

Confined ionic order in atomic nanowires of rare-earth chlorides unveiled via symmetry-guided structural screening

Corresponding Author: Dr Haitao Zhang

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Concerning 'Unveiling confined ionic order in rare-earth chloride nanowires 1 via symmetry-guided atomic modeling' (anonymous author list in submitted version), this is a very intriguing and ambitious submission and covers several topics in depth, the most important of which are (i) 'symmetry-guided atomic modeling' which is based on a systematic interpretation of heavy metal contrast of lanthanide crystals formed in carbon nanotubes; (ii) the further optimisation of these using various theory approaches including machine learning; (iii) calculation of magnetic anisotropy and conductivity using an approaches often used for molecular scale species with the former taking into account symmetry considerations. Of these (iii) is especially novel and useful and will potentially be of very great interest to the readers of Nature Communications although (i) and (ii) are also very useful.

While this manuscript is highly detailed and comprehensive (especially in terms of the high number of structural calculations that were performed), this manuscript suffers from an number of issues, some of which clearly need to be addressed in a revised version. Item 4 (i.e. providing adequate detail on how the authors produced limited diameter nanotubes) must be addressed or the Editor should reject this manuscript. The authors should address the following issues in particular:

(1) As a general comment, this paper would look better divided into subsections dealing with different aspects of the work including microscopy (identifying motifs), modelling (i.e. 'symmetry-guided atomic modeling'), spectroscopy (XAFS, XANES), calculation of physical properties, and any other subcategory defined by the authors, which would help the narrative significantly.

(2) Page 2, line 23 "...manufactory matter at the nanoscale.1" should be "...manufacturing matter at the nanoscale.1"

(3) Page 3, lines 35 to 36 – the sentence 'However, due to their often non-crystalline nature, these systems are not easily characterized using conventional X-ray diffraction techniques.' is inappropriate both because the size scale of the materials under discussion is beneath the Scherzer limit in size scale but also because the method they are referring to is really 'conventional high performance microscopy. The statement should therefore be something like sentence 'However, due to their often non-crystalline nature, these systems are not easily characterized using conventional high performance microscopy imaging methods.'

(4) Page 3, lines 51-53 (see also comment above) – the statement: 'To obtain homogeneously encapsulated nanowires, anhydrous rare-earth chlorides LnCl_3 were treated with single-walled carbon nanotubes (SWCNTs) exhibiting a narrow diameter distribution (1.4 ± 0.152 nm) using a high-vacuum sublimation method.' Is very problematic because the protocol for producing 'single-walled carbon nanotubes (SWCNTs) exhibiting a narrow diameter distribution (1.4 ± 0.152 nm)' (which is highly technically challenging) is neither referenced nor described either in the Methodology or the Supporting Information document. The authors **must** provide this information in their publication or the editor must consider **rejecting** this manuscript as the article must provide enough information for other scientists to reproduce their results. The diameter consideration is also important when contemplating the structural models that the authors are developing as they themselves have recognised.

(5) Page 4, Figure 2. This Figure contains some HAADF STEM images and also some simulations of structures based on the experimental images. To make the structures more understandable to the general reader, the authors should provide

models of the structures used to produce the simulations including, if possible, the predicted coordination scheme of the lower atomic number halogens around the lanthanide metals (i.e. 'Ln', Fig. 1 caption. Later, on page 7, lines 138-139, this is described as 'the initial positions of the chlorine atoms were derived from the YCl_3 motif placed around yttrium atoms'). Fig. 1 actually provides such a scheme for a 'zigzag' crystal as shown for the T2 structure in this Figure (i.e Fig. 2). The authors should also state which lanthanide gave rise to which image (and they should do this for all of their imaged structures in this and in all their other Figures although I note that they default to certain lanthanides later in the study).

(6) Page 7, lines 138-139 (see also point (5)), concerning 'the initial positions of the chlorine atoms were derived from the YCl_3 motif placed around yttrium atoms' – the authors should include a separate diagram, perhaps as an extra panel in Figure 1, showing a depiction of the YCl_3 motif they are using for their 'initial positions.' This motif should also include bond distances.

(7) Pages 9 and 10 (i.e. Figures 4 and 5). These Figures would be enhanced by including image simulations so that the readers can see which experimental motifs these correspond to perhaps either referring back to Fig. 2 or adding in insets from the experimental images. This will give greater confidence that their methodology 'works' in terms of 'reliable identification' as described on page 4, lines 75-77.

(8) Page 10 - Fig. 5 (also lines 188 to 190) could also be improved by including here all of the structure types (i.ee TX, T2, TZ, TB, TH and TU) for ease of interpretation in addition to the cross referencing that the authors indicate in lines 188 to 190. Don't make the readers work so hard !

(9) Page 15, Discussion, lines 316-317. Regarding the statement "Experimentally, we observed that $\{\text{LnCl}_3\}_n$ undergoes a change in its primary coordination mode upon encapsulation,..." This observation of altered coordination in nanotubes is actually quite widely reported and the authors should add some citations here and compare their results with those produced by other groups. Citations are available on further request, but I suggest the authors look this item up by themselves.

(10) Page 27, line 601, reference 12 – write chemical formulas out correctly (also check to see that this is done in the rest of the manuscript) i.e. 'Comparison between $\text{DySc}_2\text{N@C}_{80}$ and $\text{Dy}_2\text{ScN@C}_{80}$...' should be Comparison between $\text{DySc}_2\text{N@C}_{80}$ and $\text{Dy}_2\text{ScN@C}_{80}$... The authors should check all of their other references for consistency of style and the correct usage of chemical formulas.

If all of the above items are addressed, then this paper should be subject to a second review after which it may possibly be considered for publication again in Nature Communications.

Reviewer #2

(Remarks to the Author)

The authors describe the encapsulation of rare-earth chloride molecules within SWCNT together with an impressive high resolution STEM/HAADF imaging that allows to observe different structures formed by the molecules confined in the nanotubes.

The core of the manuscript is a method: the symmetry-guided structural screening workflow, that combines symmetry analysis and energetic filtering to identify realistic atomic models. The manuscript ends with somewhat disconnected magnetism and electron transport measurements.

This work is very original and has the potential to have an impact in the fields of low-dimensional materials, particularly 1D magnetic systems. However, the manuscript has, in my opinion, significant clarity and organization issues that I detail below which makes the manuscript difficult to follow.

I recommend major revision.

