

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

Referee report on manuscript COMMSPHYS-20-0754-T entitled "Symmetry mediated tunable molecular magnetism on a 2D material" by Y. Wang et al.

The authors use STM and STS to unravel changes in the total spin of a CoPc molecule adsorbed on 2H-NbSe₂. Depending on the molecular adsorption orientation they find either the preservation of the vacuum $S=1/2$ spin state or a non-magnetic ground state. In order to describe spectroscopic data of the $S=0$ molecule the authors use a Hamiltonian that includes the Dzyaloshinskii-Moriya interaction between the molecular spins.

I think that the data are excellent. The presentation is concise and accessible for a reader with solid-state physics background. The interpretations are backed by the data and are scientifically sound. However, I am concerned about the novelty aspects of the findings and several other issues that I substantiate below. On the basis of these comments I do not recommend acceptance of the paper for publication in Communications Physics in its current status. I encourage the authors to take the following questions and suggestions into account for a revision of the manuscript.

(a) In essence, the authors demonstrate that the actual adsorption geometry of a molecule on a surface determines its electronic and magnetic properties. This effect is well-known and has been explored in extenso for phthalocyanine molecules on surfaces, e.g., in J. Phys. Chem. C 112, 13650 (2008), Phys. Rev. B 85, 155437 (2012), Nat. Mater. 12, 337 (2013). In this context, the impact of adsorption site and orientation on electronic properties of a phthalocyanine molecule on 2D hexagonal boron nitride has recently been reported [ACS Nano 9, 10125 (2015)].

(b) Comparing the twist-angle physics of 2D materials with the rotational orientation of the molecule on a layered material (in the introduction of the manuscript and in the last paragraph of the discussion section) is misleading. The former situation relies on the subtle tuning of Van Hove singularity energies in order to drive transitions from a Mott insulator to a superconductor. These effects are the result of the hybridization of Dirac cones, i.e., the electronic structure of the entire 2D materials are involved. In the latter case, local charge transfer between the adsorbed molecule and the substrate plays the key role for the molecular properties.

(c) The symmetry reduction of adsorbed phthalocyanine molecules was reported before and should be cited, e.g., AIP Adv. 2, 041402 (2012) and references therein.

(d) The existence of two molecular spins – labelled S_1 , S_2 in Eq. (1) – remains vague. While one spin reflects the Co^{2+} oxidation state (and is thus coupled to the position of the central ion) it is not clear where the second spin is localized. Is it on the phenyl moieties? Would it then be more appropriate to consider the interaction of S_1 with four other spins? Moreover, it is unclear why the authors choose an isotropic Heisenberg exchange interaction. The symmetry reduction of the molecular electronic structure due to the surface suggests an anisotropic Heisenberg exchange coupling.

(e) It remains elusive what the inelastic transitions at $\sim \pm 25$ meV are due to. They seem to be inelastic spin excitations, but it is unclear which energy levels are involved. The authors may add the different energy levels and mark the observed transitions.

(f) The authors claim that Jst and A maps reveal different symmetry. I do not see that (in my version of the manuscript file): both maps exhibit two perpendicular mirror planes, in contrast to what the authors suggest.

Reviewer #2 (Remarks to the Author):

Dr. Wang and colleagues reported here on asymmetry mediated tunable molecular magnetism on a 2D material. The manuscript clearly shows that two different molecular spin states by modifying the symmetry of the molecules via the twist angle to the substrate. the author also claims that observation of significant non-collinear Dzyaloshinskii-Moriya interaction between two electron spins on the molecule induced by the strong spin-orbit coupling of the van der Waals coupled layered material with broken inversion symmetry. Although I enjoyed reading the manuscript a lot, I want to clear a few points that are listed below:

- 1.the intrinsic spin-orbit coupling in NbSe₂ is actually weak, however, due to the broken inversion symmetry of the crystal, monolayer NbSe₂ shows some sign of Ising spin-orbit coupling which leads to a resilient superconducting state upon applying an in-plane external field. being said that, the author has used a bulk NbSe₂ crystal which is different from monolayer Nbse₂ even if they have bound together with VdW forces. How the author excludes the effect of bulk?
- 2.did the author performed an experiment on monolayer NbSe₂?
- 3.The author mentioned that the charge density wave of the surface has only marginal influence on Jst. why? and what is the effect of CDW on YSR states?
- 4.author has demonstrated that the spin state of adsorbed molecules can strongly depend on subtle variations of the twist angle with respect to the substrate, however, only one twist angle is shown experimentally? it will more convincing if the author can provide more data on this?

