Peer Review File

Manuscript Title: Giant spin polarisation in an antiparallel pair of a chiral superconductor

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

Nature manuscript 2021-12-20228

The paper "Giant spin polarization emerging in an antiparallel pair in a chiral superconductor" by R. Nakajima, D. Hirobe, G. Kawaguchi, Y. Nabei, T. Sato, T. Narushima, H. Okamoto, H. M. Yamamoto" presents an important study showing very large spin polarization obtained in chiral superconductors aa result of the CISS effect.
While spin polarization was measured in such materials as a results of the Edelstein effect, in this work due to the CISS effect the spin magnetization is claimed to be larger by three orders of magnitude. The paper is therefore interesting and may be also important for superconducting spintronics devices applications.
Having say that major changes are required before publication is possible. It is very hard to understand the paper, the exact measurement techniques, and many of the figures are not clear enough.
One other main claim is wrong: "Our results will provide a missing piece of evidence for TRS breaking in CISS". This is not true and should be modified, as the authors use ac current and just present non-equilibrium metastable spin separation as was shown in several other CISS papers using both magnetic and superconducting samples {See for example: Nature Communications 8, 14567 (2017), Advanced Materials 31 1904206 (2019), Phys. Rev. Materials 5, 114801 (2021)}. With dissipation you don't break TRS {reference 3 and 24}.

In all these examples the metastable spin separation is short range. In that sense the long range spin separation that achieved in the chiral superconducting system is extraordinary, however the authors should explain the difference between this results and their previous publication "Phys. Rev. Lett. 127, 126602 (2021)" in the text.

Other issues:

• The easy axis magnetization of the Ni is in plane. Why would the CISS influence such a magnetization? Why did the authors did not chose easy axis that can be rotated easily? ACS Nano, 15, 3, 5574–5579 (2021).

• In Figure 1b it is not clear what the main claim is. If the figure aims to show that spin pair polarization in chiral systems under mirror reflection (m) and time reversal (T), is the same, it should be mentioned in the captions. The inequality signs aim is not clear.

• Figure 2 d on the CD polarization image it is not evident what we are seeing and where is the spin accumulation. I suggest to take a cross section and show the profile, also enlarge with a popup in the relevant areas.

• Figure 2 E why the resistance does not reach zero? What is the other phase transition at 20K?

• Figure 3 what is the source for large asymmetry? How come that terminal 4 and 7 have the same spin angle while 5 is very different? Please add errors to the angle numbers.

• Please improve the writing with English editor

Minor issues
• Add error bars where possible
• Explain better what are the meaningful areas in Extended Data Fig. 1

Over all the paper is interesting and indeed The observed charge-to-spin conversion in a chiral superconductor resulting long-range spin accumulation is interesting. I suggest publishing after major revisions.

Referee #2 (Remarks to the Author):

The manuscript by Nakajima and collaborators reports the results of measurements on a chiral organic superconductor, κ-(BEDT-TTF)2Cu(NCS)2, namely κ-NCS, under alternating current (a.c.) excitation. The measurements show the emergence of a voltage drop that assumes different sign at the two opposite edges of the κ-NCS crystal. This voltage, appears across the superconducting transition of the chiral superconductor, is ascribed by the authors to the accumulation of pairs of spins with opposite polarity which stems from the chirality-induced spin selectivity (CISS) effect of the crystals.
The experiment is certainly novel and original, the data sets are well presented, and the discussion is also well-structured. The manuscript provides strong insights into the mechanism underlying CISS, which is an effect currently investigated in a wide range of materials for spintronics applications, also in the superconducting state. From this point of view, the article meets the requirements of great novelty and general interest that are key for publication in Nature. Nevertheless, there are several points that the authors should consider to improve the clarity of the results presented and their robustness.
I would be happy to recommend the manuscript for publication, once the authors address all the remarks reported below.
• An important point that is never addressed in the manuscript is that the sample of κ-NCS never reach a zero-resistance state, meaning a fully superconducting state. This is evident from the graph in Fig. 2e, where the authors have decided to plot the resistance normalized to its value at 300 K.

Nevertheless, as confirmed also by the results from the same authors in their previous work (ref. 32 of the manuscript), the samples show a residual resistance. Is it clear why this is always the case? The residual resistance reminds of a behavior normally due to percolation in metal or oxide superconductors with higher density. In ref. 32, the authors also discuss that the superconductor consists of a mixture of superconducting and Mott insulating regions. Is it clear why these regions form during growth? The origin of the residual resistance in the superconducting transition should be clarified in the manuscript, as it would be more appropriate to talk about 'transition to a partially superconducting state' for these κ-NCS samples. On line 131, for instance, it would be more appropriate to replace the expression 'superconducting state' with 'across the superconducting transition', since the κ-NCS sample never reaches a fully superconducting state (also it is more appropriate, since the magnetoresistance can only be measured across a superconducting transition, but not below Tc, as the authors are well aware).
I would also suggest that other than giving the normalized resistance, it would be more informative if the authors could show the absolute resistance (to get an idea of the value of the residual resistance at low temperatures), or even better the resistivity, as this brings even more information on the electronic transport properties of the material.

• What is the transparency of the interfaces between the Ni and Au contacts with κ-NCS? Although I agree with the authors that they only observe the emergence of a Vodd signal across the superconducting transition (Extended Data Fig. 5), I am wondering if they have tried to measure a current versus voltage, I-V, characteristic between a pair of contacts, to see if it is non-linear and to determine if there are additional interface resistance contributions which may contribute to Vodd as superconductivity sets in.

