Reviewers' comments:

Reviewer #1 (Remarks to the Author):

This work describes the electronic decoupling of hydrogenated heptacene molecules on a metal surface as monitored by scanning tunneling microscopy and spectroscopy. The authors provide firm evidence for the decoupling and describe and explain in detail the spectroscopic results and their implications. This paper is very clear and well written and provides basic understanding of the charging and tunneling processes. I, therefore, recommend publication of the manuscript as is.

Reviewer #2 (Remarks to the Author):

Mohammed et.al. report an STM study on the electronic structures of hydrogenated heptacene on Ag(100). They claim that electronic decoupling of the molecule can be achieved by bending the planar geometry through sp3 carbon atoms. Although some interesting phenomenon are observed by STS measurements, additional experiments are required to confirm the statement that decoupled electronic structures can be achieved by hydrogenated carbon atoms.

1) The concept about self-decoupling of organic molecules is not completely new. Similar concept was introduced by Berndt et.al in 2010 (PNAS,2011,961-964).

2) The existence of C(sp3)-H bonds can break the planar structure of the molecule but cannot change the fact that the molecule is still adsorbed on metal substrate. The electronic structures in this case should not be decoupled from the metal substrate. A controlled experiment is required, such as the STS spectroscopy of the molecule on NaCl films. Furhermore, the authors claimed that "The zero bias resonance is a manifestation of the Kondo effect associated with the spin 1/2 of the molecule as a single electron occupies its gas-phase LUMO", which mean the unoccupied electrons of the molecules are screen by the conducting electrons of the substrate. Can the authors comment on this?

3) On page 6 the authors mentioned that "the datasets of Fig. 2b, 2c and 2d correspond to different molecules, although all of them share the same chemical structure displayed in Fig. 1b."The question is why different molecule is chosen when taking the distance and tunneling junction dependent dI/dV measurements?

4) The charging mechanism should rely on the double tunneling barrier, thus should not be temperature dependent. However, In page 9 the author mention a Kondo temperature of 73±2 K, which mean the resonance would disappear at elevated temperature.

5) I strongly recommend add a schematic diagram explaining the double tunneling barrier and the induced charging resonances.

Reviewer #3 (Remarks to the Author):

The manuscript reports a spectroscopic investigation of heptacene molecules functionalized with additional hydrogen atoms. Based on scanning tunneling spectrscopy and complemented with ab initio calcuations the authors show that the sp3 hybridization induces a reduction of the effective lenght of the acene and makes it comparable to pentacene. As an additional effect of present sp3 hybridization the authors report electronic decoupling of the molecule from the underlying substrate. This is mainly accessed through the analysis of electric field dependent charging of individual molecules and can be rationalized with a double tunneling barrier. At the same time,

observation of a Kondo resoance is observed for some particular charging configurations. While the study reports potentially interesting new insigths into acenes and ways to intrinsically decouple specific molecules, I feel that some of the points are discussed in a rather qualitative way and that overall status of the report is somewhat premature for publication. My main concerns are listed below.

- Chemical functionalization with three-dimensional moieties has been used in the past with the aim of decoupling the main part of the molecules (see e.g. Moresco and Gourdon in PNAS, 2005 [DOI: 10.1073/pnas.0500915102]). However, efficiency of the approach for large molecules is very limited due to their flexibility so that decoupling can be rahter poor. Hence, a somewhat refined discussion with respect to the validity of the described decoupling approach would be adapted.
- The authors show a DFT-based geometry of the surface-adsorbed molecule where the additioanl hydrogens point away from the surface. How is this rationalized? The opposite configuration with hydrogens pointing towards the surface seems to be equally accessible.
- A more detailed comparison between the model system pentacene and the hydrogenated heptacene would be welcome in order to better understand why the later is decoupled from the surface and the former not. The two additional hydrogens seem to only affectthe adosrption height one side of the molecule. Is the other side remaining at the same height as pentacene? In this case, an efficient decoupling would be very surprising.
- The authors emphasize the great varability of the properties of different molecules, which is assigned to varying substrate properties. Does it mean that the substrate is not clean? Can molecules be manipulated to similar orientations and lattice sites so that the show exactly the same properties?
- Oberservation of a Kondo resonance and the claim of efficient decoupling seems to be contradictory. Decoupling from the substrate implies that Kondo screening should not be effective anymore. This needs further discussion.