Comments:

- The methodology description is rather confusing. The Results and Methods sections are now mixing conceptual explanations together with technical details. Besides, the manuscript relies continuously on references to the supporting information and methods sections. The Supporting information actually exceeds 70 pages and 100 figures and the methods section contains around 11 pages. Some of the figures in the Supporting information are not even referred to in the text. All this makes the manuscript rather difficult to digest in its present form (in spite of the impressive computational effort). In my opinion, the authors should condense the most important information in the main manuscript. Move the essential information from the Supporting Information and focus the narrative.

- Related to my previous comments, the magnetic and transport measurements seem completely disconnected sections appended after the structural modeling, the core of the manuscript. The authors show AC magnetic susceptibility and electron transport but do not link those results to the predicted structure. The way they appear now seem as independent results rather than any kind of evidence that may support the structural models presented before. The author should discuss the correlation between structure and properties that may validate their model.

- The transport measurements reported in the manuscript are performed on samples that likely contain a mixture of different LnCl_3 configurations within SWCNTs. The conductivity represents therefore an averaged response. These results cannot be directly compared to the calculated electronic structures of specific models. The authors should clarify this limitation.

- Besides the authors attribute the change in conductance to deformation of the SWCNT upon encapsulation. However they do not refer to the effect of defects that are known to modify significantly the conductivity of SWCNT. These defects will definitely appear in the tubes after the encapsulation process due to the harsh conditions. However, in their transport measurements, the authors compare with pristine SWCNT, I assume before encapsulation. This is not a valid comparison. The authors should compare with empty SWCNT exposed to the same harsh conditions of temperature etc than the encapsulated ones. They may well encounter that the enhancement in conductivity happens even in empty tubes.

- The figure captions are very poorly described. It is now impossible to understand the content of some figures by reading the captions. They should be rewritten to be self contained.

- The encapsulation efficiency, and other parameters, is not described in the text. I could find some TGA graphs lost in the sea of the Supporting Information, but there is no mention nor explanation about them in the main text.

- The following assumption made by the authors: "Guided by the principle that "Nature loves simplicity",..." may be appealing but it should be justified in physical terms more rigorously.

Minor comments:

- I don't think that this sentence makes sense: "Unlike what is usually expected, LnCl_3 would present a single-type one-dimensional nanostructure in SWCNTs.14 They formed polymorphic nanowires inside SWCNTs (Fig. 2). " I think it should be rewritten.

- The sentence "If the corresponding Dy-based hybrid can be successfully synthesized, it is expected to exhibit excellent slow magnetic relaxation properties" appears out of place in the structural modeling section. It introduces speculation about magnetic behavior that is not connected to the preceding discussion. It should be moved later in the discussion.

Reviewer #3

(Remarks to the Author)

The manuscript by Zhang et al. describes the synthesis of LnCl_3 encapsulated into SWCNTs, and their comprehensive structural characterization based on a combination of STEM and an intense stepwise calculation effort.

The work is solid and detailed, and the authors have done a very good job in presenting it in the manuscript. However, I am afraid I do not think Nature Communications is the right venue for its publication. These are my reasons:

1) The novelty is limited to the characterization methodology, which in turn is very specific to these LnCl_3 type species, so the broad impact is also limited. The synthesis of lanthanide chlorides encapsulated within SWCNTs was described long ago (ref. 13). The methods used for the calculations are all also described by other groups, and fine-tuned for this specific case. In this sense, I do not agree with the authors' claim that the "approach is transferable". The problem addressed is very specific of lanthanides, as the authors correctly argue in their introduction. Other salts, molecules or coordination compounds @SWCNTs can often be characterized directly from microscopy or a combination of microscopy plus much simpler calculations.

2) The connection between precise atomic positions and physical properties does not hold for these systems. As the authors correctly describe, they find several (many) atomic arrangements within the same LnCl_3 @SWCNT sample, so the final physical properties are most likely better explained from a weighted linear combination of all those, which inherently means that the position of all atoms does not need to be determined precisely. Unless of course it is determined for ALL atoms of ALL possible species, the population of each species determined also with precision, etc. which is unfeasible.

3) The complete workflow (Fig. 3) involves an intense calculation effort in MD, DFT, and ultimately first-principles calculations, which limits its application by other groups.

All in all, this is an excellent piece of work that will be very interesting for those interested in encapsulation within SWCNTs, but it is neither sufficiently novel nor broad to merit publication in Nature Communications. I believe the right venue for publication would be a physical-chemistry focused journal.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This review is in response to the revised version of the manuscript entitled 'Unveiling confined ionic order in rare-earth chloride nanowires via symmetry-guided atomic modelling' submitted to Nature Communications.

In general the resubmitted manuscript is much improved, is (mostly) better written and the authors have done a very good job of addressing the concerns of all of the referees. Some minor issues do remain and I suggest that, in the first instance, the editor address these to the authors and that, providing that they can be addressed to the editor's satisfaction, this manuscript can now be published with only minor further revisions providing that other reviewers do not have more serious concerns.

The following should, nonetheless, be addressed at least to the satisfaction of the editor:

(i) Introduction, page 3, lines 35-36. The phrase '...encapsulation of guest molecules within single-walled carbon nanotubes...' given the context of this manuscript should be rewritten as '...encapsulation of guest molecules and nanowires within single-walled carbon nanotubes...'

(ii) Results page 4, lines 76-77 (also Methods section, Page 24) - in response to a referee's request (i.e. mine) the authors have now given the source of the nanotubes used in this project (new Ref. 52) and quote the diameter precision as "(1.4 +/- 0.1 nm)" which has been rounded from the published specification of "1.28 to 1.52" or 1.4 +/- 0.12. Although not incorrect, I would suggest this unfounded value in order to maintain consistency with the significant figures given for their mass fractions on the subsequent page i.e. "6.00%, 16.40% etc."

(iii) Fig. 1, Page 5, lines 98-99 and Fig. 2, "T2" structure and "TZ" structure. Fig. 1 seems to have been based on Fig. 1 (c) to (d) of reference 13 which the authors of reference 13 have described as a 'zig-zag' TbCl₃ structure. This appears to be isostructural with their so-called "T2" or "double-line" structure which does not look like the "TZ" "zigzag" structure claimed by the authors. I think the original "zig-zag" assignment described in Ref. 13 is correct and really should be "T2". This original "zig-zag" structure is also the basis for their Fig. 1 structure. The authors should therefore do two things: (i) reassign the "zig-zag" structure to "T2" and come up with a new description of "TZ" which is not "zig-zag" (perhaps 'alternating chain'?) and (ii) correctly acknowledge that the "T2" 'zig-zag' structure (i.e. with the correct assignment) was already observed in reference 13. These items should also be reflected in a revised caption for Fig. 2.

