

Exploring electron spin dynamics in spin chains using defects as a quantum probe.

Corresponding Author: Dr Sylvain Bertaina

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)

The manuscript reports ESR experiments on organic crystals of (o-DMTTF)X, with X=Br,Cl,I that contain S=1/2 spin chains with a modulation of the antiferromagnetic exchange on account of dimerization. The experiments focus on the spin relaxation and decoherence and are rationalized in terms of the S=1/2 that appear at the edges and defects of the spin chains of the dimerized chains. A systematic analysis of the temperature and field dependence (for 3 values of the field) is carried out and using a multi-parameter formula, the contribution of different spin relaxation mechanisms is estimated.

In addition, pulsed ESR techniques, such as two-pulse Hahn echo and 3-pulse stimulated echo is used to probe T2 as a function of temperature. Both the T1 and the T2 experiments are carried out for 3 compounds (X=Cl,Br,I). The echo experiments are also carried out as a function of the refocusing angle θ_2

The work is supplemented with DMRG calculations, that reproduce results known in the literature (namely, the presence of S=1/2 moments localized at the edges that host a weak bond), with spin-phonon calculations as well as DFT calculations of the hyperfine interactions.

I can not recommend the publication of this work in Nature Communications for the following reasons:

- 1) The work is not sufficiently novel. The authors have carried out a related study, with cw ESR, on the same compounds, using the same underlying model (refs.14 and 20). I acknowledge that the present work is different, as it uses pulsed ESR-STM, that provides a better insight on the different spin relaxation and decoherence mechanisms.
- 2) The interpretation of the data is not fully supported by experiments. The main claim is that ESR is probing the topological (edge) spin states of the chains. However, there are alternative explanations have not been ruled out (see below)
- 3) The potential significance of the claims, if they were corroborated, is not particularly outstanding. ESR experiments of topological spin chains go back to the early 90 (<https://doi.org/10.1103/PhysRevLett.65.3181>, <https://doi.org/10.1103/PhysRevLett.65.1659>). It is not clear how the spin relaxation and decoherence mechanisms of the present system would be relevant for other one-dimensional spin chains with alternate exchange.

Comments/questions/recommendations

- I could not find the conducting state of the compound. I guess it is an insulator, but in some previous paper it was mentioned that these compounds can be conductors (at higher temperatures). Of course, this would be relevant both for the origin of the resonating spins and for the spin relaxation mechanisms
- Same comment for the magnetic state of the samples (magnetization vs field, magnetization vs temperature). Authors have reported these measurements in previous work, but they are not discussed here.
- Specifically, an estimate of the density of resonating spins would help to substantiate the claim that they come from edge states. Specifically, the signal should increase with the area of the surface. Hence, a study of the signal vs surface area would help to substantiate the claim.

- Some sort of magnetic imaging (perhaps NV magnetometry) may also help to map the increased magnetic density at the surface of the single-crystals
- Introduction of some sort of non-magnetic doping that interrupts the chains, without adding free carriers would increase density of edges, and the ESR/magnetization signal, accordingly
- In reference 20, authors show some sort of magnetic transition at around 50 Kelvin. However, in the present study, data is shown up to 20 Kelvin only. In reference 20 there is evidence of magnetic impurities, that is not discussed in the present work
- I could not find the location of the magnetic moments in this compound. Perhaps DFT calculations could show that to the non-expert readers.

Reviewer #2

(Remarks to the Author)
N/A

Reviewer #3

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reviewer #4

(Remarks to the Author)

The work of Bertaina and co-workers focuses on the electron spin dynamics of topological defects (edge states) in the so-called organic Spin-Peierls chains, namely the family of *o*-DMTTF. This system has been recently studied by the authors (ref.20) in terms of cw-EPR spectroscopy that was used to quantify the dimerization parameter $\delta=0.08$, and pulse EPR methods (Rabi oscillations) that revealed the coexistence of single magnetic solitons with $S=1/2$ and exchanged-coupled solitons with $S=1$.

The present work employs well established pulse EPR methods to measure the relaxation and coherence times T_1 and T_2 of three (*o*-DMTTF)₂X species (with X=Br, Cl, and I) which are key parameters for the implementation of such entities in quantum devices. The work presents original research that is likely to attract the interest of various groups working in quantum technologies involving magnetic and paramagnetic materials. While some key challenges—such as scalability and fabrication—remain unresolved in the context of applying these many-body entities to quantum information processing, the study nonetheless represents a significant contribution to the fields of EPR spectroscopy and molecular magnetism.