• The discussion about the possible types of carriers that can account for the enhancement in spin polarization of the system is interesting. I do agree with the authors that spin-polarized quasiparticles can account for the observed effect, and this is also consistent with the fact that the Vodd signal increases at the onset of the superconducting transition, where the density of quasiparticles is larger. Regarding the spin-triplet contribution, it must be observed that although one cannot exclude sources of spin-triplet pairs of intrinsic origin in κ-NCS (this will require further studies, as the authors correctly state), the authors also use Ni contacts which introduce a magnetic exchange field at the interface with κ-NCS. This exchange field, in combination with the external applied field may lead to the magnetic inhomogeneity that is needed for spin-triplet generation. Have the authors considered such an effect and, if so, how they can rule it out?

• Since the authors talk about superconducting properties of κ-NCS, and also discuss spin-triplet superconductivity at the end of the manuscript, the couple of electron spins reported in Fig. 2c is a bit misleading. I guess the authors have in mind two electron charges or quasiparticle excitations with the same spin polarization, or are these two electrons forming a superconducting pair (i.e., a. fully polarised spin-triplet)? It is not clear to me what the authors have in mind when they introduce Fig. 2, and perhaps this should be specified before discussing the figure (also by simply referring to the discussion reported later in the manuscript).

Other very minor points are the following:

• In Extended Data Fig. 3, the authors should specify at which a.c. amplitude the curves were measured. I assume that they were both measured with an amplitude of the a.c. component equal to 0, but this must be written in the caption. Similarly, the a.c. amplitude should be specified in any other figure captions, where it is missing. For example, in extended Data Fig. 5, the a.c. amplitude value is also missing, and it should be reported, even if the authors indicated in the main text that the current used for all Vodd measurements is 2.4 μA.

• On line 69, the acronym 'a.c.' already stands for alternating current, so the word 'current' on the same line is redundant. This redundancy appears in several other positions in the manuscript (see, e.g., lines 355, 368, 442 etc.).

• In Fig. 3g, it is clear how the voltage is detected, but the authors should clarify how the current is injected. This should be clarified either in the sketch (giving one example for a given pair of Au-Ni voltage electrodes) or in the main text, as done for the non-local transport measurements.

• The authors of ref. 22 have recently demonstrated much clearer evidence for spin-triplet superconductivity (see H. Alpern et al., Phys. Rev. Mater. 5, 114801 (2021)), since the measurements in ref. 22 are local spectroscopy measurements, which can also be explained as the result of the generation of Yu-Shiba-Rusinov states due to the molecules acting as magnetic impurities.

• I personally find the labelling of the crystallographic axes in Fig. 2a confusing, as it is not clear the molecule structure in the a-b plane. In ref. 32, the authors have reported a much clearer picture on the crystal structure of κ-NCS in the ac- and bc-planes. Perhaps it would be helpful to reproduce such picture also in the Extended Data of the manuscript to help the reader understand the crystal structure of κ-NCS.

Referee #3 (Remarks to the Author):

The manuscript of Nakajima et al. reports a combination of several measurements, mostly of (magneto-)transport properties, on an organic superconducting film. The film is in contact with two reservoirs, one being a ferromagnet (Ni) the other one being a good metal (Au). The crucial point of this study is that the film is built from several layers of chiral molecules.

A motivation to work with chiral molecules may come from transport experiments that have been performed in recent years on very different molecular systems, such as single molecule junctions or self-assembled monolayers of molecules. In such systems observations have been reported on spin selectivity in transport as a consequence of the chirality, i.e. chirality induced spin selectivity (CISS). A recent review has been published in arXiv:2108.09998.

The CISS effect has caught the attention of theorists and experimentalists from early on, partially because of its possible technological relevance in spintronics. However, the recent discovery of a possible significance of CISS for chemical binding and chiral surface chemistry has increased the interest even more.

At present there is no consensus as to what is the dominating physical mechanism behind the CISS effect. Various candidate mechanisms have been proposed that produce the effect on a qualitative level, but fail to account for it quantitatively. The present authors have sketched this situation to the extent that is relevant to their work.
Before assessing the study, I would like to point out that my perspective a largely theoretical one. While I very much appreciate the experimental effort that has been invested here, I cannot judge its validity with respect to details in system synthesis or measurement procedures.

In my opinion the manuscript is not suitable for publication in the Nature journals.

(a) My main point of concern is the following: The experiment reports spin-accumulation at the interface between the superconducting film and the electrodes. While I do not doubt the experimental observation, I fail to see a clear connection to the CISS phenomenon. In other words, I am missing a “smoking gun” type of observation demonstrating that the spin-accumulation is due to chirality and nothing else. Admittedly, such a demonstration is very difficult to do and for this reason many (but not all!) of the experiments reporting the CISS effect are under debate.

Typical consistency checks that would hint at chirality as the origin of the spin accumulation include (i) magnetization reversal under chirality reversal; (ii) scaling of the magnitude of spin-accumulation with the amount of chirality breaking, controlled e.g. by the molecular length; (iii) most importantly, demonstrating that spin-accumulation yields a very large polarization of order of several 10%. (I could not the corresponding estimate in the manuscript). I recall that some spin-polarization effects due to chirality are expected. While they may very well exceed the Edelstein effect, as seen in this manuscript, they do NOT constitute the CISS phenomenon which is an effect of (almost) order unity, c.f. arXiv:2108.09998.

(b) The theory papers motivating the CISS-interpretation adopted by the present authors have been commented on in arXiv:2108.09998. The model employed in Ref. 3 is hard to motivate in terms of a microscopic model of physical reality and was therefore considered “unphysical”; its apparent simplicity is deceptive. In contrast, Ref. 24 cited points to a valid physical mechanism that however is not believed to be sufficiently strong in order to explain the experimentally observed polarizations of order of several 10%.