(iv) Page 10, line 191 - the sentence "YCl₃ monomers tend to polymerise on the graphene surface." would read better in context as "YCl₃ monomers tend to polymerise on the curved nanotube graphene surface."

As already stated, if these revisions can be completed to the satisfaction of the editor, then this article can be passed for publication in Nature Communications.

Reviewer #2

(Remarks to the Author)

The authors have addressed my comments satisfactorily. I think the manuscript has improved in clarity with a better structure. I agree with the other referees in that the results may be too specific and difficult to extrapolate to other materials. Besides, the fact that the real systems are a combination of different configurations makes it still difficult to establish a clear correspondence between theory and experiment. Still, I think the manuscript shows general trends and can be of interest to be published

Reviewer #3

(Remarks to the Author)

The revised manuscript by Zhang et al. addresses satisfactorily most of the technical comments by other reviewers. However, I was already satisfied with the quality of the initial submission, and my recommendation to publish the manuscript in a more specialised journal was based on a lack of sufficient novelty and broad interest for Nat. Comm. I am thankful to the authors for attempting to address my concerns in the response to the referees letter, but since the essence of the manuscript stays the same, I am afraid I have to stand by my initial recommendation.

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

Dear Editors,

We would like to resubmit a revised version of our manuscript “Unveiling confined ionic order in rare-earth chloride nanowires *via* symmetry-guided atomic modeling”. We would like to thank the reviewers for their careful reading of our manuscript and for their constructive comments. We have addressed them as follows:

Reviewer #1 (Remarks to the Author):

Concerning ‘Unveiling confined ionic order in rare-earth chloride nanowires 1 via symmetry-guided atomic modeling’ (anonymous author list in submitted version), this is a very intriguing and ambitious submission and covers several topics in depth, the most important of which are (i) ‘symmetry-guided atomic modeling’ which is based on a systematic interpretation of heavy metal contrast of lanthanide crystals formed in carbon nanotubes; (ii) the further optimisation of these using various theory approaches including machine learning; (iii) calculation of magnetic anisotropy and conductivity using an approaches often used for molecular scale species with the former taking into account symmetry considerations. Of these (iii) is especially novel and useful and will potentially be of very great interest to the readers of Nature Communications although (i) and (ii) are also very useful.

While this manuscript is highly detailed and comprehensive (especially in terms of the high number of structural calculations that were performed), this manuscript suffers from an number of issues, some of which clearly need to be addressed in a revised version. Item 4 (i.e. providing adequate detail on how the authors produced limited diameter nanotubes) must be addressed or the Editor should reject this manuscript. The authors should address the following issues in particular:

(1) As a general comment, this paper would look better divided into subsections dealing with different aspects of the work including microscopy (identifying motifs), modelling (i.e. ‘symmetry-guided atomic modeling), spectroscopy (XAFS, XANES), calculation of physical properties, and any other subcategory defined by the authors, which would help the narrative significantly.

We thank the reviewer for this helpful and constructive suggestion.

Following the reviewer’s recommendation, we have reorganized the Results section into several clearly defined subsections to better delineate the different aspects of the study, including:

1. Synthesis of LnCl_3 @SWCNTs hybrids
2. Electron microscopy analysis of the nanowire structure
3. Challenges in atomic structure reconstruction and need for advanced screening
4. Initial atomic model construction based on STEM imaging
5. Validation of DFT methods and ReaxFF reparameterization
6. Symmetry-guided screening of atomic structures
7. Energetic stability of encapsulated nanowires in SWCNTs
8. Spectroscopic analysis of local coordination and charge transfer

9. Magnetic properties and slow relaxation behavior
10. Electrical transport properties and underlying mechanism

This restructuring improves the logical flow of the manuscript and enhances its overall clarity and readability.

(2) Page 2, line 23 “...manufactory matter at the nanoscale.1” should be “...manufacturing matter at the nanoscale.1”

We thank the reviewer for pointing out this typographical error. The phrase “manufactory matter” has been corrected to “manufacturing matter” in the revised manuscript.

(3) Page 3, lines 35 to 36 – the sentence ‘However, due to their often non-crystalline nature, these systems are not easily characterized using conventional X-ray diffraction techniques.’ is inappropriate both because the size scale of the materials under discussion is beneath the Scherzer limit in size scale but also because the method they are referring to is really ‘conventional high performance microscopy. The statement should therefore be something like sentence ‘However, due to their often non-crystalline nature, these systems are not easily characterized using conventional high performance microscopy imaging methods.’

We thank the reviewer for this helpful comment. We agree that the difficulty in characterizing these confined systems arises from their small size and local structural disorder, rather than solely from limitations of X-ray diffraction techniques. Accordingly, we have revised the sentence to clarify that resolving the atomic structures of such confined nanowires remains challenging using conventional imaging and diffraction methods:

“However, due to their often non-crystalline nature, these systems are difficult to characterize using conventional high performance microscopy imaging, X-ray diffraction, or electron diffraction techniques”.

(4) Page 3, lines 51-53 (see also comment above) – the statement: ‘To obtain homogeneously encapsulated nanowires, anhydrous rare-earth chlorides LnCl_3 were treated with single-walled carbon nanotubes (SWCNTs) exhibiting a narrow diameter distribution (1.4 ± 0.152 nm) using a high-vacuum sublimation method.’ Is very problematic because the protocol for producing ‘single-walled carbon nanotubes (SWCNTs) exhibiting a narrow diameter distribution (1.4 ± 0.152 nm)’ (which is highly technically challenging) is neither referenced nor described either in the Methodology or the Supporting Information document. The authors must provide this information in their publication or the editor must consider rejecting this manuscript as the article must provide enough information for other scientists to reproduce their results. The diameter consideration is also important when contemplating the structural models that the authors are developing as they themselves have recognised.

We thank the reviewer for emphasizing the importance of providing detailed information about the SWCNTs used in this study.

In the revised manuscript, we have clarified the source of the nanotubes in the Methods section. The SWCNTs were obtained from Meijo Nano Carbon Co. Ltd., and their synthesis and structural characteristics have been previously reported (*Chemical Physics Letters* **323**, 580-585 (2000)). These

SWCNTs were produced using the arc plasma jet method developed by Prof. Yoshinori Ando and Prof. Sumio Iijima, and subsequently commercialized through the above-mentioned company. According to the original report, the diameter distribution of the SWCNTs ranges from 1.28 to 1.52 nm. Although this specific SWCNTs product is no longer commercially available from the above company, limited quantities remain in our laboratory and can be provided upon reasonable request for verification purposes.

