nature portfolio

Peer Review File

Waveguide quantum electrodynamics at the onset of spin-spin correlations.

Corresponding Author: Professor Fernando Luis

This file contains all editorial decision letters in order by version, followed by all author rebuttals in order by version.

Version 0:

Decision Letter:

** Please ensure you delete the link to your author homepage in this e-mail if you wish to forward it to your coauthors **

Dear Professor Luis,

Thank you for submitting your manuscript, "Waveguide quantum electrodynamics at the onset of spin-spin correlations.", to Communications Materials. It has now been seen by 3 referees, whose comments are appended below. You will see that while they find your work of interest, some important points are raised. We are interested in the possibility of publishing your study in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript before we make a decision on publication.

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

-A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.

-A clean version of the manuscript. Please select the file type 'Article File'.

-An updated Editorial Policy checklist, uploaded as a 'Related Manuscript File' type. This checklist is to ensure your paper complies with all relevant editorial policies. If needed, please revise your manuscript in response to these points. Please note that this form is a dynamic 'smart pdf' and must therefore be downloaded and completed in Adobe Reader. Clicking this link will download a zip file containing the pdf.

In the event that your manuscript is accepted we will provide detailed guidance on our journal policies and formatting. You may however wish to ensure that the manuscript complies with our house style at this stage. See our style and formatting guide (https://www.nature.com/documents/commsj-phys-style-formatting-guide-accept.pdf) and checklist (https://www.nature.com/documents/commsj-phys-style-formatting-checklist-article.pdf) for reference.

Data availability statements and data citations policy: All Communications Materials manuscripts must include a section titled "Data Availability" at the end of the Methods section or main text (if no Methods). More information on this policy, and a list of examples, is available at http://www.nature.com/authors/policies/data/data-availability-statements-data-citations.pdf.

In particular, the Data availability statement should include:
- Accession codes for deposited data
- Other unique identifiers (such as DOIs and hyperlinks for any other datasets)
- At a minimum, a statement confirming that all relevant data are available from the authors
- If applicable, a statement regarding data available with restrictions
- If a dataset has a Digital Object Identifier (DOI) as its unique identifier, we strongly encourage including this in the Reference list and citing the dataset in the Data Availability Statement.

DATA SOURCES: We strongly encourage authors to deposit all new data associated with the paper in a persistent repository where they can be freely and enduringly accessed. We recommend submitting the data to discipline-specific, community-recognized repositories, where possible and a list of recommended repositories is provided at http://www.nature.com/sdata/policies/repositories.

If a community resource is unavailable, data can be submitted to generalist repositories such as figshare or Dryad Digital Repository. Please provide a unique identifier for the data (for example a DOI or a permanent URL) in the data availability statement, if possible. If the repository does not provide identifiers, we encourage authors to supply the search terms that will return the data. For data that have been obtained from publically available sources, please provide a URL and the specific data product name in the data availability statement. Data with a DOI should be further cited in the methods reference section.

Please refer to our data policies at http://www.nature.com/authors/policies/availability.html.

Please use the following link to submit your documents:

Link Redacted

** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to receive your revised paper within three months; please let us know if you aren’t able to submit it within this time so that we can discuss how best to proceed. If we don’t hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Klaas-Jan Tielrooij, PhD
Editorial Board Member
Communications Materials
orcid.org/0000-0002-0055-6231

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

In their manuscript "Waveguide quantum electrodynamics at the onset of spin-spin correlations", Roca-Jerat and co-authors study a spin species, DPPH, which may form spin chains at low temperature through spin-exchange interactions by probing its absorption of microwave power. They characterize the properties of DPPH through several measurements as a function of temperature (magnetic susceptibility, heat capacity, continuous wave and pulsed EPR measurement, as well as the core of the paper, broadband microwave measurements), so that their analysis is well backed.

The novelty of the paper is about studying the transformation of having a spin ensemble coupled to a waveguide (which translates into microwave absorption when the microwaves matches the Larmor frequency of the spins) to having magnons coupled to the waveguide (which also translates into microwave absorption when the microwaves matches the magnon frequency). The difference in the two regimes comes from observing the frequency shift and the broadening occurred by shifting from a weakly non-interacting spin ensemble to a strongly interacting one. The analysis developed by the authors is interesting and captures a few of the features of this transitions, though not all (see questions below).