The EPR methodology employed is robust, and the work adheres to high standards within the field. The claimed results of the work are summarized as follows: first, at low temperatures T_1 is governed by the phonon bottleneck effect, and second, due to the exchange coupling of the chain spins the dipolar fields (both electronic and nuclear) are reduced leading to increased T_2 values as compared to those of isolated spins having the same concentration. While the findings are noteworthy and the manuscript is generally well written, several key aspects require further clarification in order to fully substantiate the conclusions. The following points should be addressed as major revisions:

1) From section IV it is concluded that instantaneous diffusion (ID) is the dominant decoherence mechanism in the studied systems. From the standard analysis of $1/T_2$ vs $\sin^2\theta/2$ a spin concentration of $C_{ID}=3.5\times 10^{17} \text{ cm}^{-3}$ is obtained which is about two times smaller than the concentration $C_{CW}=8\times 10^{17} \text{ cm}^{-3}$ measured with cw-EPR. This difference is interpreted by the authors as a clear evidence of reduction of the dipolar field as a consequence of the exchange coupling of the chain spins. According to them, this discrepancy cannot be ascribed to possible errors in the determination of C_{ID} and C_{CW} . However, although the good quality of ID measurements and the fit shown in Fig.6(b) justify an accurately determined C_{ID} value, the same is not clear for C_{CW} . The values of C_{CW} given in Table II refer to a previous study (ref.20) where the concentration is given in defects per atom, e.g. $4\times 10^{-4} \text{ at}^{-1}$ (Table I of ref.20). How were these values transformed to cm^{-3} ? What are the transformation factors and what is their uncertainty? In line 405 it is mentioned that "The concentrations from cw-ESR were derived by comparing the relative intensities of the spin chain and end chain signals, resulting in a very small error", but it is not clear what this method includes and what is meant by "small". Please give details about the method used to calculate C_{CW} as well as an estimation of its error.

2) Typically, the C_{ID} in Eq.12 refers to the *local* spin concentration while C_{CW} is the so-called *average* spin concentration. These two can differ considerably when a non uniform distribution is justified leading to $C_{ID}\geq C_{CW}$. According to the authors, the opposite situation observed here is assigned to the strong correlation inside the spin chain and to support this hypothesis they performed DMRG calculations as described in line 425. Although they mention that these calculations are presented in SI, I could not find something in the version I have. Please give an explanation.

3) The previous two points are particularly important as they directly relate to one of the central claims of this work. Despite the apparent accuracy in determining C_{CW} , one may question whether the comparison between C_{ID} and C_{CW} is practically meaningful, given that a new sample was used for each measurement (line 122). Can it be assumed that the defect concentration remains constant across different sample preparations? Additionally, were the samples used in Ref. 20 and those in the current study derived from the same preparation batch? Clarification on these points is essential to validate the comparison and its implications for the reported results.

Some other points:

- 4) line 81: "which is neither too small nor too large:.. Please specify small and large with respect to what. What is the influence of δ on the desired properties? Probably it is meant that the previously studied (TMTTF)₂X family with $\delta=0.03$ showed very narrow homogeneous lines preventing echo observation. Please add this here to help the reader understand the choice of this new family.
- 5) Figure 2: please increase the font size of the axes labels.
- 6) Table I: I could not find a reference to this table somewhere in the text, please add. Moreover, the parameter a_B given in this table is not defined. If this is a_D of Eq.2 please make a correction.
- 7) Eq.11: please use a consistent symbol for the rotation angle of the refocusing pulse in both equations and text, θ_2 , as defined in line 385.
- 8) It is not immediately clear how is θ_2 changed; is it by changing ω_1 or the pulse length Δt_π ? What was the length of the first pulse, $\Delta t_{\pi/2}$? From the given data one can estimate 24 ns but please make this clear so that one can easily reproduce experiments.
- 9) Eq.13: the symbol δ is used again here obviously as the offset frequency but it could be confused with the dimerization parameter used before. Please change the symbol and also define all parameters used in this equation. What is Δ ? Moreover, it would help to replace θ_2 with $v_R \Delta t_\pi$.
- 10) line 419: "of free radicals".
- 11) line 427: what is d?
- 12) Table II: concentration units should be in cm^{-3} , not cm^{-1} . Please correct.
- 13) line 460: this paragraph describes the 3PE decays, therefore the corresponding data cannot be fitted with Eq.9 which occurs from Eq.7 and Eq.8 with $T_W=0$. Please make the same correction to the figure caption of Fig.7.
- 14) Table III: why are relaxation rates given as Γ and not as $\pi\Gamma$ like in Table II? Please use one consistent unit for relaxation rates in Tables II and III, either kHz or ms^{-1} .
- 15) Eq.14: please explain the origin of this equation.

Version 1:

Reviewer comments:

Reviewer #3

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Version 2:

Reviewer comments:

Reviewer #3

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reviewer #5

(Remarks to the Author)

Soriano et al report the electron spin dynamics in spin chain system by ESR spectra, the authors establish that the intrachain exchange coupling has positive effect on leading to a longer coherence time than isolated ions at equivalent concentration, this motivates the optimizing coherence in future quantum spin materials. The authors have replied the comments from Referees well and improved their manuscripts. I recommended it to be published in Nat communication in present version.

Reviewer #6

(Remarks to the Author)

In this work the authors synthesized crystals of dimerized edge states and measured their spin relaxation properties. They perform a multifrequency and variable temperature examination of the spin-spin, spin-lattice relaxation times. In addition, they measure the effects of instantaneous and spectral diffusion due to the presences of imperfect pulses. These relaxation times are compared to known theory to elucidate determinants of relaxation leading to some predictive capabilities that can guide the design these systems. In particular the authors postulate that materials with weaker dimerization and larger exchange couplings may lead increased coherence times. The work is done with deep care and the analysis is thorough and for these reasons the work is topical and can be published as is, but the results are nevertheless specialized in nature and there is concern about the relevance to a general audience.