(5) Page 4, Figure 2. This Figure contains some HAADF STEM images and also some simulations of structures based on the experimental images. To make the structures more understandable to the general reader, the authors should provide models of the structures used to produce the simulations including, if possible, the predicted coordination scheme of the lower atomic number halogens around the lanthanide metals (i.e. ‘Ln’, Fig. 1 caption. Later, on page 7, lines 138-139, this is described as ‘the initial positions of the chlorine atoms were derived from the YCl₃ motif placed around yttrium atoms’). Fig. 1 actually provides such a scheme for a ‘zigzag’ crystal as shown for the T2 structure in this Figure (i.e Fig. 2). The authors should also state which lanthanide gave rise to which image (and they should do this for all of their imaged structures in this and in all their other Figures although I note that they default to certain lanthanides later in the study).

We thank the reviewer for this helpful suggestion.

a). To improve the clarity of Fig. 2 for general readers, we have added the final optimized ball-and-stick atomic structure models corresponding to the simulated HAADF-STEM images. These models illustrate the coordination environment of chlorine atoms around the lanthanide centers and help visualize the structural motifs used in the simulations. In the models, cyan spheres represent Ln atoms, while green spheres represent chlorine atoms.

b). We apologize for any confusion. The “double-line” (T2) and “zigzag” (TZ) structures indeed appear very similar; however, the addition of the ball-and-stick models should facilitate clearer distinction between the two.

c). The HAADF-STEM images in Fig. 2 correspond to distinct lanthanide systems, namely: TX (Er), TB (Dy), T2 (Gd), TZ (Dy), TH (Er), and TU (Dy), and this information has been clarified in the revised figure caption. We further note that the assignment of specific structures to particular lanthanide elements reflects the systems investigated here and does not exclude the possibility of similar configurations occurring in other lanthanides. Based on observations across multiple samples, we have compiled a summary table, which is now provided in the Supplementary Information.

Table 1. Nanowire structures in LnCl₃@SWCNTs (Ln = Y, Gd, Dy, Er) observed by STEM.

Systems	Types of nanowires
YCl ₃ @SWCNTs	N/A, STEM measurements were not performed.
GdCl ₃ @SWCNTs	T2; poorly ordered
DyCl ₃ @SWCNTs	TB; TZ; TU; TX; poorly ordered
ErCl ₃ @SWCNTs	TX; TH; poorly ordered

(6) Page 7, lines 138-139 (see also point (5)), concerning ‘the initial positions of the chlorine atoms were derived from the YCl_3 motif placed around yttrium atoms’ – the authors should include a separate diagram, perhaps as an extra panel in Figure 1, showing a depiction of the YCl_3 motif they are using for their ‘initial positions.’ This motif should also include bond distances.

We thank the reviewer for this helpful suggestion. To improve clarity, we have added a new schematic diagram (Fig. 4) illustrating the procedure for constructing the initial structural model from STEM images. The figure outlines the key steps, including identification of heavy atoms from HAADF imaging, estimation of structural parameters, construction of the initial model, and subsequent parameter grid search for molecular dynamics simulations. In addition, the template YCl_3 unit is included, with its bond lengths and angles labeled, showing an equilateral triangular geometry with a Y-Cl bond length of 2.0 Å.

(7) Pages 9 and 10 (i.e. Figures 4 and 5). These Figures would be enhanced by including image simulations so that the readers can see which experimental motifs these correspond to perhaps either referring back to Fig. 2 or adding in insets from the experimental images. This will give greater confidence that their methodology ‘works’ in terms of ‘reliable identification’ as described on page 4, lines 75-77.

We thank the reviewer for this helpful suggestion. To facilitate a direct comparison between the experimental observations and the proposed structural models, we have integrated the content of the original Fig. 5 into Fig. 2, allowing the corresponding STEM image simulations to be more intuitively matched with the experimental data. These revisions clarify the relationship between the experimental results and the structural models, and further support the reliability of our structure identification methodology.

(8) Page 10 - Fig. 5 (also lines 188 to 190) could also be improved by including here all of the structure types (i.ee TX, T2, TZ, TB, TH and TU) for ease of interpretation in addition to the cross referencing that the authors indicate in lines 188 to 190. Don’t make the readers work so hard !

We thank the reviewer for this helpful suggestion. Figure 5 has now been incorporated into Fig. 2, with the corresponding ball-and-stick models for TX, T2, TZ, TB, TH, and TU included. Extended periodic representations are provided in the Supplementary Figs. 44–49. This revision reduces the need for cross-referencing between figures and improves the overall continuity of the presentation, allowing readers to more readily identify the corresponding structures directly in Fig. 2.

(9) Page 15, Discussion, lines 316-317. Regarding the statement “Experimentally, we observed that $\{\text{LnCl}_3\}_n$ undergoes a change in its primary coordination mode upon encapsulation,...” This observation of altered coordination in nanotubes is actually quite widely reported and the authors should add some citations here and compare their results with those produced by other groups. Citations are available on further request, but I suggest the authors look this item up by themselves.

We sincerely thank the reviewer for this helpful suggestion. We agree that changes in coordination

mode for materials confined inside carbon nanotubes have been reported previously. To clarify this point, we have added new references in the Introduction section of the revised manuscript and included the following statement:

“For example, lanthanide ions, which generally favor high coordination numbers, typically exhibit sixfold coordination after encapsulation, (*Chemical Communications*, 2427-2428 (2000)) whereas potassium iodide and cobalt iodide transform from sixfold to fourfold coordination.” (*Chemical Physics Letters* **329**, 61-65 (2000), *Nat Mater* **2**, 788-791 (2003)).

In addition, to avoid any implication that this is the first observation of such a phenomenon, we have revised the corresponding sentence in the Discussion section as follows:

“We found that $\{\text{LnCl}_3\}_n$ exhibits the commonly observed change in primary coordination mode upon encapsulation”.

(10) Page 27, line 601, reference 12 – write chemical formulas out correctly (also check to see that this is done in the rest of the manuscript) i.e. ‘Comparison between DySc(2)N@C(80) and Dy(2)ScN@C(80)...’ should be Comparison between DySc₂N@C₈₀ and Dy₂ScN@C₈₀...’ The authors should check all of their other references for consistency of style and the correct usage of chemical formulas.

We thank the reviewer for pointing out this formatting issue. The chemical formulas in the reference have been corrected to follow standard stoichiometric notation (DySc₂N@C₈₀ and Dy₂ScN@C₈₀). We have also carefully checked the entire manuscript and reference list to ensure that chemical formulas are consistently formatted throughout.

If all of the above items are addressed, then this paper should be subject to a second review after which it may possibly be considered for publication again in Nature Communications.