Previous work on this type of experiment has already been published (ref 29-32 in the paper), and the main difference between this article and these works is that the current article use a waveguide to study the spins absorption (broadband characterization) instead of a superconducting resonator (narrow-band). The authors argue that although their technique becomes less sensitive, it allows them to probe a large scale of energy range. However, in the current article, this broadband property does not seem to be used. For example, it should become possible to explore different regimes comparing the interaction exchange versus the Zeeman energy but this is not realized here (i.e how would vary the spin linewidth versus magnetic field below the antiferromagnet transition ? it's hinted at in the analysis of the supp mat, but not measured).

The paper is overall well written, with details analysis in the supplementary material and appropriate summary of the corresponding model in the main text. I believe these datasets are quite thorough and represent a very good study of magnon coupled to microwave physics, but the novelty of the paper (being broadband) does not play a large role in it. The application to characterization of spin-spin exchange interaction could be interesting, but as far as I understand, the authors' analysis falls slightly short in that regard. I am thus hesitant to recommend publication in Nature's Communications Materials.

Remarks and questions:

- Why does the title mention "at the onset of" ? It hints at some threshold of spin-spin correlations being crossed, but this is not discussed in the main text. To me, it looks like the experiment described here ise clearly in a regime where the spin-spin correlations play a significant role, and can not be neglected.

- I do not understand the fit of the antiferromagnetism anisotropy. How are the authors able to characterize separately \epsilon and the distribution in \phi ? In particular, I can't make sense of this sentence : "Results obtained for \epsilon=-0.086...". Especially since \phi = ~60\degrees seems the median choice in Fig 3c. It does not make sense to me that In the supp mat, fig 15 is not at all helpful to understand the conventions chosen by the authors.

- It seems to me the important role of anisotropy could be better characterized by tuning the magnetic field orientation, have the authors tried doing so ?

- In fig 4b, the authors make a model for "distinguishable chains" and "undistinguishable chains", and the expected linewidth in each case. In the text, they argue that the difference comes from the anisotropic spin-spin interaction, and its angular distribution, yet a few paragraphs earlier they also state that the more considerable broadening in their experiment (which correspond to the distinguishable chains chase) can only partially be explained by this effect - so what is the good conclusion ?

Reviewer #2 (Remarks to the Author):

Referee report on the manuscript "Waveguide quantum electrodynamics at the onset of spin-spin correlations" by Sebastián Roca-Jerat et al.

This is a comprehensive experimental-theoretical study on the collective coupling of an array of interacting spins to propagating photons. This is realized by coupling an array of organic molecules to photons in a superconducting waveguide. The authors observe that at large temperatures the spin-spin interaction is not important, and the photon interacts with spins as if those were independent. The transmission is then determined by the coupling to the (broadened) collective superradiant mode. At low temperatures, the interaction between the spins in different sublattices becomes important. This results in the broadening of the transmission spectrum.

The subject is fundamentally interesting and definitely worthy of investigation. Experimental works where emitters interact not only with photons but also directly with each other are still scarce. The manuscript is well-written, and the results look solid. I do not have any reservations about recommending this work for publications, but I think it will actually be useful to the community.

I still have some minor questions and suggestions.

1) the whole model assumes photons interacting with a collective superradiant mode of the array (at least, at large temperature). I assume the distance between the spins is much smaller than the photon wavelength (that is in the order of cm), so this seems like a very good approximation. Still, I wonder if there are any signatures or possibilities to probe subradiant modes of the array, maybe not in this particular experiment but in this platform.

2) all the results are in the linear optics regime. That is, they assume weak coherent light with much less than one photon incident upon the array. I understand this is probably beyond the current study, but I still wonder whether something could be said about attaining a quantum nonlinear optics regime with several interacting photons in this system.