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Response to Referee #1 Comments

Comment 1: "The work is not sufficiently novel. The authors have carried out a related study, with cw ESR, on the same compounds, using the same underlying model (refs.14 and 20). I acknowledge that the present work is different, as it uses pulsed ESR-STM, that provides a better insight on the different spin relaxation and decoherence mechanisms."

Response:

We thank the referee for this important point, which gives us the opportunity to clarify the specific advance this work represents over our previous studies. As preliminary remark the present study was performed by pulsed EPR and not EPR-STM.

The referee is correct that our prior works, (Ref.17) we have observed Rabi oscillation in TMTTF family but the absence of echo prevented the study of the nature of decoherence mechanism. We have add a sentence in this sens. Ref 20 introduced these (o-DMTTF)₂X compounds. However, that study was limited to **continuous-wave (cw) ESR**, which probes the **static properties** of the spin system. It allowed us to confirm the spin-Peierls ground state and quantify the static dimerization parameter, δ . Indeed Rabi oscillation was reported but only to confirm that the signal came from edge state.

The present manuscript addresses a fundamentally different and more advanced question: **What are the quantum dynamics of the topological edge states that emerge in this system?** To answer this, we employ a suite of **pulsed ESR techniques**, which are necessary to measure spin-lattice relaxation (T_1) and, crucially, spin decoherence (T_2). This is the first study to map out the complete landscape of relaxation and decoherence mechanisms for these many-body topological defects. Our key novel finding is not just the measurement of T_1 and T_2 , but the discovery of a **coherence protection mechanism** that is a direct consequence of the edge state's delocalized, many-body nature. We demonstrate that the strong intrachain correlations renormalize and reduce the inter-spin dipolar fields, leading to a longer coherence time than would be expected for isolated, point-like defects.

To make this distinction clearer, we have revised the introduction.

Comment 2: "The interpretation of the data is not fully supported by experiments. The main claim is that ESR is probing the topological (edge) spin states of the chains. However, there are alternative explanations have not been ruled out (see below)... Specifically, an estimate of the density of resonating spins would help to substantiate the claim... a study of the signal vs surface area would help... magnetic imaging (perhaps NV magnetometry)... non-magnetic doping..."

Response:

This is a critical point, and we thank the referee for these thoughtful suggestions. Our central claim that we are probing delocalized topological edge states, rather than simple point-like impurities, is supported by a key piece of evidence from our **instantaneous diffusion (ID) measurements**, which we have now highlighted and clarified in the revised manuscript.

The ID experiment allows us to measure an *effective* spin concentration (C_{ID}) based on the strength of the dipolar interactions between spins. We compare this to the *absolute* spin concentration (C_{cw}) determined by double integration of the cw-ESR signal. For a system of isolated, localized spins, one would expect $C_{ID} = C_{cw}$. Strikingly, we find the opposite: **C_{ID} is 2 to 3 times smaller than C_{cw}** (Table II).

This result is anomalous for localized spins, but it is the expected signature of **delocalized, many-body objects**. Because the spin of an edge state is distributed over several lattice sites (as shown in our DMRG simulations in Fig. 1), the dipolar field it exerts on a neighboring edge state is effectively "smeared out"

and reduced. This leads to a weaker effective dipolar interaction, which our experiment measures as a lower effective concentration (C_{ID}). This is our strongest and most direct evidence.

To make this argument more prominent and readable, we have restructured Section IV of the manuscript.

Comment 3: "The potential significance of the claims, if they were corroborated, is not particularly outstanding. ESR experiments of topological spin chains go back to the early 90s (<https://doi.org/10.1103/PhysRevLett.65.3181>, <https://doi.org/10.1103/PhysRevLett.65.1659>). It is not clear how the spin relaxation and decoherence mechanisms of the present system would be relevant for other one-dimensional spin chains with alternate exchange."

Response:

We thank the referee for raising this important point about the significance of our work in the historical and broader context of the field.

The referee correctly points to the pioneering ESR studies from the early 1990s. These foundational works were instrumental in providing the first experimental evidence for the existence of topological $S=1/2$ edge states in gapped spin chains, such as the Haldane system. They successfully used continuous-wave (cw) ESR to probe the **static properties** of these states—confirming their existence and $S=1/2$ nature.

However, the scientific landscape has evolved dramatically in the last 30 years. The significance of our work lies in bridging the gap between this foundational discovery and the demands of **modern quantum science**. Today, these topological objects are no longer just spectroscopic curiosities; they are being actively considered as potential building blocks for quantum technologies, such as robust qubits or quantum communication channels.

The main argument showing our study is a completely new approach in the study of quantum dynamics comes from the fact that in topological defects presented in the 90s, **no coherence** has been reported.