Reviewer #2 (Remarks to the Author):

The authors describe the encapsulation of rare-earth chloride molecules within SWCNT together with an impressive high resolution STEM/HAADF imaging that allows to observe different structures formed by the molecules confined in the nanotubes.

The core of the manuscript is a method: the symmetry-guided structural screening workflow, that combines symmetry analysis and energetic filtering to identify realistic atomic models. The manuscript ends with somewhat disconnected magnetism and electron transport measurements.

This work is very original and has the potential to have an impact in the fields of low-dimensional materials, particularly 1D magnetic systems. However, the manuscript has, in my opinion, significant clarity and organization issues that I detail below which makes the manuscript difficult to follow.

I recommend major revision.

Comments:

- The methodology description is rather confusing. The Results and Methods sections are now mixing conceptual explanations together with technical details. Besides, the manuscript relies continuously on references to the supporting information and methods sections. The Supporting

information actually exceeds 70 pages and 100 figures and the methods section contains around 11 pages. Some of the figures in the Supporting information are not even referred to in the text. All this makes the manuscript rather difficult to digest in its present form (in spite of the impressive computational effort). In my opinion, the authors should condense the most important information in the main manuscript. Move the essential information from the Supporting Information and focus the narrative.

We thank the reviewer for this insightful comment regarding the clarity and organization of the manuscript. In the revised version, we have substantially reorganized the manuscript to improve readability and streamline the presentation.

Specifically, the Results section has been restructured into clearly defined subsections to better guide the reader through each stage of the study, and several figures have been redrawn to more clearly illustrate the methodology. Key information previously presented in the Supplementary Information has been incorporated into the main text to make the narrative more self-contained and reduce the need for cross-referencing.

In addition, the Supplementary Information has been carefully streamlined by removing non-essential content (e.g., the full summary of 263 structures, now provided as a separate file).

- Related to my previous comments, the magnetic and transport measurements seem completely disconnected sections appended after the structural modeling, the core of the manuscript. The authors show AC magnetic susceptibility and electron transport but do not link those results to the predicted structure. The way they appear now seem as independent results rather than any kind of evidence that may support the structural models presented before. The author should discuss the correlation between structure and properties that may validate their model.

We thank the reviewer for this insightful comment. We agree that the relationship between the predicted atomic structures and the measured physical properties should be more clearly articulated. Accordingly, we have expanded the discussion in the sections “Magnetic properties and slow relaxation behavior” and “Electrical transport properties and underlying mechanism” to explicitly address these structure–property correlations.

For the magnetic analysis, we calculated the effective energy barriers (U_{eff}) for all 2554 coordination polyhedra across the 263 optimized structures using the CASSCF method. The results were classified and analyzed according to polyhedron type. This analysis reveals that the dominant nanowire motifs exhibit significantly enhanced U_{eff} values, with average barriers of 105.8 cm⁻¹ for octahedral coordination, 246.4 cm⁻¹ for trigonal prismatic units, and 102.8 cm⁻¹ for capped trigonal prismatic units, all markedly higher than that of the distorted square-antiprismatic coordination in DyCl₃ crystals (42.3 cm⁻¹).

For the transport properties, a full modelling of all 263 structures would be computationally prohibitive. We therefore selected the representative T2 nanowire, which has a relatively simple structural configuration, for detailed electronic structure and transport calculations. This approach enables a tractable yet physically meaningful analysis that captures the essential features of the system.

Overall, these additions clarify how the calculated coordination environments of lanthanide ions in the identified structural motifs provide a consistent framework for interpreting both the AC magnetic susceptibility and electron transport measurements.

- The transport measurements reported in the manuscript are performed on samples that likely contain a mixture of different LnCl_3 configurations within SWCNTs. The conductivity represents therefore an averaged response. These results cannot be directly compared to the calculated electronic structures of specific models. The authors should clarify this limitation.

We thank the reviewer for raising this important point. We agree that the transport measurements were performed on samples containing a distribution of different LnCl_3 configurations within the SWCNTs, and thus the measured conductivity reflects an ensemble-averaged response of multiple structural motifs. In the revised manuscript, we have modified the text as follows:

“Transport measurements on LnCl_3 @SWCNTs reflect an ensemble-averaged conductivity arising from structural and compositional heterogeneity, which precludes a fully quantitative description of charge transport. To capture the essential physics, we employ a simplified Y_6Cl_{18} @SWCNT(14,7) model (Figs. 10d–e), with the semiconducting SWCNT(14,7) chosen as representative of the dominant nanotube species. A supercell of the T2 nanowire ($\{\text{Y}_6\text{Cl}_{18}\}_n$), optimized *via* the above screening protocol, was placed in the SWCNT(14,7) model. The structure of the hybrid was optimized. Accordingly, the calculated electronic structures should be interpreted as indicative trends rather than direct quantitative predictions, while still offering valuable insight into how the encapsulated nanowires modulate the electronic structure of the host SWCNT.”.

We have now explicitly clarified this limitation and emphasized that the calculated electronic structures should be interpreted as representative trends rather than as direct quantitative comparisons with the experimental transport data.

- Besides the authors attribute the change in conductance to deformation of the SWCNT upon encapsulation. However they do not refer to the effect of defects that are known to modify significantly the conductivity of SWCNT. These defects will definitely appear in the tubes after the encapsulation process due to the harsh conditions. However, in their transport measurements, the authors compare with pristine SWCNT, I assume before encapsulation. This is not a valid comparison. The authors should compare with empty SWCNT exposed to the same harsh conditions of temperature etc than the encapsulated ones. They may well encounter that the enhancement in conductivity happens even in empty tubes.

We appreciate the reviewer’s comment. The SWCNTs used in this study were purified prior to the experiments *via* high-temperature treatments at 1200 °C and 550 °C. Although this procedure has been reported previously, we have now explicitly included these details in the Methods section to avoid potential misunderstanding.

As a consequence of this purification process, the surface defect density of pristine SWCNTs and LnCl_3 @SWCNTs is expected to be comparable. This is further supported by Raman spectroscopy: the D-band and 2D-band intensities show no significant differences between SWCNTs and LnCl_3 @SWCNTs.

In addition, we have revised the terminology in the manuscript by replacing “pristine SWCNTs” with “purified SWCNTs” in the experimental section to ensure clarity and avoid ambiguity.