As an additional comment, I suggest the Authors consider moving some of the information from the Supplementary to the main text or to the Appendices or Methods. I fully understand that when writing a work aiming for certain journals, that appreciate experimental results, we have to present calculation details in Supplementary. Moving some of the results back at the current stage might feel like too much of an effort. But I still think that for a future reader, it might be helpful to have more information (e.g., Hamiltonian, transmission calculation details, spin mode interaction details) in a separate file, rather than having to download it separately. I was missing some of this info when reading the main text. I trust the judgment of the Authors on how to implement this in the best way.

Reviewer #3 (Remarks to the Author):

The manuscript titled "Waveguide Quantum Electrodynamicss at the Onset of Spin-Spin Correlations" explores the interplay between light-mediated and intrinsic matter-matter interactions in waveguide quantum electrodynamicss (wQED). The authorrs investigate the coupling of a superconducting transmission line to a model magnetic material composed of organic free radical molecules with spin S=1/2.. The study probes a wide range of temperatures, magnetic fields, and frequencies, revealing how temperature influences intrinsic spin correlations and the collective coupling of spins to propagating photons.

The work addresses a relatively unexplored area in wQED by focusing on the competition between light-mediated and intrinsic spin-spin interactions. This is a good contribution given the growing interest in quantum technologies and the need to understand photon-induced correlations. The experimental setup is well-described and appropriately designed to measure microwave transmission across various conditions. The use of a superconducting transmission line coupled to organic free radical molecules is innovative and provides a unique platform for studying spin-photon interactions. The manuscript presents a deep analysis of the experimental results, supported by theoretical models and simulations. The authors use mean-field theory and input-output theory to interpret their findings, providing a robust framework for understanding the observed phenomena.

The paper is well-structured, with clear sections for methods, results, and discussion. The figures and supplementary information are comprehensive and support the main text effectively.

I think the manuscript should be published but some improuvement on the clarity should be done. While the introduction provides a good overview of the field, it could benefit from a more explicit statement of the main findings and their significance. Highlighting the key results early on would help readers understand the importance of the work.
1/ Although the theoretical models are well-referenced, a more detailed explanation of how these models were applied to the specific system under study would be beneficial. This would help readers unfamiliar with the theoretical framework to follow the analysis more easily.
2/ The manuscript would benefit from a more detailed discussion of the limitations of the study. For example, how do the results depend on the specific choice of organic free radical molecules? Are there any potential sources of error or uncertainty in the measurements that could affect the conclusions?
3/ figure 2a is a bit strange to me. One expect one line and not a serie of undefined spots. I think the problem is the way the authors plot the 2D plot. Moreover the is a second line weaker but presents on the right of the main line. What it's orgin ? why there are some horizontal line ?

Overall, the manuscript presents a significant contribution to the field of waveguide quantum electrodynamicss. The experimental design is robust, and the analysis is thorough. With some improvements in clarity, explanation of theoretical models, discussion of limitations, comparison with previous work, and potential applications, the manuscript would be well-suited for publication.

Version 1:

Decision Letter:

** Please ensure you delete the link to your author homepage in this e-mail if you wish to forward it to your coauthors **

Dear Professor Luis,

Your manuscript titled "Waveguide quantum electrodynamics at the onset of spin-spin correlations." has now been seen again by our referees, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials.

We therefore invite you to edit your manuscript to comply with our journal policies and formatting style in order to maximise the accessibility and therefore the impact of your work.

EDITORIAL REQUESTS
* Your manuscript should comply with our policies and format requirements, detailed in our style and formatting guide (https://www.nature.com/documents/commsj-phys-style-formatting-guide-accept.pdf).

* Please edit your manuscript according to the editorial requests in the attached table, and outline revisions made in the right hand column. If you have any questions or concerns about any of our requests, please do not hesitate to contact me. It is important that each request be addressed in order to avoid delays in accepting your manuscript. Please upload the completed table with your manuscript files as a Related Manuscript file.

* The editorial requests table also includes a full list of the files that must be provided upon resubmission. Please upload your files according to this table.

OPEN ACCESS
Communications Materials is a fully open access journal. Articles are made freely accessible on publication. For further information about article processing charges, open access funding, and advice and support from Nature Research, please visit https://www.nature.com/commsmat/open-access

At acceptance, you will be provided with instructions for completing the open access licence agreement on behalf of all authors. This grants us the necessary permissions to publish your paper. Additionally, you will be asked to declare that all required third party permissions have been obtained, and to provide billing information in order to pay the article-processing charge (APC).