(c) There are a number of smaller issues that I would like to mention. The authors say (in line 123) that all samples display the same handedness despite the fact that “no intentional symmetric induction” was made in the process of sample preparation. How is this possible? My general concern is that unknown sources of symmetry breaking (of whatever kind) may manifest in measurements that are interpreted as broken spin-symmetry (“accumulation”) in an unknown way.

(d) In the present measurement the presence of CISS is tested in the superconducting phase. Why would one employ a superconducting sample for devising a “smoking gun experiment” on the CISS? Taken at face value to get a superconductor involved looks like an extra complication, e.g., the combined effect of chirality and spin-orbit interaction on the superconducting state is not very well known, given that there is a CISS effect.

Ideally, I would be able to assist the authors by suggesting how to improve the manuscript in such a way that a publication in Nature would be indicated. Very much to my regret, I am unable to make constructive suggestions the main reason being the complexity of the experimental setup combining superconductivity, magnetic interfaces, chirality and the spin-orbit interaction.

Author Rebuttals to Initial Comments:

Referee #1 (Remarks to the Author):

The paper… presents an important study showing very large spin polarization obtained in chiral superconductors as a result of the CISS effect. While spin polarization was measured in such materials as a results of the Edelstein effect, in this work due to the CISS effect the spin magnetization is claimed to be larger by three orders of magnitude. The paper is therefore interesting and may be also important for superconducting spintronics devices applications… Over all the paper is interesting and indeed The observed charge-to-spin conversion in a chiral superconductor resulting long-range spin accumulation is interesting. I suggest publishing after major revisions.

We are grateful for your appreciation and recommendation of publication after we address your comments properly.

Referee #1's comment 1

It is very hard to understand the paper, the exact measurement techniques, and many of the figures are not clear enough.

Authors' reply 1

We apologize for these concerns. In response to the comment, we have revised the logic of the manuscript and further described measurement techniques so that researchers can understand the experimental details better. We also have improved the figures to clarify our claims. These changes are detailed in the following replies to your comments.

Referee #1's comment 2

One other main claim is wrong: "Our results will provide a missing piece of evidence for TRS breaking in CISS". This is not true and should be modified, as the authors use ac current and just present non-equilibrium metastable spin separation as was shown in several other CISS papers using both magnetic and superconducting samples {See for example: Nature Communications 8, 14567 (2017), Advanced Materials 31 1904206 (2019), Phys. Rev. Materials 5, 114801 (2021)}. With dissipation you don't break TRS {reference 3 and 24}.

Authors' reply 2

Thank you for your technical comment. Second symmetry consideration led us to learn that an antiparallel pair of spin polarizations does not break time reversal symmetry but exhibits T-odd symmetry (arXiv:2208.06071v2). Additionally, nonequilibrium metastable spin separation has been reported in preceding studies, as Referee #1 pointed out. Accordingly, we have replaced "TRS breaking" with "spin accumulation" or equivalent phrases in the revised manuscript.

The main changes in response to your comment are listed below.

…two microscopic phenomena have been hypothesised based on experimental results (lines 16-17)

CISSs in various chiral materials have several characteristics. One characteristic is the efficient spin polarisation rate…Experiments have also suggested that a CISS accompanies a pair of opposite spins…We reason that both the effective enhancement of the SOI and a pair of opposite spins are universal features of molecular CISS (lines 43-54)

Referee #1's comment 3

In all these examples the metastable spin separation is short range. In that sense the long range spin separation that achieved in the chiral superconducting system is extraordinary, however the authors should explain the difference between this results and their previous publication "Phys. Rev. Lett. 127, 126602 (2021)" in the text.

Authors' reply 3

The main difference lies in the detection of an antiparallel pair of spin accumulations, namely evidence for spatial spin separation. The PRL paper just reported a spin-dependent voltage signal which is consistent with the symmetry of the Edelstein effect and is ascribable to a bulk magnetization over a long distance. We should stress, however, that the PRL paper failed to detect an antiparallel pair of spin accumulations. This point is explained in the following.

Sourcing an electric current j to chiral metals yields a bulk magnetization M via the Edelstein effect (i.e., $M \propto j$). Within this framework, M is *bipolar* with respect to j, and M changes sign upon reversal of the polarity of j. Indeed, the PRL paper is consistent with this current-induced *bipolar* magnetization prevailing over a long distance.

However, the PRL paper did not find evidence for an antiparallel pair of spin accumulations; such a spin pair should result in *unipolar* spin accumulation at crystal edges, independently of the polarity of j. Our present study showed that a *d.c.* spin-dependent voltage is generated by sourcing an *a.c.* electric current. This observation is compatible with the *unipolar* spin accumulation at crystal edges due to an antiparallel pair of spin accumulations. This clearly differentiates the present paper from the PRL paper.

The following description has been added in the main text in response to your comment.

Similar results for nonlocal chirality-dependent spin polarisation have been reported for chiral crystals[41, 42], although no evidence for an opposite-spin pair has been reported (lines 229-230)

Referee #1's comment 4

The easy axis magnetization of the Ni is in plane. Why would the CISS influence such a magnetization? Why did the authors did not chose easy axis that can be rotated easily? ACS Nano, 15, 3, 5574–5579 (2021).