Dear editor,

We thank both reviewers for their careful consideration of our manuscript and their overall very positive and thoughtful critiques which we believe allowed us to improve the manuscript significantly. Below, we provide our response to their comments in blue. Additions or changes to the manuscript and the supplementary information are marked in red.

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(a) Q: In essence, the authors demonstrate that the actual adsorption geometry of a molecule on a surface determines its electronic and magnetic properties. This effect is well-known and has been explored in extenso for phthalocyanine molecules on surfaces, e.g., in J. Phys. Chem. C 112, 13650 (2008), Phys. Rev. B 85, 155437 (2012), Nat. Mater. 12, 337 (2013). In this context, the impact of adsorption site and orientation on electronic properties of a phthalocyanine molecule on 2D hexagonal boron nitride has recently been reported [ACS Nano 9, 10125 (2015)].

(c) Q: The symmetry reduction of adsorbed phthalocyanine molecules was reported before and should be cited, e.g., AIP Adv. 2, 041402 (2012) and references therein.

We highly appreciate that the reviewer points us to some significant previous publications which we have partly missed to acknowledge correctly. We also agree with him/her that the novelty and motivation of our work was not as clear as it should be.

To account for previous publications we have updated the references throughout the manuscript and added the references 6, 12–14, and 20.

Additionally, we changed the introduction and discuss previous work in more detail by now writing (lines 43–48):

... The molecular symmetry of phthalocyanine molecules has been shown to be modified by manipulating the molecule and additional atoms¹². Alternatively, the molecular symmetry can be changed without modifying its structure by adsorbing the molecule on a sample with a dissimilar point-group^{13–15}. While these previous works mainly focus on the influence of the chemical bonds between sample and molecule, and on the influence of the symmetry and local environment on the molecular charge and spin state, the physical properties of the intramolecular spin-spin interaction has not been studied in detail. ...

Later in the text where we discuss the CoPc_v species we write now (lines 73–74):

... Contrarily, molecules in which the σ_v of the sample and of the molecule are aligned couple stronger to the substrate and enable charge transfer between the molecular orbitals and the sample^{6,19,20}. ...

To be more precise with the main novelty of our research in which we study the physics of intramolecular spin-spin interaction, we write now in the introduction (lines 25–30):

... While many studies address the influence of angle mismatch between layered 2D materials^{3–5} in which the twisting leads to symmetry breaking and a subtle tuning of Van-Hove singularities that drives the system into different phases, the impact of the absorption alignment on the physical properties of planar molecules on 2D substrates has not been studied in detail; in particular the intramolecular spin-spin interactions and the arising of non-collinear molecular spin states. ...

(b) Q: Comparing the twist-angle physics of 2D materials with the rotational orientation of the molecule on a layered material (in the introduction of the manuscript and in the last paragraph of the discussion section) is misleading. The former situation relies on the subtle tuning of Van Hove singularity energies in order to drive transitions from a Mott insulator to a superconductor. These effects are the result of the hybridization of Dirac cones, i.e., the electronic structure of the entire 2D materials are involved. In the latter case, local charge transfer between the adsorbed molecule and the substrate plays the key role for the molecular properties.

We thank the referee for mentioning this point. He/She is right that the twist-angle physics of 2D materials is different from our work. Therefore, we changed the introduction and last paragraph as reviewer suggested. However, even though the charge transfer is crucial for the molecule’s spin state as we mention in our manuscript, the symmetry breaking plays the key role in our system for the intramolecular spin-spin interaction. In this regard, we made the following changes in the revised manuscript:

(1) The second and third sentence of the introduction (see above).

(2) The last paragraph of the discussion section in line 165:

... Our work demonstrates that the intramolecular spin-spin interaction of adsorbed molecules can strongly depend on subtle variations of the adsorption geometries with respect to the substrate which opens a new path for controlling and engineering more complex spin structures. ...