Please use the following link to submit your revised files:

Link Redacted

** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to hear from you within two weeks; please let us know if the process may take longer.

Best regards,

Klaas-Jan Tielrooij, PhD
Editorial Board Member
Communications Materials
orcid.org/0000-0002-0055-6231

REVIEWERS' COMMENTS:

Reviewer #2 (Remarks to the Author):

I am happy to recommend publication of the revised manuscript as is.

Reviewer #3 (Remarks to the Author):

The authors have answered to all of my comments. I think the manuscript is suitable for publication

Reviewer #1

We would like to thank the referee for his/her insightful comments, which have helped us to improve the manuscript and clarify some aspects of our work. In the following, we provide responses to all questions in the same order as they appear in the report.

Question 1: Previous work on this type of experiment has already been published (ref 29-32 in the paper), and the main difference between this article and these works is that the current article use a waveguide to study the spins absorption (broadband characterization) instead of a superconducting resonator (narrow-band). The authors argue that although their technique becomes less sensitive, it allows them to probe a large scale of energy range. However, in the current article, this broadband property does not seem to be used. For example, it should become possible to explore different regimes comparing the interaction exchange versus the Zeeman energy but this is not realized here (i.e how would vary the spin linewidth versus magnetic field below the antiferromagnet transition ? it's hinted at in the analysis of the supp mat, but not measured).

Response 1: We thank the referee for raising this point. We certainly think it is a very important aspect which reinforces our observations and which perhaps we have not emphasized as much as it deserves. The broadband nature of our experiments is key to different aspects of this work. In particular, it allows reaching high spin polarizations and, therefore, quite strong collective spin-photon couplings and high visibilities in the paramagnetic regime (e.g. at T = 2 K as shown in Figure 2 of the main text). It also enables observing directly the whole spin resonance, and how it gets broader and weaker as spin-spin correlations grow on decreasing T. Besides, and as the referee correctly points out in his/her comment, the magnetic field contributes to make different DPPH spins equivalent to each other, thus compete against the effect of anisotropic exchange interactions. This is confirmed by field-dependent heat capacity experiments, shown in Supplementary Fig. 5, which suggest that the paramagnetic behavior is recovered for $B \gtrsim 2$ T. In the new version, we have addressed these questions in the following way:

1) We have emphasized the usefulness of measuring the spin resonance over a wide frequency (and magnetic field) region, both in the paramagnetic regime and in the crossover to a situation dominated by intrinsic spin-spin correlations. The relevant text fragments are
   a. “Detecting this remarkable enhancement in spin-photon coupling and its visibility has been made possible by the broadband nature of these transmission experiments. It reflects the increase in the photon-induced decay rate from superradiant collective states.” See page 3, paragraph following after Eq. (2).
   b. “The access to a wide frequency window allows observing that this is accompanied by a significant broadening, by a factor ten between 1.5 K to 10 mK and, as Fig. 3c shows, by a 7 % upwards shift of the resonance center frequency.” Page 4, left column.
2) We have added an additional Supplementary Note 4 that shows transmission data and other parameters, such as the collective spin-photon coupling, the spin resonance line width and the spin resonance frequency shift, measured for different magnetic fields. Although the highest magnetic fields, and frequencies, reached in these very low T transmission experiments (< 300 mT and < 14 GHz) do not seem strong enough to

revert the system back to the paramagnetic regime, in agreement with the heat capacity results, the competition between the Zeeman and the spin-spin interactions can still be observed. We have also reinforced the discussion in the main text with these observations. Relevant text fragments are:

a. “ This qualitative behavior persists for magnetic fields up to 300 mT (see Supplementary Figs. 13-15), although its magnitude, as gauged by the resonance broadening and by the drop in its visibility, seems to get somewhat reduced by increasing B.“ Page 4, left column.
b. “By contrast, increasing B brings the spins closer to the paramagnetic state, as shown by field-dependent heat capacity experiments (Supplementary Fig. 5), and would then reduce such effects, as it is indeed observed (see Supplementary note 4 and Supplementary Fig. 15).” Page 4, right column.
c. “Increasing magnetic field tends to reduce those effects that we have associated with the onset of spin-spin interactions: the changes in Γ, $\delta\Omega$ and visibility become smaller, and take place less abruptly. However, fields much higher than 0.3 T, corresponding to frequencies beyond our experimentally accessible window, would still be required to completely erase spin correlations and recover the paramagnetic regime, as can be seen from heat capacity data shown in Fig. 5”. New Supplementary Note 4.