Reviewer #1:

This work describes the electronic decoupling of hydrogenated heptacene molecules on a metal surface as monitored by scanning tunneling microscopy and spectroscopy. The authors provide firm evidence for the decoupling and describe and explain in detail the spectroscopic results and their implications. This paper is very clear and well written and provides basic understanding of the charging and tunneling processes. I, therefore, recommend publication of the manuscript as is.

We thank the referee for her/his appreciation of our work.

Reviewer #2:

Mohammed et.al. report an STM study on the electronic structures of hydrogenated heptacene on Ag(100). They claim that electronic decoupling of the molecule can be achieved by bending the planar geometry through sp3 carbon atoms. Although some interesting phenomenon are observed by STS measurements, additional experiments are required to confirm the statement that decoupled electronic structures can be achieved by hydrogenated carbon atoms.

We thank the referee for her/his positive evaluation of our work and answer in the following to each of the criticisms raised in the report.

1) The concept about self-decoupling of organic molecules is not completely new. Similar concept was introduced by Berndt et.al in 2010 (PNAS,2011,961-964).

We agree with the referee. Our novelty claim lies in the demonstration of the decoupling effect of a specific type of functionalization not reported to date, which is much less "bulky" and "distorting" than the functional groups utilized to promote the self-decoupling in previous works. However, we do not claim novelty for the self-decoupling of the molecules in general. To further clarify this, we have modified the introductory text and have added references to various papers having reported the self-decoupling concept (including the reference suggested by the referee). The text now reads:

"The chemical addition of bulky side groups to the molecular structure of interest, which can act as molecule-substrate spacers and thereby reduce their coupling strength, has also been proved successful.[24–26] The efficiency of this self-decoupling strategy is generally poor due to the flexibility of the carbon backbones, which allows them coming close to the substrate by molecular deformations.[24] Nevertheless, it has been sufficient e.g. to regain the functionality of molecular switches that is otherwise quenched by the stronger interaction with the substrate.[27]

Herein we report the decoupling of polyacenes from an underlying Ag(100) surface by exploiting the non-planarity of the organic backbone imposed by sp^3-type functional groups. Interestingly, this approach could easily be extrapolated to other organic species and thereby allow important advances in timely research fields like carbon-based magnetism.[28–34]„

2) The existence of C(sp3)-H bonds can break the planar structure of the molecule but cannot change the fact that the molecule is still adsorbed on metal substrate. The electronic structures in this case should not be decoupled from the metal substrate. A controlled experiment is

required, such as the STS spectroscopy of the molecule on NaCl films. Furhermore, the authors claimed that "The zero bias resonance is a manifestation of the Kondo effect associated with the spin 1/2 of the molecule as a single electron occupies its gas-phase LUMO", which mean the unoccupied electrons of the molecules are screen by the conducting electrons of the substrate. Can the authors comment on this?

We agree with the referee in that the molecule is still adsorbed on the metal substrate and its decoupling is not intuitively expected. However, the unambiguous observation of several spectroscopic fingerprints that are unequivocally associated to electronically decoupled molecules is proof for this unexpected finding. These observations are (i) the charging resonances in conductance spectra, which require a double tunneling barrier with a bias drop across the molecule-tip junction that can only exist with sufficiently electronically decoupled molecules; (ii) the strong vibronic resonances following the first charging peak, which imply that tunneling electrons may efficiently couple to vibrational levels of the transiently charged molecule and show up stronger the more decoupled the molecules are; (iii) the observed Kondo resonance on molecules that are charged at zero bias. This last point is explicitly addressed by the referee, since it is used in the paper as proof for the decoupling but actually requires a sufficient interaction with the substrate to allow the screening of the molecular spin by the substrate electrons. We would like to clarify that these two points are not contradictory. An exceedingly strong decoupling would indeed cause the Kondo resonance to disappear. However, the same applies if the coupling becomes too strong, which would broaden the molecular levels and decrease correlations, quenching the spin of the singly charged molecule. Those two limits are explicitly addressed and explained in the initial section describing the case of pentacene on Ag(001) with and without a decoupling (MgO) layer, reported in reference 35.