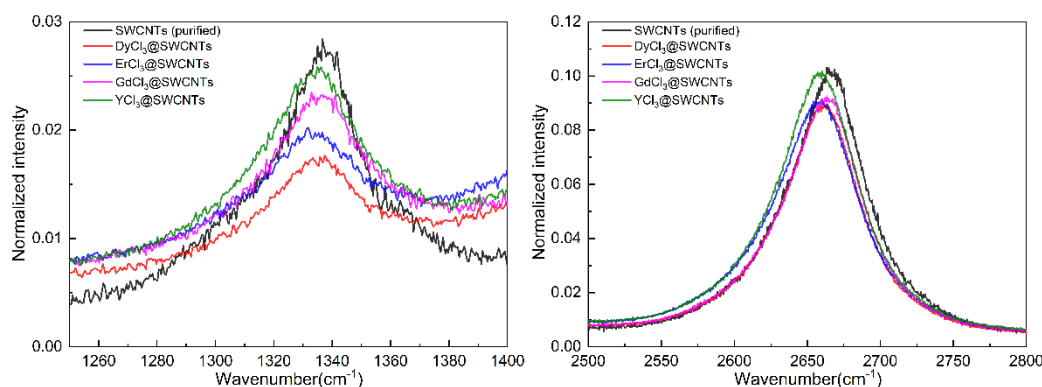


Fig. 1 The D band (left) and 2D band (right) region Raman spectrum for purified SWCNTs, DyCl₃@SWCNTs, ErCl₃@SWCNTs, GdCl₃@SWCNTs, and YCl₃@SWCNTs respectively. The intensities were normalized to their respective G-band intensities.

- The figure captions are very poorly described. It is now impossible to understand the content of some figures by reading the captions. They should be rewritten to be self contained.

We thank the reviewer for this helpful comment. In response, we have revised all figure captions to improve their clarity and completeness. The captions have been expanded to be more descriptive and self-contained, with each now including a brief statement of the figure's purpose as well as detailed explanations of all panels, thereby enhancing the overall readability of the manuscript.

- The encapsulation efficiency, and other parameters, is not described in the text. I could find some TGA graphs lost in the sea of the Supporting Information, but there is no mention nor explanation about them in the main text.

We thank the reviewer for this valuable suggestion. In response, we have moved the discussion of the conclusions derived from the TGA data from the Methods section to the subsection "Synthesis of LnCl₃@SWCNTs hybrids" in the Results, where it is now more appropriately contextualized:

"Thermogravimetric analysis confirmed successful encapsulation in LnCl₃@SWCNTs (Ln = Y, Gd, Dy, Er), yielding mass ratios of 6.00%, 16.40%, 9.46%, and 12.03%, respectively".

It should be noted that TGA analysis provides only the mass fraction of LnCl₃ relative to the total sample and does not directly yield the spatial packing fraction. This is because different nanowire configurations can exhibit substantially different packing efficiencies within SWCNTs.

Based on the analysis presented in the subsection "Energetic stability of encapsulated nanowires in SWCNTs", the theoretical mass fraction under full filling depends on the nanowire type. For T2 nanowires, the expected mass fraction ranges from 33.0% to 40.4% for YCl₃ (37.0%–44.7% for DyCl₃). For TX nanowires, the corresponding range is 40.1%–48.0% for YCl₃ (44.1%–52.0% for DyCl₃). Taking an approximate average value (e.g., ~45%) as a reference for ideal full filling, the filling efficiencies can be roughly estimated to be 13.3%, 36.4%, 21.0%, and 26.7%. However, we emphasize that these values should be regarded as only semi-quantitative estimates due to the structural variability of the confined nanowires.

- The following assumption made by the authors: “Guided by the principle that "Nature loves simplicity",...” may be appealing but it should be justified in physical terms more rigorously.

We thank the reviewer for this insightful comment. We agree that the statement “Nature loves simplicity” was overly informal. In the revised manuscript, we have replaced this expression with a more rigorous formulation and revised the relevant section as follows:

“Guided by Pauling’s fifth rule (the rule of parsimony), we aim to identify structures with minimal polyhedral diversity, that is, those composed of as few distinct polyhedral species as possible with uniform coordination environments. Although this rule is not universally obeyed, statistical analyses of large structural databases indicate that many systems nevertheless exhibit a preference for a limited number of local coordination environments”.

Although Pauling’s fifth rule lacks a strict theoretical derivation, statistical analyses from the Cambridge Structural Database (CCDC) indicate that it applies to approximately 70% of crystal structures, with deviations primarily occurring in alkali and alkaline-earth metals that more readily adopt multiple coordination environments. (*Angew Chem Int Ed Engl* **59**, 7569-7575 (2020)) In light of this statistical support, we consider the use of this rule to be a reasonable and well-justified guiding principle in our study.

Minor comments:

- I don’t think that this sentence makes sense: “Unlike what is usually expected, LnCl_3 would present a single-type one-dimensional nanostructure in SWCNTs.¹⁴ They formed polymorphic nanowires inside SWCNTs (Fig. 2). “ I think it should be rewritten.

We thank the reviewer for pointing this out. We agree that the original sentence was unclear. In the revised manuscript, we have rewritten this sentence,

“Contrary to the expectation of a single one-dimensional nanostructure, LnCl_3 forms polymorphic nanowires inside SWCNTs.”,

to clarify that, while a single structural motif might be expected for LnCl_3 confined in SWCNTs, the experimental observations reveal multiple polymorphic nanowire structures.

- The sentence “If the corresponding Dy-based hybrid can be successfully synthesized, it is expected to exhibit excellent slow magnetic relaxation properties” appears out of place in the structural modeling section. It introduces speculation about magnetic behavior that is not connected to the preceding discussion. It should be moved later in the discussion.

We thank the reviewer for this helpful suggestion. We agree that the sentence discussing the potential magnetic properties of the Dy-based hybrid was not ideally placed in the structural modelling section. In the revised manuscript, we have moved this discussion to the subsection entitled “Magnetic properties and slow relaxation behavior”. This revision improves the overall coherence of the manuscript and avoids abrupt transitions in the text.

Reviewer #3 (Remarks to the Author):

The manuscript by Zhang et al. describes the synthesis of LnCl_3 encapsulated into SWCNTs, and their comprehensive structural characterization based on a combination of STEM and an intense stepwise calculation effort.

The work is solid and detailed, and the authors have done a very good job in presenting it in the manuscript. However, I am afraid I do not think Nature Communications is the right venue for its publication. These are my reasons:

1) The novelty is limited to the characterization methodology, which in turn is very specific to these LnCl_3 type species, so the broad impact is also limited. The synthesis of lanthanide chlorides encapsulated within SWCNTs was described long ago (ref. 13). The methods used for the calculations are all also described by other groups, and fine-tuned for this specific case. In this sense, I do not agree with the authors' claim that the "approach is transferable". The problem addressed is very specific of lanthanides, as the authors correctly argue in their introduction. Other salts, molecules or coordination compounds @SWCNTs can often be characterized directly from microscopy or a combination of microscopy plus much simpler calculations.