Q2: The paper is overall well written, with details analysis in the supplementary material and appropriate summary of the corresponding model in the main text. I believe these datasets are quite thorough and represent a very good study of magnon coupled to microwave physics, but the novelty of the paper (being broadband) does not play a large role in it. The application to characterization of spin-spin exchange interaction could be interesting, but as far as I understand, the authors' analysis falls slightly short in that regard. I am thus hesitant to recommend publication in Nature's Communications Materials.

R2: The main focus of our work is to explore how spin-spin interactions compete with the spin-photon couplings in a model situation, a 1D spin chain, which allows tuning the former by means of temperature changes. However, perhaps we have not properly emphasized the information that these experiments provide also about the existence, intensity and nature (sign and anisotropy) of spin-spin exchange interactions in such low-dimensional spin systems. In the revised text, we have reformulated the analysis and discussion of these aspects to emphasize their interest. Relevant text fragments are:

a. “The comparison with experimental data allows to determine both $|\epsilon|$, from the resonance broadening, and its sign, from the observed shift in the resonance center frequency (grey dots in Fig. 3c). In particular, a negative ϵ leads to higher frequencies for angles closer to $\pi/2$, which then dominate the average in a random distribution. We then find $\epsilon = -0.086$, which accounts well for the experimental results in Fig. 3. Note that the solid black curve in Fig. 3c emerges naturally from the resonance curves shown in Fig. 3b. Therefore, it is not an additional fit.” Page 5, top of left column.
b. “However, as can be seen in this plot, the sources of broadening present in isotropic antiferromagnetic chains are not sufficient to account for the experimentally observed Γ. Only when we include in the model an anisotropic exchange (i.e. we take a nonzero ϵ) with randomly oriented anisotropy axes does it account for Γ measured at very low temperatures.” Page 5, right column.

c. "Besides, they provide a method to characterize in detail the strength and nature of spin-spin interactions in low-dimensional systems". Concluding paragraph on page 5.

Q3: Why does the title mention "at the onset of" ? It hints at some threshold of spin-spin correlations being crossed, but this is not discussed in the main text. To me, it looks like the experiment described here is clearly in a regime where the spin-spin correlations play a significant role, and cannot be neglected.

R3: This is a key question, indeed. As we have mentioned above, the main focus of this work is to study how the growth of AF spin correlations along 1D chains of DPPH molecules, which can be controlled by temperature changes, modifies their coupling to photons propagating through a transmission line. The experiments evidence a clear crossover between two different regimes that takes place near T = 0.8 K, thus close to the specific heat maximum that characterizes the onset of quasi-long-range spin correlations (Fig. 1). The main experimental facts that characterize the two regimes, in connection to wQED are:

a. Paramagnetic regime (e.g. at T = 2 K, as shown in Fig. 2 of the main text): Here, DPPH molecules act as independent spins that emit collectively in a superradiant manner. The main signature is the sqrt(Neff) enhancement of the spin photon coupling that leads to visibilities above 1/2. As we state in the manuscript, this shows that "...it is possible to reach a regime in which collective spin-photon couplings become dominant over the individual spin decay rates".
b. Regime of spins correlated by their intrinsic exchange interactions, in which it is the magnons that emit (also collective). A crucial point is, in our opinion, that transmission experiments can resolve the different nature of matter excitations that dominate both regimes (i.e. correlated through the coupling to photons or via exchange interactions) because:
    - The changes in the temperature dependence of the visibility (Fig. 4a)
    - Increase in the spin resonance line width (Fig. 4b), which reveals the crossover from a situation in which all spins are quasi-identical emitters to another one in which they depend on the orientation of the spin chain with respect to the magnetic field

Q4: I do not understand the fit of the antiferromagnetism anisotropy. How are the authors able to characterize separately \epsilon and the distribution in \phi ? In particular, I can't make sense of this sentence: "Results obtained for \epsilon=-0.086...". Especially since \phi = ~60\degrees seems the median choice in Fig 3c. It does not make sense to me that In the supp mat, fig 15 is not at all helpful to understand the conventions chosen by the authors.