(d) Q: The existence of two molecular spins – labelled S1, S2 in Eq. (1) – remains vague. While one spin reflects the Co^{2+} oxidation state (and is thus coupled to the position of the central ion) it is not clear where the second spin is localized. Is it on the phenyl moieties? Would it then be more appropriate to consider the interaction of S1 with four other spins? Moreover, it is unclear why the authors choose an isotropic Heisenberg exchange interaction. The symmetry reduction of the molecular electronic structure due to the surface suggests an anisotropic Heisenberg exchange coupling.

We thank the referee for bringing the effect of anisotropic Heisenberg coupling into the discussion. We believe that her/his question is so important that we updated our supplemental information (section 4) to explain in detail why an anisotropic Heisenberg coupling without Dzyaloshinskii-Moriya interaction is not sufficient to describe our observations.

The referee is fully right in that the molecule’s symmetry suggests some kind of XXZ coupling between the central spin and the distributed spin on the ligands. The simplest models are either a pure Ising-like coupling in which only J_z is unequal to zero, or an in-plane coupling in which J_x and J_y are the dominant terms. As we now show in the SI, both models lead to results inconsistent with our observations (Fig. S6). We note that this holds also for any combination of these two models. Thus, we need an additional Dzyaloshinskii-Moriya interaction which originates from the broken in-plane symmetry and the spin-orbit coupling of the hosting NbSe_2 substrate.

As the reviewer correctly mentions, it is as such not clear how many spins are distributed on the ligands of the molecule. However, we have evidence that the formerly $S = 1/2$ CoPc_d changes its ground state when it is rotated by 15° becoming CoPc_v to a non-magnetic singlet state which neither influences the superconductor nor shows some spin excitations at low energy when a magnetic field is applied. Thus, the additional spin moment over the ligands must be half integer and can not be an integer, excluding 4 additional spins on the ligands as suggested by the referee.

We believe that there is only one additional unpaired electron spin distributed over the ligands, because we have no hints of a higher spin in the system from the magnetic field dependent measurements. Also our Kelvin probe force measurements points to a single charge difference between both species (Fig. S2).

This additional spin is in contrast to the well localized Co^{2+} moment distributed over the phenyl moieties as our spatially resolved measurements in Figure 4 clearly shows. We believe that it is localized in a singly occupied molecular orbital (SOMO) of the molecule.

(e) Q: It remains elusive what the inelastic transitions at $\sim \pm 25$ meV are due to. They seem to be inelastic spin excitations, but it is unclear which energy levels are involved. The authors may add the different energy levels and mark the observed transitions.

The reviewer's suggestion can indeed help readers better understand our model. We have therefore updated the figure in the SI (Fig. S6) with the quantum numbers of the states and marked the allowed transition at out-of-plane magnetic field.

(f) Q: The authors claim that the J_{ST} and A maps reveal different symmetry. I do not see that (in my version of the manuscript file): both maps exhibit two perpendicular mirror planes, in contrast to what the authors suggest.

We again thank the referee for mentioning this point. We believe that this crucial point was not well elaborated by us. Therefore, we have updated Fig. 4 of the main text with panels which compare the relative differences between the A and spin-excitation energy maps ε to perfect 4-fold symmetry. We found that relative difference of the ε map is less than 4% supporting our claim that it has remained mainly 4-fold symmetric, while the difference is $\approx \pm 20\%$ in the A -map. We hope that this comparison makes it easier for the reader to clearly see the different symmetries in the ε and A -maps.

Reviewer 2 (Remarks to the Author):

Dr. Wang and colleagues reported here on asymmetry mediated tunable molecular magnetism on a 2D material. The manuscript clearly shows that two different molecular spin states by modifying the symmetry of the molecules via the twist angle to the substrate. the author also claims that observation of significant non-collinear Dzyaloshinskii-Moriya interaction between two electron spins on the molecule induced by the strong spin-orbit coupling of the van der Waals coupled layered material with broken inversion symmetry. Although I enjoyed reading the manuscript a lot, I want to clear a few points that are listed below:

1. Q: the intrinsic spin-orbit coupling in NbSe_2 is actually weak, however, due to the broken inversion symmetry of the crystal, monolayer NbSe_2 shows some sign of Ising spin-orbit coupling which leads to a resilient superconducting state upon applying an in-plane external field. Being said that, the author has used a bulk NbSe_2 crystal which is different from monolayer NbSe_2 even if they are bound together with VdW forces. How does the author excludes the effect of bulk?