Authors' reply 4

The present measurement technique was used to detect a voltage drop at the interface of Ni/κ-NCS. The interfacial voltage drop is determined by a relative angle between the magnetization M of Ni and spin accumulation σ at the crystal edge of κ-NCS (please also see Fig. 2c). This method was derived from TMR (tunneling magnetoresistance) measurement in the field of spintronics, and the direction of M is assumed to be determined exclusively by external magnetic field. Therefore, our method does not require tilting of

M by σ-induced effective magnetic field, although such tilting is essential to an experimental technique used in the ACS Nano paper. Since both electric currents and the screw axis of κ-NCS were in the plane, σ was predicted to be in the plane as well. Accordingly, M should be varied in the plane to get a variable angle between σ and M.

Referee #1's comment 5

In Figure 1b it is not clear what the main claim is. If the figure aims to show that spin pair polarization in chiral systems under mirror reflection (m) and time reversal (T), is the same, it should be mentioned in the captions. The inequality signs aim is not clear.

Authors' reply 5

We would like to state that an antiparallel pair of spin accumulations breaks mirror symmetry while it is T-odd and respects time reversal symmetry. To be short, such a spin pair exhibits T-odd chirality. We apologize for the confusion caused. Following the comment, we have added explanations of the T-odd chirality in the main text, the caption and the figure.

The inequality sign in Fig. 1 was intended to emphasize that an antiparallel pair of spin polarizations is NOT T-even. In the revised manuscript, we have deleted the inequality sign to prevent possible confusion in response to the comment.

The main changes in response to your comment are listed below.

Moreover, it changes sign or handedness under the time-reversal ($\mathcal{T}$) operation; therefore, it can be regarded as $\mathcal{T}$-odd. This chirality differs from simple molecular chirality because the latter is invariant under the same operation and is thus $\mathcal{T}$-even (lines 49-52)

On one hand, the chiral molecular structure and the antiparallel-spin pair are not invariant under m, and they are converted into their own mirror images. This interconversion is denoted by "Odd". On the other hand, the chiral molecular structure is invariant under T, denoted by "Even", while the antiparallel-spin pair goes through interconversion under T, and likewise, m (lines 380-384)

Fig. 1b (inequality sign deleted. "Even" and "Odd" added)

Referee #1's comment 6

Figure 2 d on the CD polarization image it is not evident what we are seeing and where is the spin accumulation. I suggest to take a cross section and show the profile, also enlarge with a popup in the relevant areas.

Author's reply 6

We apologize for insufficient explanation of the CD data in the main text. We stress that the CD method probes chiral lattice structure, not spin accumulation. Additionally, the CD data was taken at room temperature well above the superconducting transition temperature. Therefore, the CD data in Fig. 2d is not relevant to the superconducting state of k-NCS. To resolve possible confusion regarding the CD data, we have deleted Fig. 2d in the main text and explained CD imaging in detail in the Extended Data section.

The main changes in response to your comment are listed below.

We confirmed the uniform sign and intensity over the entire area of the□ κ-NCS (device #1), which demonstrated a uniform enantiomeric excess of the crystal (Extended Data Fig. 3) (lines 124-126)

CD image reconstructed from the small ones, taken at room temperature, well above the superconducting transition temperature of 7.5 K. (lines 603-604)

CD microscopy directly probed the chiral lattice structure at room temperature, rather than spin accumulation (lines 610-611)

Referee #1's comment 7

Figure 2 E why the resistance does not reach zero? What is the other phase transition at 20K?

Authors' reply 7

One possible cause of residual resistance is a small volume fraction of the superconducting state. To resolve this issue, we employed annealing at the glass transition temperature ~ 80 K [Phys. Rev. B, 55, 14140 (1997), Physica B 284-288, 519 (2000) and Phys. Rev. B 65, 144521 (2002)], in which terminal ethylene groups of BEDT-TTF molecules tend to be regularly ordered. As a result, we successfully suppressed residual resistance below the superconducting transition temperature [R(2 K)/R(300 K) ~ 1e-05 (Extended Data Fig. 4), cf. 1e-02 in the previous measurement.

An anomaly of resistance at 20 K is unlikely to arise from a phase transition of κ-NCS, because such a change does not appear in bulk crystals (ref. 25). We suspect that the anomaly is caused by a temperature-dependent difference in the thermal expansion coefficients of the substrate material (polyethylene naphthalate) and κ-NCS. Because the superconductivity of κ-NCS is based on strong electron correlation, the resistance of κ-NCS is sensitive to the thermal expansion difference via the resulting effective pressure (please also refer to refs. 33).

Referee #1's comment 8

Figure 3 what is the source for large asymmetry? How come that terminal 4 and 7 have the same spin angle while 5 is very different? Please add errors to the angle numbers.

Authors' reply 8

We reviewed analysis of spin-polarization angles, and found a mistake for terminal 5. The correct angle is -65 deg., not -25 deg. We deeply apologize for this mistake and acknowledge for the comment. In the revised manuscript, we have presented the correct angle. We also have added error bars of ±5 deg. to the angle values, taking into account the accuracy of a custom-made sample rotator.

Referee #1's comment 9

Please improve the writing with English editor

Author's reply 9

We apologize for unproficiency in English. We have the manuscript polished by an English editing service.

Referee #1's comment 10

Add error bars where possible

Authors' reply 10

We have added error bars of $\pm$5 deg. to the angle values of external magnetic field, taking into account the accuracy of a custom-made sample rotator.

Referee #1's comment 11

Explain better what are the meaningful areas in Extended Data Fig. 1

Authors' reply 11

The meaningful area is a thin-film crystal of κ-NCS except the electrodes. This is because calculation of the CD signal involves subtraction of the reference signal for circularly polarized lights transmitted only through the PEN substrate. Therefore, only a difference in the CD signal between "PEN" and "PEN + κ-NCS" is important. In response to the comment, we have explained at which area the magnitude of the CD signal is meaningful in the Extended Data section.