We thank the reviewer for raising this important and insightful point.

While the synthesis of LnCl_3 encapsulated within SWCNTs has been reported previously, the central contribution of the present work does not lie in the synthesis itself, nor in the specific chemistry of LnCl_3 systems. Instead, it is the development of a symmetry-guided structural screening framework that enables reliable atomic structure determination for confined nanomaterials.

Determining atomic structures inside nanotubes is inherently challenging, as conventional diffraction techniques are often inapplicable, and microscopy images typically provide only partial or ambiguous structural information. More broadly, there exists a wide class of systems, including confined materials, amorphous phases, quasicrystalline structures, and systems with short-range order (e.g., metallic glasses), for which atomic structure determination is intrinsically underdetermined. In these cases, the lack of long-range periodicity and limited experimental contrast prevent direct extraction of atomic positions from XRD or STEM alone, and reliable structural models necessarily require support from simulations.

To address this challenge, our workflow integrates symmetry analysis, energetic filtering, STEM image simulations, and multiscale modeling (MD and DFT) to systematically narrow down candidate structures from a large configurational space. Importantly, the key aspect of our approach is that structural selection is not based solely on energetic criteria. Instead, we explicitly introduce symmetry as an additional, quantifiable constraint, which can be used to evaluate and rank candidate configurations. This symmetry-guided criterion enables an efficient reduction of the structural search space, significantly improving the robustness and tractability of atomic structure determination in complex systems.

Although certain systems can be resolved using direct imaging or relatively simple calculations, our approach is specifically designed for more challenging cases where conventional crystallographic or imaging-based methods are insufficient. In this context, lanthanide chlorides encapsulated in SWCNTs serve as a stringent test system due to their complex electronic structures and coordination environments. Successfully resolving these systems demonstrates the robustness and reliability of the proposed framework.

It is worth noting that, while the present study focuses on LnCl_3 nanowires, the underlying strategy is not restricted to this specific system. It is broadly applicable to a wider class of systems exhibiting local symmetry but lacking long-range order. At the same time, we have revised the manuscript to clarify the scope of applicability and to avoid overgeneralizing the transferability of the method.

2) The connection between precise atomic positions and physical properties does not hold for these systems. As the authors correctly describe, they find several (many) atomic arrangements within the same $\text{LnCl}_3@\text{SWCNT}$ sample, so the final physical properties are most likely better explained from a weighted linear combination of all those, which inherently means that the position of all atoms does not need to be determined precisely. Unless of course it is determined for ALL atoms of ALL possible species, the population of each species determined also with precision, etc. which is unfeasible.

We thank the reviewer for raising this important point. We agree that the experimental samples likely contain a distribution of different LnCl_3 configurations within the SWCNTs, and therefore the measured physical properties represent ensemble responses rather than those of a single structural motif.

In the revised manuscript, we have clarified that the purpose of the structural modelling in this work is not to establish a one-to-one correspondence between a specific atomic configuration and the measured macroscopic properties. Instead, the identified structural models serve as representative atomic arrangements that help rationalize how different coordination environments may influence the electronic and magnetic behavior of the confined nanowires.

Accordingly, we have emphasized the limitations of the model scheme adopted. For example, in the magnetic section, we stated:

“Interpreting the magnetic behavior of $\text{DyCl}_3@\text{SWCNT}$ at the microscopic level is challenging because the experimental sample is inherently a mixed system. The SWCNT host possesses a diameter distribution, while the encapsulated DyCl_3 nanowires may adopt several energetically similar structures according to the above structural analysis. Therefore, the measured magnetic response likely reflects the combined contribution of multiple structural motifs. Since exhaustive modeling of all possible configurations is impractical, we instead selected the 263 optimized nanowire structures for theoretical analysis.”;

in the conductivity section, we stated:

“Transport measurements on $\text{LnCl}_3@\text{SWCNTs}$ reflect an ensemble-averaged conductivity arising from structural and compositional heterogeneity, which precludes a fully quantitative description of charge transport. To capture the essential physics, we employ a simplified $\text{Y}_6\text{Cl}_{18}@\text{SWCNT}(14,7)$ model”.

Although it is difficult to exhaustively calculate and statistically average all possible configurations to quantitatively reproduce experimental observations, the key objective here is to provide a qualitative understanding of the observed trends. These points have now been explicitly clarified in the revised manuscript.

3) The complete workflow (Fig. 3) involves an intense calculation effort in MD, DFT, and ultimately first-principles calculations, which limits its application by other groups.

We thank the reviewer for this insightful comment. We agree that the complete workflow involves multiple computational steps, including molecular dynamics, density functional theory, and higher-

level first-principles calculations.

However, the proposed approach is intentionally designed as a hierarchical screening strategy. Symmetry constraints and computationally inexpensive force-field simulations are first employed to significantly reduce the structural search space, such that only a small subset of candidate structures is subjected to more demanding first-principles refinement. This design avoids exhaustive high-level calculations and ensures that the overall workflow remains computationally tractable for realistic systems.

Importantly, similar multi-tiered high-throughput screening paradigms are widely adopted in other fields, such as computer-aided drug discovery and materials informatics, where large candidate spaces are efficiently narrowed down through successive levels of theory. In this context, the computational cost of our workflow is comparable to that of many established modern structure prediction and screening frameworks.

In addition, the workflow can be naturally decomposed into modular steps (force-field parameter optimization, structure generation, screening, and refinement) that are amenable to automation and parallel execution. This further improves its accessibility and scalability for broader community use.

All in all, this is an excellent piece of work that will be very interesting for those interested in encapsulation within SWCNTs, but it is neither sufficiently novel nor broad to merit publication in Nature Communications. I believe the right venue for publication would be a physical-chemistry focused journal.

We are looking forward to your response.

Thank you and with best regards,

Haitao Zhang

Dear Editors,

We would like to resubmit a revised version of our manuscript “Confined ionic order in atomic nanowires of rare-earth chlorides unveiled via symmetry-guided structural screening”. We would like to thank the reviewers for their careful reading of our manuscript and for their constructive comments. We have addressed them as follows:

Reviewer #1 (Remarks to the Author):

This review is in response to the revised version of the manuscript entitled 'Unveiling confined ionic order in rare-earth chloride nanowires via symmetry-guided atomic modelling' submitted to Nature Communications.

In general the resubmitted manuscript is much improved, is (mostly) better written and the authors have done a very good job of addressing the concerns of all of the referees. Some minor issues do remain and I suggest that, in the first instance, the editor address these to the authors and that, providing that they can be addressed to the editor's satisfaction, this manuscript can now be published with only minor further revisions providing that other reviewers do not have more serious concerns.