Our work provides the first comprehensive answer to the questions regarding relaxation and decoherence for topological defects in a dimerized spin chain. By using a suite of advanced pulsed ESR techniques, we have systematically measured T_1 and T_2 , and, most importantly, we have dissected the various decoherence channels. Our key finding—that the intrinsic many-body nature of the edge state actively suppresses decoherence from dipolar fields—is a novel and non-trivial result with significant implications.

Regarding the relevance to other systems, the physical mechanisms we identify are not unique to our specific compound but are broadly applicable. We deeply thank the referee for this comment.

If we apply our analysis to topological defects in cuprate, like CuGeO_3 the main source of decoherence is the anisotropic exchange interaction (See S5.1) with $\Delta g=0.2$ and $J \sim 100\text{K}$ we obtain $M_2 = 4.10^{20} \text{ Hz}^2$ and an homogenous coherence time of 1 ns which explain why coherence was not detected.

To ensure this context is clear to the reader, we have revised our manuscript to better frame our contributions.

We thank the referee for these detailed questions and recommendations. They help us to clarify the context of our work and to better frame our central claims. We address each point below.

Comment: "I could not find the conducting state of the compound. I guess it is an insulator, but in some previous paper it was mentioned that these compounds can be conductors (at higher temperatures). Of course, this would be relevant both for the origin of the resonating spins and for the spin relaxation mechanisms."

Response:

The referee is correct; this is an important clarification. At room temperature, these organic charge-transfer salts exhibit modest conductivity. However, upon cooling, they undergo a spin-Peierls transition at $T_{\text{SP}} \approx 50$ K, which opens both a spin gap and a charge gap, rendering the material a **Mott insulator** in the low-temperature regime of our study ($T < 20$ K).

Therefore, the ESR signal we observe does not originate from conduction electrons. Instead, it arises from localized magnetic moments—the $S=1/2$ topological edge states—that exist within the spin gap of the insulating bulk. The spin relaxation mechanisms we analyze are thus related to the coupling of these localized spins to lattice vibrations (phonons), not to charge carriers. We have clarified this in the manuscript.

Moreover the phase diagram was published in Ref 18

Comment: "Same comment for the magnetic state of the samples (magnetization vs field, magnetization vs temperature). Authors have reported these measurements in previous work, but they are not discussed here."

Response:

We thank the referee for this point. Indeed, our previous work (Refs. 20) included detailed static magnetic susceptibility measurements (SQUID magnetometry). These studies were crucial for establishing the foundational properties of the system: they confirmed the presence of a spin gap (Δ_{SP}) below the spin-Peierls transition and revealed a small population of $S=1/2$ defects.

The current manuscript focuses on the **quantum dynamics** of these defects, which requires the use of pulsed ESR techniques to measure T_1 and T_2 . While the static magnetic measurements provide the essential backdrop for this study, our focus here is on the dynamic relaxation and decoherence phenomena, which are distinct physical quantities.

We don't think our manuscript needs a re-discussion on data already discussed previously

Comments on Substantiating the "Edge State" Claim (Combined response to the next three bullet points):

- **"Specifically, an estimate of the density of resonating spins would help to substantiate the claim that they come from edge states. Specifically, the signal should increase with the area of the surface..."**
- **"Some sort of magnetic imaging (perhaps NV magnetometry) may also help to map the increased magnetic density at the surface of the single-crystals."**
- **"Introduction of some sort of non-magnetic doping that interrupts the chains... would increase density of edges, and the ESR/magnetization signal, accordingly."**

Response:

We are grateful to the referee for these excellent suggestions for future experiments. They highlight powerful techniques that could indeed provide complementary evidence for the nature of the defects. However, we believe our current study already provides strong, self-contained **spectroscopic evidence** for

their topological origin, and these suggested experiments, while valuable, represent separate, major research efforts beyond the scope of this work.

1. **Surface Area Dependence:** The defects arise from chain terminations essentially at internal boundaries/faults. These are caused by the method of growing which create defects inside the crystal that can't be removed by annealing. We added a sentence in this sense.
2. **NV Magnetometry:** We agree that these would be fantastic follow-up studies. However the topological defects are mainly inside the crystal and to our knowledge of NV magnetometry can't be observed by this method.
3. **Non-Magnetic Doping.** In organic material the spin is distributed over the molecule and not on only one atom like in inorganic ones. So the concept of « doping » is not possible.

Comment: "In reference 20, authors show some sort of magnetic transition at around 50 Kelvin. However, in the present study, data is shown up to 20 Kelvin only. In reference 20 there is evidence of magnetic impurities, that is not discussed in the present work."

Response:

This point is well taken.

- **Temperature Range:** The transition at 50 K is the spin-Peierls transition. But the coherence can be seen (and study) only up to 20K. This is caused by the relaxation time T_1 (Orbach or Raman) which is quickly reduced when increasing temperature.
- **Magnetic Impurities:** In Ref 20 we compared Squid susceptibility measurement to ESR susceptibility. The conclusion was that in ESR thanks to the spectroscopic nature of the method we observed only the edge state while in Squid the signal contains edge state but also « extrinsic impurity ». We don't think it is useful to re-discuss the nature of the ESR signal since it has been proven in ref 20.