The change in response to your comment is as follows:

We did not consider the modulation of circularly polarised light transmitted through the metal electrodes. Accordingly, the magnitude of the CD signal is significant for a thin-film crystal of κ-NCS, except for the electrodes (lines 608-610)

Referee #2 (Remarks to the Author):

The experiment is certainly novel and original, the data sets are well presented, and the discussion is also well-structured. The manuscript provides strong insights into the mechanism underlying CISS, which is an effect currently investigated in a wide range of materials for spintronics applications, also in the superconducting state. From this point of view, the article meets the requirements of great novelty and general interest that are key for publication in Nature. Nevertheless, there are several points that the authors should consider to improve the clarity of the results presented and their robustness.

I would be happy to recommend the manuscript for publication, once the authors address all the remarks reported below.

We are grateful for your appreciation and recommendation of publication after we address your comments properly.

Referee #2's comment 1

• An important point that is never addressed in the manuscript is that the sample of κ-NCS never reach a zero-resistance state, meaning a fully superconducting state. This is evident from the graph in Fig. 2e, where the authors have decided to plot the resistance normalized to its value at 300 K. Nevertheless, as confirmed also by the results from the same authors in their previous work (ref. 32 of the manuscript), the samples show a residual resistance. Is it clear why this is always the case? The residual resistance reminds of a behavior normally due to percolation in metal or oxide superconductors with higher density. In ref. 32, the authors also discuss that the superconductor consists of a mixture of superconducting and Mott insulating regions. Is it clear why these regions form during growth? The origin of the residual resistance in the superconducting transition should be clarified in the manuscript, as it would be more appropriate to talk about 'transition to a partially superconducting state' for these κ-NCS samples. On line 131, for instance, it would be more appropriate to replace the expression 'superconducting state' with 'across the superconducting transition', since the κ-NCS sample never reaches a fully superconducting state (also it is more appropriate, since the magnetoresistance can only be measured across a superconducting transition, but not below Tc, as the authors are well aware).

I would also suggest that other than giving the normalized resistance, it would be more informative if the authors could show the absolute resistance (to get an idea of the value of the residual resistance at low temperatures), or even better the resistivity, as this brings even more information on the electronic transport properties of the material.

Authors' reply 1

One possible cause of residual resistance is a small volume fraction of the superconducting state. To resolve this issue, we employed annealing at the glass transition temperature ~ 80 K, in which terminal ethylene groups of BEDT-TTF tend to be regularly structured. As a result, we successfully suppressed residual resistance below the superconducting transition temperature [R(2 K)/R(300 K) ~ 1e-05 cf. 1e-02 in the previous measurement]. (4)

As Referee #2 pointed out, the spin-dependent voltage intensifies in the vicinity of Tc, and it disappears well below Tc. Thus, it is more appropriate to say that spin accumulation emerges “across the superconducting transition” rather than “in the superconducting state”.

In response to the comment, we have added the explanation of the residual resistance in the revised manuscript. We have also presented the absolute value of the resistance. Lastly, we have used the phrase “across the superconducting transition” to specify where an antiparallel pair of spin accumulations is detectable.

The main changes in response to your comment is listed below.

Here, we report the simultaneous observation of these two phenomena in an organic chiral superconductor by magnetoresistance measurement in the vicinity of the superconducting transition temperature (lines 19-21)

The residual resistance may have originated from the small volume fraction of the superconducting state. The residual resistance was found to be reduced by several orders of magnitude after an annealing procedure at glass transition temperature (~ 80 K), at which the terminal ethylene groups of BEDT-TTF molecules tend to be regularly structured (Extended Data Fig. 4) (lines 134-138)

Subsequently, we discuss the magnetoresistance measurements in the vicinity of the superconducting transition of the *κ*-NCS (lines 139-140)

Fig. 2d (absolute value of the resistance presented)

Extended Data Fig. 4 (newly added to show zero resistance after an annealing procedure)

Extended Data Fig.8 (newly added to show spin-dependent voltages in a device which reaches zero resistance well below T_c)

Referee #2’s comment 2

• What is the transparency of the interfaces between the Ni and Au contacts with κ-NCS? Although I agree with the authors that they only observe the emergence of a Vodd signal across the superconducting transition (Extended Data Fig. 5), I am wondering if they have tried to measure a current versus voltage, I-V, characteristic between a pair of contacts, to see if it is non-linear and to determine if there are additional interface resistance contributions which may contribute to Vodd as superconductivity sets in.

Authors’ reply 2

In response to the comment, we investigated the current dependence of voltage and found a linear relation both in the normal conducting state and around the superconducting transition. Therefore, we can preclude the possibility that a nonlinear interfacial resistance is responsible for V_{odd}. The linear I-V curve has been discussed in the main text in response to the comment.

The main changes in response to your comment are listed below.

We obtained a linear current-voltage curve for the junction between the Au-capped Ni electrode and κ-NCS (Extended Data Fig. 2). This precludes the possibility that d.c. voltage signals simply originate from rectification via asymmetric current-voltage relations (lines 117-120)

Extended Data Fig. 2 (newly added to show a linear I-V curve)

Referee #2's comment 3

• The discussion about the possible types of carriers that can account for the enhancement in spin polarization of the system is interesting. I do agree with the authors that spin-polarized quasiparticles can account for the observed effect, and this is also consistent with the fact that the Vodd signal increases at the onset of the superconducting transition, where the density of quasiparticles is larger. Regarding the spin-triplet contribution, it must be observed that although one cannot exclude sources of spin-triplet pairs of intrinsic origin in κ-NCS (this will require further studies, as the authors correctly state), the authors also use Ni contacts which introduce a magnetic exchange field at the interface with κ-NCS. This exchange field, in combination with the external applied field may lead to the magnetic inhomogeneity that is needed for spin-triplet generation. Have the authors considered such an effect and, if so, how they can rule it out?