We thank the referee for contrasting the difference between monolayer and bulk NbSe_2 . As she/he emphasized, it is not appropriate to state that bulk

NbSe₂ is an Ising superconductor. Although the staggered spin-orbit coupling of each layers in bulk restores inversion symmetry as a whole, the layers are weakly coupled and hence the resulting SOC in the bulk NbSe₂ is not as strong as a monolayer, however SOC in bulk 2H-TMDs still exists [2H-NbSe₂ Nature Communications 7, 11711 (2016), 2H-WSe₂ Nature Physics 10, 835–839 (2014)].

Therefore, in compliance with the referee’s point, we made the following changes in the revised manuscript:

- (1). Line 17: We changed "...the strong spin-orbit coupling..." to "...the spin-orbit coupling..."
- (2). Line 37: "Because the Ising superconductor 2H-NbSe₂..." is changed to "Because 2H-NbSe₂..."
- (3). Line 37: Reference 8 which discusses the SOC in bulk 2H-NbSe₂ has been added. Furthermore we changed "...lacks inversion symmetry..." to "...lacks in-plane inversion symmetry..." and "... has strong spin-orbit coupling..." to "...has spin-orbit coupling..."
- (4). Line 176: We changed "...the strong spin-orbit coupling..." to "...the spin-orbit coupling..."

2. Q: Did the author performed an experiment on monolayer NbSe₂?

We have not yet performed any measurement on monolayer NbSe₂ mainly due to technical difficulties in our experimental set-up where we have neither *x-y* coarse motion nor optical access to the sample which would be requirement to locate monolayer NbSe₂ flakes. However, the experiment on single-layer material proposed by the reviewer is certainly an interesting research topic due to the stronger SOC in monolayer NbSe₂, out-of-plane inversion symmetry breaking, and a more pronounced 2D character.

3. Q: The author mentioned that the charge density wave of the surface has only marginal influence on J_{ST} . Why? and what is the effect of the CDW on the YSR states?

The referee points to a very interesting question regarding the effect of the CDW on the YSR states. The energy and particle-hole asymmetry of the YSR states depends on the magnetic and potential scattering of the substrate’s Cooper pairs on the impurity, as well as on the local density of state (DOS) of the substrate which indeed is modulated by the CDW on the atomic corrugation of the substrate. We did not focus our study on this topic because it has been studied recently in great detail on Fe adatoms in the following reference: Nano Lett. 20, 339–344 (2020). However, we would like to note that the force the approaching tip exerts on the molecule will change the energy of the YSR states at CoPc molecules on NbSe₂ [Ref. 18, Nano Lett. 18, 2311–2315 (2018)] similar to our observation that J_{ST} changes approximately linearly with the short-range force acting between the tip apex and the central Co-ion in CoPc_v molecules (Fig. S4c–f).

Because we do not observe any Kondo or YSR states on the CoPc_v molecules, the spin scattering exchange energy J between the molecule and the substrate must be much smaller than the intramolecular spin-spin interaction J_{ST} . Therefore, the substrate's CDW only marginally renormalizes J_{ST} as Fig. S4a, b shows.

4. Q: The author has demonstrated that the spin state of adsorbed molecules can strongly depend on subtle variations of the twist angle with respect to the substrate, however, only one twist angle is shown experimentally? It will more convincing if the author can provide more data on this?

According to our symmetry analysis (see section 1, SOM), we conclude that there are only two stable adsorption sites with high symmetry. We have measured thousands of molecules and observed only these two stable geometries. In fact, we found that the population rate of the stable CoPc_v is much higher than of the meta-stable CoPc_d. Therefore we were not able to study other rotational configurations with lower symmetry.

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

Referee report on manuscript COMMSPHYS-20-0754A entitled "Symmetry mediated tunable molecular magnetism on a 2D material" by Y. Wang et al.

The authors have thoroughly responded to my questions and suggestions. The manuscript has been revised accordingly. In particular, the novelty aspect of the findings has persuasively been clarified and well embedded into the available literature. Moreover, the symmetry discussion of inelastic excitations across the molecule has substantially been improved by the new figure 4 and the additional statements on anisotropic Heisenberg coupling in the supporting online material.

I recommend acceptance of the paper for publication in Communications Physics.

Reviewer #2 (Remarks to the Author):

the author has addressed all of my concerns, therefore I recommend for publications