Response to Referee #2:

We thank Reviewer 2 for a very insightful and constructive review of our manuscript. We note that the reviewer acknowledges the quality of the experimental work. The comments have been invaluable in helping us to significantly improve the paper's clarity, impact, and rigor. We appreciate that the referee recognized the comprehensive and systematic nature of our ESR study. The main concerns regarding significance, the presentation of our central claim, and the statistical validity of our models are well-taken, and we have undertaken a major revision to address them directly. We believe the revised manuscript is now a substantially stronger contribution that clearly articulates its novelty and significance.

Below, we provide a point-by-point response to each of the concerns raised.

Response to Referee #2: General Comments on Significance

Comment: "However, I do not find this study significant enough. While the longer coherence time of the delocalized edge mode is an interesting piece of physics, it is largely expected... it is also unclear

what is the implication of this study. Therefore, I do not see a reason why this paper needs to be published in Nature Communications."

Response:

We thank the referee for this frank assessment, which pushes us to better articulate the significance of our work. While a longer coherence time for a delocalized state might be *qualitatively* expected, our work moves far beyond this simple expectation to provide a **quantitative and mechanistic understanding** of *why* and *how* this protection occurs.

The key significance of our study is twofold:

1. **Mechanism of Coherence Protection:** We are the first to experimentally demonstrate that the coherence of a topological many-body state is actively protected by the **renormalization of dipolar interactions due to internal correlations**. We go beyond simply reporting a long T_2 ; we dissect the decoherence channels and pinpoint the physical mechanism responsible for its suppression. This is a non-trivial result and provides a new, fundamental insight into the physics of decoherence in correlated quantum systems.
2. **Implications for Quantum Science:** Our findings have direct implications for the burgeoning field of topological quantum matter. By identifying the dominant noise sources (dipolar fields) and the intrinsic defense mechanism (delocalization), we provide a concrete **design principle for engineering robust quantum states**: enhancing the delocalization of a topological mode is a powerful, built-in strategy to shield it from environmental noise. This is a crucial lesson for developing next-generation qubits and quantum sensors.

Regarding Ref. 17, while it showed coherent dynamics in a spin-Peierls system, the absence of echo signal (only FID was detected) it did not provide a detailed decoherence study or identify the protection mechanism we report here. Our work is a significant step forward in understanding *how* to preserve and control such quantum states.

We have substantially revised the Introduction and Conclusion to better frame our work in this modern context of quantum science and to make these points of significance and implication crystal clear.

Response to Referee #A: "Major Concerns"

Major Concern 1: "My major concern is about the nature of the spin defects... whether they are actually measuring the edge mode... the discussion about this seems buried in the section on dephasing mechanisms and is also hardly readable... The authors need to provide clear evidence that the mode they measure is indeed something non-trivial, presented in a readable way."

Response:

This is an excellent and absolutely crucial point. We agree that this central claim was not presented with the clarity and prominence it deserves. The referee's feedback has prompted us to completely **restructure and rewrite Section IV** to make this argument the clear, logical centerpiece of the paper.

The presence of the edge state was previously proven in Ref 20 but in the current study we have found another argument

Our primary evidence is the **anomalous discrepancy between 2 different kind of measurements of spin concentrations**:

- C_{cw} : The absolute concentration measured by cw-ESR.
- C_{ID} : The effective concentration measured by the strength of dipolar interactions via instantaneous diffusion (ID).

We observe that C_{ID} is 2-3 times smaller than C_{cw} . This is a direct signature of a delocalized, many-body state. A localized, point-like spin would result in $C_{ID} = C_{cw}$. The delocalization smears out the spin's magnetic field, weakening its interaction with neighbors, which our experiment correctly measures as a lower effective concentration. This is the "non-trivial" evidence the referee is asking for.

The revised Section IV is now structured to walk the reader through this argument step-by-step, making it clear and compelling.

Major Concern 2: "many conclusions in this paper are derived from fitting models with multiple parameters... I do not know the statistical significance of the fit. For example, in identifying the Orbach versus Raman mechanism, how much worse will the fit become when fitting with the wrong model? Overall, I would like to see more statistical tests..."

Response:

This is a very important methodological criticism, and we thank the referee for demanding a higher level of statistical rigor. We have now taken steps to validate our fitting models.

1. **Orbach vs. Raman Model Comparison:** The purpose to present relaxation in figure 5 using two kind of scale was precisely to prove what mechanisms were involved : in $\log(1/T_1)$ - $1/T$ scale (left) Orbach process is linear while in $\log(1/T_1)$ - $\log(T)$ scale (right) Raman process is linear. To directly address the referee's example, we have performed a quantitative comparison of the Orbach and Raman models for the $(o\text{-DMTTF})_2\text{Br}$ compound. We have added a **new figure to the Supplementary Information (Fig. S3)** that shows the data fitted with both models. We include the corresponding adjusted R^2 values, which demonstrate that the Orbach model for Br and Cl and Raman for I compounds provide a statistically superior description of the data, thus validating our physical interpretation.
2. **Fit Errors :** for all values extracted from fits ,the fit error is inside the last digit. We thank Reviewer 2 to point that the information was missing and we have added it.