Authors' reply 3

We reason that inhomogeneous magnetic field is irrelevant to spin-triplet generation on the basis of the angular dependence of V_{odd}. If the idea of inhomogeneous magnetic field was true, then the spin-polarization direction $\boldsymbol{\sigma}$ of the spin-triplet Cooper pairs would be determined by the magnetization direction $\boldsymbol{M}$ of the nickel electrode. In this case, rotation of $\boldsymbol{M}$ accompanies rotation of $\boldsymbol{\sigma}$. Therefore, a relative angle is unchanged between $\boldsymbol{M}$ and $\boldsymbol{\sigma}$. This does not produce an angle-dependent V_{odd}: inconsistent with our observations. Therefore, we reason that spin-triplet generation is more likely to be intrinsic to the chiral structure of κ-NCS.

Referee #2's comment 4

• Since the authors talk about superconducting properties of κ-NCS, and also discuss spin-triplet superconductivity at the end of the manuscript, the couple of electron spins reported in Fig. 2c is a bit misleading. I guess the authors have in mind two electron charges or quasiparticle excitations with the same spin polarization, or are these two electrons forming a superconducting pair (i.e., a. fully polarised spin-triplet)? It is not clear to me what the authors have in mind when they introduce Fig. 2, and perhaps this should be specified before discussing the figure (also by simply referring to the discussion reported later in the manuscript).

Authors' reply 4

We intended to simply mean spin-1 carriers in Fig. 2c and refrained from specifying which the carriers are, quasiparticles or spin-triplet Cooper pairs. As Referee #2 rightly understands, our experiment does not offer a conclusion on spin carrier type being relevant. In the revised manuscript, we have stated that spin-

1 carriers are depicted in Fig. 2c and that discussion on spin carrier type is to be given at the end of the manuscript.

The corresponding change in the main text is as follows.

This experimental protocol is expected to hold true irrespective of the spin carrier type in the superconductor because it is essentially based on angular momentum conservation. The possible spin carriers in the superconductor are discussed at the end of the main text (lines 112-115)

Referee #2's comment 5

• In Extended Data Fig. 3, the authors should specify at which a.c. amplitude the curves were measured. I assume that they were both measured with an amplitude of the a.c. component equal to 0, but this must be written in the caption. Similarly, the a.c. amplitude should be specified in any other figure captions, where it is missing. For example, in extended Data Fig. 5, the a.c. amplitude value is also missing, and it should be reported, even if the authors indicated in the main text that the current used for all Vodd measurements is 2.4 μA.

Authors' reply 5

In response to your technical comment, we have specified the a.c. amplitude wherever possible in the captions. Additionally, we have described technical details of electric a.c. excitation in more detail in the main text (Referee#2's comment 7). Since our excitation method was based on mutual inductance, we directly controlled a.c. voltage Vac applied to the 1st coil outside the main circuit, rather than an alternating electric current Iac in the main circuit. In high-frequency measurements like ours, conversion from Vac to Iac is susceptible to circuit impedance, so that Vac is the most controllable parameter in long-run measurements, rather than Iac. Considering this, we have specified the amplitude of Vac in the revised manuscript alongside a measured coefficient of conversion from Vac to Iac.

The main changes in response to your comment are list below.

An a.c. voltage, $V_{\mathrm{ac}}(t) = \frac{V_{\mathrm{ac}}}{2}\sin(2\pi f)$, with a frequency ($f$) of 10 MHz was converted into an a.c. excitation in the *κ*-NCS, $I_{\mathrm{ac}}(t) = \frac{I_{\mathrm{ac}}}{2}\sin(2\pi f + \varphi)$ (a phase shift φ caused by circuit impedance), along the screw axis by a mutual inductance method[33] (lines 92-95)

The ratio of I_{ac} to V_{ac} was approximately 24 μA V^{-1} (line 142)

Having investigated the I_{ac} dependence of V_{odd}, we present the data obtained at V_{ac} = 100 mV (lines 157-158)

An electric current was applied between the two Au electrodes for excitation by setting V_{ac} to 100 mV (lines 206-207)

Fig. 2b (equivalent circuit for electric a.c. excitation added)

Fig. 3g (details of electric a.c. excitation explained)

Fig. 4a (equivalent circuit for electric a.c. excitation added)

Referee #2's comment 6

• On line 69, the acronym 'a.c.' already stands for alternating current, so the word 'current' on the same line is redundant. This redundancy appears in several other positions in the manuscript (see, e.g., lines 355, 368, 442 etc.).

Authors' reply 6

Thank you for your comment. In the revised manuscript, we have deleted the word "current" when using "a.c.".

Referee #2's comment 7

• In Fig. 3g, it is clear how the voltage is detected, but the authors should clarify how the current is injected. This should be clarified either in the sketch (giving one example for a given pair of Au-Ni voltage electrodes) or in the main text, as done for the non-local transport measurements.

Authors' reply 7

In response to the comment, we have clarified how to source an electric current by a mutual inductance method.

The correspond changes are listed below.