R4: The DPPH sample we work with is a powder. Therefore, the spin chains have all possible orientations, thus fixing the solid angle distribution. To determine the value of \epsilon we rely on two aspects. On the one hand, the absolute value of this parameter fixes the spread in frequencies present at T -> 0. On the other hand, the sign determines which angles of the distribution have a higher frequency than in the paramagnetic case. Thus, we are able to estimate the value for \epsilon based on the experimental results. The main text on page 5, top of the left column, has been modified to highlight this procedure more clearly: "The comparison with experimental data allows to determine both $|\epsilon|$, from the resonance broadening, and its sign, from the observed shift in the resonance center frequency (grey dots in Fig. 3c). In particular, a negative ϵ leads to higher frequencies for angles closer to $\pi/2$, which then dominate the average in a random distribution. We then find $\epsilon = -0.086$, which accounts well for the experimental results in Fig. 3. Note that the solid black curve in Fig. 3c emerges naturally from the resonance curves shown in Fig. 3b. Therefore, it is not an additional fit."

Moreover, a new Supplementary Fig. 17 has been designed (old Supp Fig 15 that the referee mentions) to improve clarity in the angle convention chosen.

Q5: It seems to me the important role of anisotropy could be better characterized by tuning the magnetic field orientation, have the authors tried doing so?

R5: Since the sample we are working with is a powder sample, all possible orientations are present and therefore we do not expect the results to vary with the orientation of the field. For this, another experiment would have to be designed where a crystal with a defined axis is synthesized. However, we feel that working with a powder sample represents an advantage for this study. On the one hand, it fixes the angular distribution of DPPH spin chains (see the response to the previous comment). On the other, the onset of intrinsic spin-spin correlations, and their anisotropic character, manifests itself directly in the transmission experiments, in the form of a broadening and a shift of the spin resonance. In this way, it both helps visualizing the crossover between the two regimes described above and eases its theoretical modelling.

Q6: In fig 4b, the authors make a model for "distinguishable chains" and "undistinguishable chains", and the expected linewidth in each case. In the text, they argue that the difference comes from the anisotropic spin-spin interaction, and its angular distribution, yet a few paragraphs earlier they also state that the more considerable broadening in their experiment (which correspond to the distinguishable chains chase) can only partially be explained by this effect - so what is the good conclusion?

R6: The two paragraphs mentioned by the referee point to the same physical origin. On page 4, right hand column, we provide a physical qualitative explanation of the additional line broadening observed at very low T, based on the existence of anisotropic spin-spin interactions along randomly oriented chains of DPPH molecules. Then, (Fig. 4 and related text) this interpretation is backed by calculations of the microwave transmission that allow extracting how the spin resonance line width and visibility, as well as the shift of the spin resonance frequency are affected by such interactions. Therefore, the two interpretations are mutually consistent. Its basic ingredients are the following.

The enhancement of the resonance width has several components. On the one hand, a system with antiferromagnetic correlations has a larger width than a system with paramagnetic or ferromagnetic correlations. That is, if the interaction in the chains were isotropic and had no angular dependence, we would also observe an increase in width (as reflected in the so-called 'indistinguishable chains' curve). However, this is still far below the experimental data (Fig. 4). If one adds the fact that the interaction is anisotropic and therefore dependent on the angular orientation, this adds an inhomogeneous broadening from the solid angle distribution that accounts perfectly for the experiment without any additional fitting parameter. Therefore, the conclusion is that the experimentally measured resonance width is a clear indication not only that antiferromagnetic correlations exist, but also that they are anisotropic, validating the proposed model. We have rewritten part of the main text to give more clarity to this discussion (see points a and b in our response to the second comment above).