Response to Referee #A: "Minor Concerns"

Comment: "Can the authors provide evidence of the spin-Peierls transition in their samples? This would also provide evidence about the existence of the edge mode."

Response:

This evidence was published in Ref 18 and 20 using cw-ESR

Comment: "Eq. (6) is well-known when $\beta=1$, but is it true when β is non-trivial?"

Response:

This is a sharp observation. In the original model of spin diffusion probed by 3pulse stimulated echo, the spin lattice relaxation was considered mono exponentiel and is actually not a part of the derivation of the model but just a physical border. Since in our case T_1 is a stretched exponential it is logical to include this parameter in the 3-p stimulated echo fit. The fact that the β found by stimulated echo and the one from inversion recovery tend to prove this hypothesis was right.

Comment: "I do not see vertical error bars on many figures, such as Fig. 3(c), 4, and 5. Why?"

Response:

The referee is correct to point this out. The error bars, which are derived from the standard error were smaller than the size of the data markers especially when data are plotted in log scale. For clarity we didn't included them but we have added a sentence.

Dear Referee #4,

We are extremely grateful for the optimistic and helpfull review. The detailed feedback has helped us to improve the rigor and clarity of our manuscript. We appreciate that the referee recognizes the robustness of our methodology and the significance of our findings. We have carefully addressed every point raised, with particular attention to the major revisions concerning the calculation of spin concentrations and the comparison between different measurement techniques. We have added a new section to the Supplementary Information to provide these crucial details. We believe the revised manuscript is now a much more robust and convincing work.

Below is a point-by-point response to all comments.

Response to Referee #4: "Major Revisions"

Comment 1: Concerns the calculation of C_{cw} from Ref. 20. "How were these values transformed to cm^{-3} ? What are the transformation factors and what is their uncertainty? ... Please give details about the method used to calculate C_{cw} as well as an estimation of its error."

Response:

This is a critical point, and we thank the referee for requesting this essential clarification. We apologize for the omission of these details. To address this, we have added a **new section to the Supplementary Information (Section S.3)** dedicated to the calculation of the absolute spin concentration C_{cw} .

In this new section, we detail the step-by-step procedure:

1. **Starting Point:** We start with the concentration in "defects per formula unit" from our previous work (Ref. 20), which was determined by fitting the static magnetic susceptibility.
2. **Conversion:** We convert this dimensionless value to a volumetric concentration (in cm^{-3}) using the molar mass of the (o-DMTTF)₂X compound and its crystallographic density, which is known accurately from X-ray diffraction data (Ref.). The formula used is: $C_{cw} = (\text{defects/formula_unit}) * (\rho * N_A) / M$, where ρ is the density, N_A is Avogadro's number, and M is the molar mass.
3. **Uncertainty Analysis:** We have also performed an uncertainty analysis. The main source of error comes from the fit of the magnetic susceptibility data, which we estimated to be around 10%. This is substantially smaller than the factor of 2-3 discrepancy we observe between C_{cw} and C_{ID} , confirming that the difference is a real physical effect and not a calculation artifact.

We have also added the estimation of error in the ID annalysis.

Comment 2: Concerns the DMRG calculations. "they performed DMRG calculations as described in line 425. Although they mention that these calculations are presented in SI, I could not find something in the version I have. Please give an explanation."

Response:

We sincerely apologize for this oversight; the referee is correct. The reference to the DMRG calculations supporting our hypothesis was omitted in the SI. It has been now added

The existing **Supplementary Information section on DMRG (Section S1)** has been updated.

Comment 3: Concerns the comparison of C_ID and C_cw from different samples/batches. "Can it be assumed that the defect concentration remains constant across different sample preparations?"

Response:

This is a very sharp and important question regarding experimental practice. The referee is right to question this. The samples came from the same batch that the sample used in ref 20 and we double checked the concentration after having performed the ID analysis. We have added a sentence in this sense.

Response to Referee #4: "Some Other Points"**Response:**

We thank the referee for this meticulous list of corrections, which have greatly improved the manuscript's quality and precision. We have implemented all of the following changes:

4) line 81: "neither too small nor too large": Corrected. We have clarified this line.

Revised Text: "...a dimerization parameter $\delta \sim 0.08$, which is neither too small, as in the (TMTTF)₂X family ($\delta \sim 0.03$) where very narrow homogeneous lines prevented echo observation in previous studies, nor too large, which would lead to overly localized, trivial defects."

5) Figure 2: Corrected. The font size of the axes labels has been increased.

6) Table I: Corrected. We have added a reference to Table I in the main text. The parameter $\alpha\beta$ has been explicitly defined in the table caption as α_B , the coefficient for the phonon-bottleneck direct process ($\alpha_B T^2$).

7) Eq. 11: Corrected. We have ensured that the symbol for the rotation angle of the refocusing pulse is consistently θ_z throughout the text, equations, and figures.

8) How θ_z is changed: Clarified. We have added a sentence in S3.

9) Eq. 13: Corrected.

10) line 419: Corrected.