Fig. 2b (equivalent circuit for electric a.c. excitation added)

Fig. 3g (details of electric a.c. excitation explained)

Referee #2's comment 8

• The authors of ref. 22 have recently demonstrated much clearer evidence for spin-triplet superconductivity (see H. Alpern et al., Phys. Rev. Mater. 5, 114801 (2021)), since the measurements in ref. 22 are local spectroscopy measurements, which can also be explained as the result of the generation of Yu-Shiba-Rusinov states due to the molecules acting as magnetic impurities.

Authors' reply 8

Thank you for directing our attention to a recent paper on spin-triplet superconductivity. We have cited the introduced paper in the revised manuscript in the context of spin-triplet superconductivity induced by CISS.

The corresponding changes are listed below.

The capability of producing high spin polarisation has triggered the active application of CISS to …induction of spin-triplet superconductors[22, 23] (lines 40-42)

23. Alpern, H. et al. Unconventional Meissner screening induced by chiral molecules in a conventional superconductor. *Phys. Rev. Mater.* **5**, 114801 (2021) (lines 300-301)

Referee #2's comment 9

• I personally find the labelling of the crystallographic axes in Fig. 2a confusing, as it is not clear the molecule structure in the a-b plane. In ref. 32, the authors have reported a much clearer picture on the crystal structure of κ-NCS in the ac- and bc-planes. Perhaps it would be helpful to reproduce such picture also in the Extended Data of the manuscript to help the reader understand the crystal structure of κ-NCS.

Authors' reply 9

We have newly added Extended Data Fig. 1 in which the molecular arrangement is projected onto the conduction plane (crystal *bc* plane).

Referee #3 (Remarks to the Author):

… In my opinion the manuscript is not suitable for publication in the Nature journals… Ideally, I would be able to assist the authors by suggesting how to improve the manuscript in such a way that a publication in Nature would be indicated. Very much to my regret, I am unable to make constructive suggestions the main reason being the complexity of the experimental setup combining superconductivity, magnetic interfaces, chirality and the spin-orbit interaction.

Thank you for your critical comments. We admit that our experimental setup is quite different from previous ones in an effort to find a superconducting analogue of CISS. We have tried resolving your concerns step by step in the following.

Referee #3's comment 1

The manuscript of Nakajima et al. reports a combination of several measurements, mostly of (magneto-)transport properties, on an organic superconducting film. The film is in contact with two reservoirs, one being a ferromagnet (Ni) the other one being a good metal (Au). The crucial point of this study is that the film is built from several layers of chiral molecules.

Authors' reply 1

We apologize for confusion caused. κ-NCS consists of achiral molecules and does not contain chiral molecules. The chirality of κ-NCS is given by a relative arrangement of the achiral molecules in the unit cell. The macroscopic conduction layers are stacked along the *a*-axis to form C_2 symmetric lattice (space group $P2_1$) which is chiral.

Referee #3's comment 2

A motivation to work with chiral molecules may come from transport experiments that have been performed in recent years on very different molecular systems, such as single molecule junctions or self-assembled monolayers of molecules. In such systems observations have been reported on spin selectivity in transport as a consequence of the chirality, i.e. chirality induced spin selectivity (CISS). A recent review has been published in arXiv:2108.09998.

Authors' reply 2

Thank you for directing our attention to a topical review paper on CISS. We have cited it in the revised manuscript.

Referee #3's comment 3

(a) My main point of concern is the following: The experiment reports spin-accumulation at the interface between the superconducting film and the electrodes. While I do not doubt the experimental observation, I fail to see a clear connection to the CISS phenomenon. In other words, I am missing a "smoking gun" type of observation demonstrating that the spin-accumulation is due to chirality and nothing else. Admittedly, such a demonstration is very difficult to do and for this reason many (but not all!) of the experiments reporting the CISS effect are under debate.

Authors' reply 3

In response to the comment, we grew different batches of κ-NCS crystals and managed to fabricate a device in which excitation electrodes were located in areas of opposite handedness. With this device, we newly found the polarity reversal of the spin accumulations by exciting the chiral superconductor at two different positions with opposite handedness. We believe that this is direct evidence for chirality origin of the spin-dependent voltage V_{odd}. The data have been added to the Extended Data section in the revised manuscript. We appreciate your critical comment.

Major changes in response to your comment is listed below.

The chirality origin of spin polarisation is demonstrated through its polarity reversal, which occurs when the crystal handedness is switched (lines 72-74)

We performed the same measurements on samples from different batches and found that a majority of them exhibited the same handedness, in agreement with Ref. 31; however, domains of opposite handedness were also found in the crystal (device #2). These domains were used in reference experiments to investigate the handedness dependence of the magnetoresistance signals (lines 126-130)

The nonlocal voltage measurement was also conducted with another device (device #2), in which domains of opposite handedness coexisted. We selectively applied I_{ac} through one of the two domains, measured the nonlocal voltage drops, and determined the polarisation direction of spin accumulation, **σ**, (Extended Data Fig. 8). We observed a pair of opposite spin accumulations, as shown in Fig. 3. Moreover, the spin pair exhibited polarity reversal from outwards to inward when the handedness of *κ*-NCS was switched at the excitation positions. This handedness-dependent polarity reversal is evidence of the chirality origin of voltage signals (lines 222-229)

Extended Data Fig. 8 (newly added to show the handedness dependence of nonlocal voltage signals)

Referee #3's comment 4

Typical consistency checks that would hint at chirality as the origin of the spin accumulation include (i) magnetization reversal under chirality reversal; (ii) scaling of the magnitude of spin-accumulation with the amount of chirality breaking, controlled e.g. by the molecular length; (iii) most importantly, demonstrating that spin-accumulation yields a very large polarization of order of several 10%. (I could not the corresponding estimate in the manuscript). I recall that some spin-polarization effects due to chirality are expected. While they may very well exceed the Edelstein effect, as seen in this manuscript, they do NOT constitute the CISS phenomenon which is an effect of (almost) order unity, c.f. arXiv:2108.09998…. (d) In the present measurement the presence of CISS is tested in the superconducting phase. Why would one employ a superconducting sample for devising a "smoking gun experiment" on the CISS? Taken at face value to get a superconductor involved looks like an extra complication, e.g., the combined effect of chirality and spin-orbit interaction on the superconducting state is not very well known, given that there is a CISS effect.