Reviewer #2

We thank the referee for his/her useful comments and appreciate his/her positive opinion of our work. In the following, we respond to all questions in the same order as they appear in the report.

Q1: The whole model assumes photons interacting with a collective superradiant mode of the array (at least, at large temperature). I assume the distance between the spins is much smaller than the photon wavelength (that is in the order of cm), so this seems like a very good approximation. Still, I wonder if there are any signatures or possibilities to probe subradiant modes of the array, maybe not in this particular experiment but in this platform.

R1: We thank the referee for this interesting suggestion, although we feel that probing such modes lies beyond the reach of our experimental system. First, we clarify the experimental conditions described in the manuscript: needless to say, all measurements are performed at finite temperatures and, furthermore, temperature is essential to the physics we aim to explore. It is by changing temperature that we tune the relative strengths of spin-photon and intrinsic spin-spin correlations. Referring to super- or sub-radiant states is, in our view, a delicate question, as we are probing thermal ensembles. To our knowledge, the quantum-optics literature contains no discussion of thermal effects on super- or sub-radiant states.

Besides, because the DPPH ensemble is fully thermalized, we cannot prepare a specific initial state. Our measurements give access to collective light–matter dynamics and, since the photon wavelength exceeds the sample size, it is dominated by the coupling to superradiant modes, as noted by the referee. Accessing subradiant modes would require selective excitation of individual emitters, a capability presently beyond our setup. Partial control might be achieved by driving the system beyond the linear regime and comparing the relaxation of single-emitter and collective excitation. For example, coupling the material to a cavity or resonator and performing an echo experiment. Our setup is not suited to this approach.

Q2: All the results are in the linear optics regime. That is, they assume weak coherent light with much less than one photon incident upon the array. I understand this is probably beyond the current study, but I still wonder whether something could be said about attaining a quantum nonlinear optics regime with several interacting photons in this system.

R2: Unfortunately, we are afraid that we cannot provide a clear-cut answer to this interesting question. Working at finite temperatures and with large (N = 10^17) spin ensembles again complicates any comparison with the usual quantum-optical experiments, which can be modelled on basis of simple T = 0 physics. In our case, the results are independent of the input power (see Fig. 16 in the supplementary information document), thus we are likely far from observing nonlinear or saturation effects. Increasing the single spin to single photon coupling, as we have e.g. achieved by decreasing locally the width of the inductor line of coplanar resonators (here, the transmission line) and reported in reference [10] of the SI, could perhaps provide a basis to work with much smaller spin samples, thus investigate phenomena arising when the number of photons approaches or overcomes N.

Q3: As an additional comment, I suggest the Authors consider moving some of the information from the Supplementary to the main text or to the Appendices or Methods. I fully understand that when writing a work aiming for certain journals, that appreciate experimental results, we have to present calculation details in Supplementary. Moving some of the results back at the current stage might feel like too much of an effort. But I still think that for a future reader, it might be helpful to have more information (e.g., Hamiltonian, transmission calculation details, spin mode interaction details) in a separate file, rather than having to download it separately. I was missing some of this info when reading the main text. I trust the judgment of the Authors on how to implement this in the best way.

R3: We agree that the methods section lacked some theoretical content. Therefore, we have moved the previous Supplementary Note 6, dealing with the modelling of microwave transmission experiments, into the Methods section. We believe that the clarity and readability of the manuscript has now been improved as a result.

Reviewer #3

We thank the referee for his/her useful comments, and for his/her favorable opinion of our work. In the following, we answer each question in the same order as they appear in the report.

Q1: While the introduction provides a good overview of the field, it could benefit from a more explicit statement of the main findings and their significance. Highlighting the key results early on would help readers understand the importance of the work.

Following the referee's advice, we have added a brief summary of the main findings at the end of the introductory section. We hope this text helps the reader to identify the main focus of our work, namely the competition between spin-photon and intrinsic spin-spin interactions in a model system and how it leads to a change in the nature of elemental spin excitations that can be evidence by means of transmission experiments. It reads as follows:

"The results show the possibility of attaining a very high collective spin-photon coupling in the paramagnetic regime, at sufficiently high T, which then competes with intrinsic spin-spin correlations as T decreases. When the latter take over, the microwave transmission bears evidence for a change in the statistics governing the elemental spin excitations, from single spin flips to bosonic magnons."