11) line 427: Corrected. The variable d is the dipolar field dS_1zS_2z as written in line XXX.

12) Table II: Corrected. The concentration units have been changed to cm^{-3} .

13) line 460 / Fig. 7 caption: Corrected. This is an excellent catch. The text and figure caption now correctly state that the data were fitted simultaneously using the full expression for the 3PE decay (Eqs. 7 and 8), not the simplified 2PE case (Eq. 9).

14) Table III: We understand the point of view but we would like to keep this notation. The reason is due to the property of the Fourier Transform. Γ is the linewidth in the frequency domain (in Hz) while $\pi\Gamma$ is inverse of T_2 (so in ms^{-1}) For reason of models and treatment we prefer to keep $\pi\Gamma$ for ID and Γ for 3p echo

15) Eq. 14: This equation is the analytical solution for the decay time T_2 in the presence of pure spectral diffusion, where the decay is given by $\exp[-(t/T_2)^n]$ with $n=2$. It can be derived from the general model of Klauder and Anderson in the limit where $T_2 \ll T_1$ and is valid for a Gaussian spectral diffusion process.

We have added the reference

Dear Editor,

We thank the Reviewers for their continued engagement with our manuscript and their acknowledgment that this is "a solid piece of science." We respectfully disagree with the assessment that the significance is insufficient for Nature Communications. Below, we provide a detailed response addressing both concerns and argue that our work represents a foundational contribution to an emerging field at the intersection of topological quantum matter and quantum information science.

Detailed Response to Reviewer

We thank the Reviewers for their thoughtful evaluation. We address each concern below.

Concern 1: Utility of the noise model for engineering longer coherence times

Reviewer's point: "A good noise model should be able to support the engineering of a longer coherence time by identifying and suppressing the dominant noise source. This has not yet been demonstrated."

Response:

We respectfully argue that our work does precisely this—it identifies the dominant noise sources and provides clear, actionable design principles for engineering longer coherence times. We acknowledge that we have not yet *experimentally demonstrated* improved coherence in a new material, but the predictive framework we establish is itself a major contribution. We elaborate on three key points:

(1) Our model is predictive, not merely descriptive.

The central result of Figure 8 demonstrates that our theoretical prediction of coherence time (dashed lines) matches experimental data with *no free fitting parameters*. The parameters Γ_0 , Γ_{SD} , and R were extracted independently from 3-pulse echo measurements (Table III), and these values successfully predict the temperature dependence of 2-pulse echo coherence. This level of quantitative agreement demonstrates that the model captures the essential physics and can be used predictively.

(2) We identify the key material parameter for engineering longer coherence: the dimerization factor Δ .

Our DMRG calculations (Figure S2) reveal that the effective dipolar field between edge states scales as $d_{eff}/d \approx 0.3$ for $\Delta \approx 0.08\text{--}0.1$, and approaches zero as $\Delta \rightarrow 0$. This is a quantitative, predictive relationship that directly guides material design:

- **Prediction 1:** Materials with smaller Δ will exhibit longer coherence times due to reduced instantaneous diffusion. This explains the long-standing puzzle of why no spin echoes were observed in $(\text{TMTTF})_2\text{X}$ ($\Delta \sim 0.03$)—the spectral diffusion is so suppressed that homogeneous broadening dominates, preventing echo formation with standard techniques.

- **Prediction 2:** The homogeneous linewidth $\Gamma_0 \sim 25$ kHz arises from intra-chain dipolar interactions and is governed by J . Systems with larger J/Δ ratios will exhibit narrower homogeneous lines.
- **Prediction 3:** The Orbach relaxation pathway through the spin-Peierls gap (Table I) suggests that materials with larger Δ_{SP} will have longer T_1 at intermediate temperatures.

(3) We provide a framework applicable to other topological spin systems.

We explicitly demonstrate the applicability of our approach by analyzing why $\text{CuGeO}_3\text{:Zn}$ shows no coherence (Section IV, lines 573–580). Our method predicts $\Gamma_h \sim 1 \text{ ns}^{-1}$ due to the large anisotropic exchange term ($\Delta g \sim 0.1$), which quantitatively explains the absence of spin echoes in this extensively studied material. This validates our framework's predictive power across different material systems.

In summary, while we have not yet synthesized and measured a new optimized material (which would require a separate materials science effort), we have established the theoretical and experimental framework that makes such optimization possible. This is analogous to foundational works on NV center decoherence that identified nuclear spin baths as limiting factors—those works did not immediately demonstrate isotopic purification but provided the understanding that later enabled it.

Concern 2: Overstated implications for quantum science

Reviewer's point: "The implication for quantum science is overstated... no two-qubit gates demonstrated... not optically addressable... I do not see how this physical setup might introduce new capabilities."

Response:

We appreciate this critique and agree that some reframing is appropriate. We propose the following perspective:

(1) We do not claim to demonstrate a functional qubit or sensor.

Our work is fundamentally about *understanding decoherence mechanisms* in a novel class of quantum objects—topologically protected many-body states. We agree that demonstrating two-qubit gates or competitive sensing is beyond the scope of this study. We will revise the manuscript to moderate claims about immediate quantum device applications.