Authors' reply 4

We recognize that an impact of the molecular CISS lies in its high spin polarization, because it appears to be incompatible with small SOI. This point is respected by our argument in the manuscript that the spin-dependent voltage is 100,000% larger than expected from a representative spin-orbit effect, or the Rashba-Edelstein effect. This means that the resulting spin accumulation density n_s is so high that the spin polarization defined by $P \equiv n_s/n_c$ exceeds unity (n_c: the conducting-hole density which mediates an electric current at the Fermi level). This situation is described as "effective enhancement of SOI" in the original manuscript. If n_c is replaced with the total hole density in the crystal, P will be well below unity. Please note that the spin polarization in molecular CISS is experimentally evaluated by using the number of tunneling electrons as denominator, not the number of all electrons in the molecule [for example, Q. Qian, et al., Chiral molecular intercalation superlattices. *Nature* (2020)].

Additionally, we intended to explore a superconducting analogue of CISS, motivated by ideas in the context of CISS. We admit that as such, it is an open question how characteristics of the molecular CISS carry over to chiral crystals.

In the revised manuscript, we stressed that the purpose of this study was to explore a superconducting analogue of CISS instead of duplicating the molecular CISS and that effective enhancement of SOI was found to be a common characteristic.

The main change is as follows.

Our results demonstrate a solid-state analogue of spin accumulations hypothetically assumed for chiral molecules and may provide clues to the origin of their molecular counterparts (lines 24-26)

Referee #3's comment 5

(b) The theory papers motivating the CISS-interpretation adopted by the present authors have been commented on in arXiv:2108.09998. The model employed in Ref. 3 is hard to motivate in terms of a microscopic model of physical reality and was therefore considered "unphysical"; its apparent simplicity is deceptive. In contrast, Ref. 24 cited points to a valid physical mechanism that however is not believed to be sufficiently strong in order to explain the experimentally observed polarizations of order of several 10%.

Authors' reply 5

In response to this comment, we have refrained from introducing ref. 3 as a major motivation of this study. Instead, we have cited different papers on different views of CISS for fairness, because the mechanism of CISS remains to be clarified.

Referee #3's comment 6

(c) There are a number of smaller issues that I would like to mention. The authors say (in line 123) that all samples display the same handedness despite the fact that “no intentional symmetric induction” was made in the process of sample preparation. How is this possible? My general concern is that unknown sources of symmetry breaking (of whatever kind) may manifest in measurements that are interpreted as broken spin-symmetry (“accumulation”) in an unknown way.

Authors’ reply 6

It is frequently observed in chiral crystal growth that one particular handedness surpasses the other. For example, the handedness of B20 MnSi and its sister compounds are known to choose left-handed crystal structure (PRL 102, 037204 (2009) and J. Phys. Soc. Jpn. 54, 2970 (1985)). The origin of this symmetry breaking is unknown, but the thermodynamic process for crystal nuclei formation is so complicated that any subtle difference such as parity violation in weak interaction may affect the asymmetry. Another possible source of the crystal asymmetry is organic impurities from biological sources such as L-amino acids or D-sugars. Regarding our chiral superconductor, after analyzing many samples, we were able to find left-handed domains in some of the crystals, although right-handed crystals are preferentially formed (ref. 31). Based on this fact, we have modified the expression on the crystal handedness in the main text accordingly. Note that the change in the crystal handedness in our device has shown inversion of the accumulated spins, which means that the source of symmetry breaking in the crystal formation does not affect the spin-asymmetry in our electrical measurements.

The corresponding change is as follows.

We performed the same measurements on samples from different batches and found that a majority of them exhibited the same handedness, in agreement with Ref. 31; however, domains of opposite handedness were also found in the crystal (device #2). These domains were used in reference experiments to investigate the handedness dependence of the magnetoresistance signals (lines 126-130)

Reviewer Reports on the First Revision:

Referees' comments:

Referee #1 (Remarks to the Author):

I am very happy with the manuscript modifications and the answers to my and the other reviewers questions.
I can now recommend the publication of the manuscript in Nature.

Referee #2 (Remarks to the Author):

I have read the revised version of the manuscript and also the answers that the authors have given to all the Referees' comments including mine.

I think that the manuscript has significantly improved since the last revision, and that the authors have addressed the Referees' comments and their points of criticism properly and at the best of their possibilities.

I would therefore recommend the article now for publication in Nature.

Referee #3 (Remarks to the Author):

In my earlier report I have requested from the authors a smoking gun experiment: A control experiment should demonstrate that the very large accumulation of spin, which they report, is indeed due to the chirality of the molecular material \kappa-NCS that they use. (3rd comment)d

The authors have presented now in Fig. 8 a fresh control experiment that in my mind gives convincing evidence for the validity of their claim.

Further, also the other points I have raised have been answered to my full satisfaction.

For this reason, I come to the conclusion that the improved manuscript is suitable for publication in Nature. A really amazing experimental observation is reported. Indeed amazing.