Q2: Although the theoretical models are well-referenced, a more detailed explanation of how these models were applied to the specific system under study would be beneficial. This would help readers unfamiliar with the theoretical framework to follow the analysis more easily.

R2: We thank the referee for the comment as we believe that a more direct reference to the theoretical methods used was missing. In the revised version, we have moved to the Methods section the former Supplementary Note 6, which deals with the input-output formalism and which underpins the expressions for transmission and reflection that we used to analyze the experimental data. The theory is developed in such a way that it can be applied to both the paramagnetic regime and to the case in which AF spin-spin correlations play a major role.

Q3: The manuscript would benefit from a more detailed discussion of the limitations of the study. For example, how do the results depend on the specific choice of organic free radical molecules? Are there any potential sources of error or uncertainty in the measurements that could affect the conclusions?

R3: DPPH is a suitable material for this study because: a) it is commercially available, b) it has been characterized previously at higher temperatures, where it is often used as an standard for paramagnetic resonance, and c) it forms AF coupled spin chains, thus enabling a simple and monotonic control of spin-spin correlations via changes in temperature. But these properties, especially the last one, are certainly not unique and we believe that the physics uncovered by our experiments can be found in other low-dimensional systems. Concerning experimental limitations, we have done our best to deal with the usually very small influence that spins have on the transmission of an open line. Uncovering such effects, and in particular separating them from unavoidable spurious signals arising from an imperfect transmission at the chip boundaries or at the microcontacts with the PCB, required us to set-up a proper normalization method for the transmission and reflection data. This is described in detail in the Supplementary note 2 and illustrated by Supplementary Figs. 8-11. Besides, we have added to page 2, right hand column, in the main text a reference to these "imperfections":

"Note that the normalization of the data induces an additional line of |S21| maxima to the right of the resonance curve in Fig. 2a, as shown in Supplementary Fig. 8. Besides, the data show also contributions from spurious modes, caused by unavoidable imperfections at the chip boundaries or contact bonds, which manifest themselves as horizontal lines in Fig. 2a."

Q4: Figure 2a is a bit strange to me. One expect one line and not a serie of undefined spots. I think the problem is the way the authors plot the 2D plot. Moreover the is a second line weaker but presents on the right of the main line. What it's orgin ? why there are some horizontal line?

R4: This comment is linked with our response to the previous one. The advantages of working with a broadband setup also bring some disadvantages such as the presence of noise for some of the frequencies. The horizontal lines arise as spurious modes due to imperfections at the edges of the chip, as described in the main text. On the other hand, the second weaker line is a product of normalisation [see Fig.8 of Supplementary Note 2]. As mentioned above, a sentence explaining this extra line has been added to the main text.

Summary of changes

Main text

We have added or reformulated explanations to all aspects that were not found sufficiently clear by the three referees. This includes: a) the usefulness of broadband microwave transmission measurements (pages 3 and 4); b) the effect of increasing magnetic fields on microwave transmission (page 4); c) the analysis of spin-spin exchange interactions in DPPH (page 5); d) a summary of the main findings and their relevance (new sentences at the end of the introductory section and of the concluding paragraph).

Methods

Following the suggestions made by two referees, we have moved from the SI to the methods section the description of the model that we use to describe microwave transmission and how it depends on the spin-spin correlations as T decreases.

Figures

We have made a few changes in order to help visualizing the information:

- Figures 1 and 2: New and larger (a), (b) and (c) labels
- Figure 4: We have replaced "thin" vs "thick" lines with "dashed" vs "solid" lines, to represent different theoretical results more clearly.

Supplementary Information file

We have added a new Supplementary Note 4, with two new figures, dealing with the effect that increasing magnetic field has on the microwave transmission results. Besides, former Supplementary Note 6, dealing with the theory of microwave transmission, has been moved to the methods section in the main text.

References

References included in former Supplementary Note 6 are now part of the main text.