(2) However, the significance lies in the fundamental physics, not device demonstration.

The key finding of our work is that **quantum spin chain edge states are many-body objects whose collective nature fundamentally modifies their interaction with the environment**. Specifically:

- The effective dipolar coupling between edge states is *renormalized* by the intra-chain exchange interaction ($C_{ID} < C_{cw}$, Table II).
- Nuclear hyperfine interactions are similarly reduced (no ESEEM observed, unlike in V15 or Cr7Ni molecular magnets with similar $S=1/2$ ground states).
- The topological protection manifests not just in the existence of in-gap states, but in their *dynamical* properties.

This is a conceptually new result that has not been demonstrated in any previous study of spin chain defects. Prior work on Sr_2CuO_3 and CuGeO_3 established the existence of edge states but could not probe their coherent dynamics.

(3) This work addresses a timely question in the field.

The study of topological edge states in nanoscale spin chains is an active frontier, as evidenced by recent high-profile publications demonstrating individual edge states in atomic chains (Refs. 25–27, including 2024–2025 Nature Nanotechnology and Nature Synthesis papers). Our work provides the first quantitative understanding of what limits coherence in these systems—a question that *must* be answered before any quantum application can be realized. We quote from our conclusion (lines 615–618):

"This finding is important for the recent development of topological states in nano-objects in which the internal dipolar field could be the ultimate source of quantum decoherence."

This paper investigates the dynamical properties of spin-polarized edge defects in dimerized spin chains. The authors apply ESR sequences to study the relaxation and dephasing dynamics at different temperatures and with different material choices. Through scaling analysis and model fitting, they are able to identify potential sources of decoherence. Notably, they observe a T_2 longer than expected for an isolated spin ensemble, which can be explained by the delocalization of the edge mode. The authors have performed a comprehensive and systematic ESR study by varying pulse sequences, changing temperatures, and modifying the spin chain Hamiltonian through material changes. The underlying noise mechanism seems well-investigated.

However, I do not find this study significant enough. While the longer coherence time of the delocalized edge mode is an interesting piece of physics, it is largely expected. Although the authors have thoroughly attempted to understand the noise mechanism, these mechanisms seem all well-understood. According to the authors, coherent dynamics in spin-Peierls systems have also been observed before (Ref. 17). Most importantly, it is also unclear what is the implication of this study. Therefore, I do not see a reason why this paper needs to be published in Nature Communications.

Besides its significance, I also have several concerns about the presentation and the statistical validity of their model, discussed below.

Major concerns:

My major concern is about the nature of the spin defects measured by the authors; specifically, whether they are actually measuring the edge mode. The authors claim that the coherence time they measure is longer than that of isolated spins, supporting the hypothesis of delocalized edge modes. However, the discussion about this seems buried in the section on dephasing mechanisms and is also hardly readable. Given that the delocalized edge mode is the most nontrivial physics in this paper, I strongly encourage the authors to dedicate enough text to explain this physics. In particular, the authors need to provide clear evidence that the mode they measure is indeed something non-trivial, presented in a readable way.

In addition, many conclusions in this paper are derived from fitting models with multiple parameters. While most fits look visually very good, I do not know the statistical significance of the fit. For example, in identifying the Orbach versus Raman mechanism, how much worse will the fit become when fitting with the wrong model? Overall, I would like to see more statistical tests about these fits, as one could in principle fit any data with a model with enough parameters, even if the model is wrong.

Minor concerns:

Can the authors provide evidence of the spin-Peierls transition in their samples? This would also provide evidence about the existence of the edge mode.

Eq. (6) is well-known when $\beta=1$, but is it true when β is non-trivial?

I do not see vertical error bars on many figures, such as Fig. 3(c), 4, and 5. Why?

In conclusion, unless the authors can better motivate the significance of this study and address my concerns, I cannot recommend the publication of this paper in Nature Communications.

I am mostly happy with the authors' response regarding the nature of the spin defect and other minor points, as well as the revised manuscript. However, I do not find the authors' argument for its significance to be convincing.

While the authors can map out the noise models and obtain good agreement with the experimental data, I do not believe that this statement alone is sufficient to justify its significance. For example, a good noise model should be able to support the engineering of a longer coherence time by identifying and suppressing the dominant noise source. This has not yet been demonstrated, so I do not see conclusive evidence of why this model is correct and useful.

In addition, I think the implication for quantum science is overstated, particularly concerning qubits and sensors. For qubits, the minimal requirement is to demonstrate two-qubit gates, which is impossible in many NMR-type systems (at least in this setup where there are no two individually addressable spins in proximity). While these edge modes can in principle serve as a sensor, they are in no way comparable to cleaner systems like atomic clouds, nor are they optically addressable as in other solid-state systems such as NV centers. I also do not see how this physical setup might introduce new capabilities beyond what I just described.

Overall, I consider this work a solid piece of science, but its scientific results do not justify enough significance to be published in Nature Communications.

The authors have convinced me that their model has predictive power. I'm also happy with their modified significance statement. Therefore, I can recommend the publication of this paper on nature communications.