast indicated by the arrow. When I see the simulation in figure 5, that contrast is very different in the simulated image, the green dash oval is very weak in signal, while in the experimental image is very strong, equivalent to the metal node and it should be very weak as in theory that contrast is owed to C and O only. In the simulated data, aberrations or distortions or electron dose can be added, could they try to find a better fit between experimental and simulation?.

Regarding the GPA analysis, after finding the small white square, I still have the concern if that can be considered as an areas of reference due to its small size. Even, in that a small region different strain is considered as reference.