The following should, nonetheless, be addressed at least to the satisfaction of the editor:

(i) Introduction, page 3, lines 35-36. The phrase '...encapsulation of guest molecules within single-walled carbon nanotubes...' given the context of this manuscript should be rewritten as '...encapsulation of guest molecules and nanowires within single-walled carbon nanotubes...'

We thank the reviewer for the helpful and precise suggestion. In accordance with the reviewer's comment and the editor's recommendation, we have revised the relevant sentence in the Introduction. The phrase now reads:

“...encapsulation of guest molecules and atomic nanowires within single-walled carbon nanotubes...”.

(ii) Results page 4, lines 76-77 (also Methods section, Page 24) - in response to a referee's request (i.e. mine) the authors have now given the source of the nanotubes used in this project (new Ref. 52) and quote the diameter precision as "(1.4 +/- 0.1 nm)" which has been rounded from the published specification of "1.28 to 1.52" or 1.4 +/- 0.12. Although not incorrect, I would suggest this unfounded value in order to maintain consistency with the significant figures given for their mass fractions on the subsequent page i.e. "6.00%, 16.40% etc."

We thank the reviewer for this careful comment and helpful suggestion. We agree that using the value directly derived from the published specification provides a more consistent expression. Accordingly, we have revised the nanotube diameter from “ 1.4 ± 0.1 nm” to “ 1.4 ± 0.12 nm” in both the Results and Methods sections.

(iii) Fig. 1, Page 5, lines 98-99 and Fig. 2, "T2" structure and "TZ" structure. Fig. 1 seems to have been based on Fig. 1 (c) to (d) of reference 13 which the authors of reference 13 have described as a 'zig-zag' TbCl_3 structure. This appears to be isostructural with their so-called "T2" or "double-line" structure which does not look like the "TZ" "zigzag" structure claimed by the authors. I think the original "zig-zag" assignation described in Ref. 13 is correct and really should be "T2". This original "zig-zag" structure is also the basis for their Fig. 1 structure. The authors should therefore do two things: (i) reassign the "zig-zag" structure to "T2" and come up with a new description of "TZ" which is not "zig-zag" (perhaps 'alternating chain' ?) and (ii) correctly acknowledge that the "T2" 'zig-zag' structure (i.e. with the correct assignation) was already observed in reference 13. These items should also be reflected in a revised caption for Fig. 2.

We thank the reviewer for this careful and helpful comment. We agree that the terminology should be consistent with the original assignment in Ref. 13. Accordingly, we have followed the naming convention used in the previous literature and reassigned the structures throughout the revised manuscript. Specifically, the structure previously denoted as "T2" has now been renamed "TZ" to reflect its zigzag configuration, consistent with Ref. 13. The structure previously denoted as "TZ" has been renamed "TS", referring to its staggered configuration. We have made the corresponding changes throughout the main text and figure labels. In addition, we have revised the discussion of the STEM observations to more clearly acknowledge that the zigzag structure,

"The zigzag nanowire structure previously observed in SWCNTs^[13] corresponds to the TZ structure in our classification",

now assigned as the "TZ" structure in our manuscript, was previously observed in Ref. 13. The caption of Fig. 2 has also been revised accordingly to reflect the corrected structural assignments.

(iv) Page 10, kibe 191 - the sentence " YCl_3 monomers tend to polymerise on the graphene surface." would read better in context as " YCl_3 monomers tend to polymerise on the curved nanotube graphene surface."

We thank the reviewer for this helpful suggestion. We would like to clarify that the original sentence referred to a simplified graphene model system used to examine the interaction between YCl_3 species and graphitic carbon, rather than directly describing the confined SWCNT system. To avoid this misunderstanding and to better connect the model calculations with the real nanotube-confined structure, we have revised the relevant text as follows:

"To clarify the interaction between YCl_3 species and graphitic carbon, we examined the adsorption of a YCl_3 monomer and a Y_2Cl_6 dimer on a graphene surface as simplified model systems. The calculations show that YCl_3 monomers tend to polymerize on the graphene surface, indicating that the formation of polymeric $\{\text{YCl}_3\}_n$ nanowires is favored under confinement by the curved graphitic surface of SWCNTs. Consequently, in a $\{\text{YCl}_3\}_n@\text{SWCNT}$ system, yttrium atoms would be wrapped within the chlorine shell, effectively suppressing any yttrium-carbon interactions".

As already stated, if these revisions can be completed to the satisfaction of the editor, then this article can be passed for publication in Nature Communications.

We sincerely thank the reviewer for the positive evaluation and valuable comments, and we greatly appreciate their support for our revised manuscript.

Reviewer #2 (Remarks to the Author):

The authors have addressed my comments satisfactorily. I think the manuscript has improved in clarity with a better structure. I agree with the other referees in that the results may be too specific and difficult to extrapolate to other materials. Besides, the fact that the real systems are a combination of different configurations makes it still difficult to establish a clear correspondence between theory and experiment. Still, I think the manuscript shows general trends and can be of interest to be published

We sincerely thank the reviewer for the positive assessment and for acknowledging the improvements in clarity and structure. We also appreciate the reviewer's insightful comments on the specificity of our results and the challenges in establishing a direct theory–experiment correspondence in complex real systems. We agree with these points and have clarified in the manuscript that our results are intended to reveal general trends and provide useful structural and mechanistic insights, rather than exhaust all possible configurations. We are grateful for the reviewer's constructive evaluation and encouraging recommendation.

Reviewer #3 (Remarks to the Author):

The revised manuscript by Zhang et al. addresses satisfactorily most of the technical comments by other reviewers. However, I was already satisfied with the quality of the initial submission, and my recommendation to publish the manuscript in a more specialised journal was based on a lack of sufficient novelty and broad interest for Nat. Comm. I am thankful to the authors for attempting to address my concerns in the response to the referees letter, but since the essence of the manuscript stays the same, I am afraid I have to stand by my initial recommendation.

We sincerely thank the reviewer for the careful assessment of our revised manuscript and for acknowledging that most of the technical comments raised by the other reviewers have been satisfactorily addressed. We also appreciate the reviewer's positive view of the quality of the initial submission. We fully understand the reviewer's remaining concern regarding the level of novelty and broad interest for Nature Communications. Although the reviewer maintains the initial recommendation, we are grateful for the constructive feedback, which has helped us better clarify the scope, significance, and positioning of our work in the revised manuscript.

We are looking forward to your response.

Thank you and with best regards,

Haitao Zhang