These cases also serve as the control experiment requested by the referee. The idea behind the control experiment being the demonstration of the electronic decoupling, the hydrogenated heptacene needs to be compared to a non-decoupled molecule. Comparing hydrogenated pentacene on Ag(001) with hydrogenated pentacene on a decoupling layer (e.g. NaCl, as suggested by the referee) would compare two decoupled molecules due to its self-decoupling ability (although the stronger decoupling on the NaCl would presumably result in an absent Kondo resonance, as it occurred for pentacene on MgO). Instead it needs to be compared to an electronically equivalent but non-decoupled molecule, which is exactly the pentacene on Ag(001) case.

In order to clarify these issues, the text has been rephrased as follows:

"For that reason, whenever the zero bias point coincides with a molecule in its charged state (occupied LUMO), an additional zero bias resonance appears in the spectra (Fig. 2c-d), but not if the molecule at zero bias is in its neutral state (Fig. 2b-c). As opposed to the charging resonances, this zero bias resonance does not shift for varying tip heights (Fig. S2b) and is a manifestation of the Kondo effect associated with the spin 1/2 of the molecule as a single electron occupies its gas-phase LUMO.[41,42] This is confirmed by its anomalously fast broadening with temperature, whose width evolution is in agreement with a Kondo temperature of 73±2 K (Fig. S3). The presence of this Kondo resonance is further proof of the decoupling effect that the "pentacene functionalization" at C-2 and C-3 with sp^3 carbon atoms brings about. If that were not the case, a broader LUMO level and reduced electron correlations would cause an equal population of spin up and spin down LUMO orbitals,[36,37]

resulting in no net spin and no Kondo peak, as occurs with pristine pentacene.[35] On the other hand, the Kondo resonance still implies a minor molecule-substrate coupling, since it relates to the screening of the molecular spin by the substrate electrons and would thus be absent for a more efficient decoupling as observed for pentacene on an insulating MgO buffer layer. We can thus conclude that on Ag(001) the "pentacene functionalization" by sp^3 carbon atoms results in sufficiently decoupled molecules to show charging resonances and stabilize a singly charged molecule with net spin 1/2, but with sufficient molecule-substrate interaction to reveal a Kondo resonance. In other words, more decoupled than pristine pentacene on Ag(001) but, as could be expected, less than pentacene on a MgO bilayer on Ag(001)."

3) On page 6 the authors mentioned that "the datasets of Fig. 2b, 2c and 2d correspond to different molecules, although all of them share the same chemical structure displayed in Fig. 1b."The question is why different molecule is chosen when taking the distance and tunneling junction dependent dI/dV measurements?

In the following panels and supplementary information figures we show systematic measurements addressing the dependence on tunneling barrier height, on the probe and on the adsorption or molecular environment. However, panels 2b-d are shown as representative examples of utterly different scenarios, namely with the parabola made up by the charging resonances entirely at negative bias, crossing the Fermi level, and entirely at positive bias. Because we don´t have similarly nice looking examples that show the entire range of variations as a function of only one of the involved parameters, we prefer to leave it as is: Panels b-d simply show the range of variation, and the dependence on each of the parameters involved is systematically explained thereafter.

4) The charging mechanism should rely on the double tunneling barrier, thus should not be temperature dependent. However, In page 9 the author mention a Kondo temperature of 73±2 K, which mean the resonance would disappear at elevated temperature.

We realize that the text was not clear enough and has led to a misunderstanding. The charging mechanism is indeed not temperature dependent and the temperature dependence described in the text refers only to the Kondo resonance. As readily shown in the response to point 2), the text has now been rephrased to make this more clear and to avoid such misunderstanding.

5) I strongly recommend add a schematic diagram explaining the double tunneling barrier and the induced charging resonances.

Following the referee´s suggestion we improve Fig. S3 and move it to the main text becoming the new Fig. 3.

Reviewer #3:

The manuscript reports a spectroscopic investigation of heptacene molecules functionalized with additional hydrogen atoms. Based on scanning tunneling spectrscopy and complemented with ab initio calcuations the authors show that the sp3 hybridization induces a reduction of the effective lenght of the acene and makes it comparable to pentacene. As an additional effect of present sp3 hybridization the authors report electronic decoupling of the molecule from the underlying substrate. This is mainly accessed through the analysis of electric field dependent

charging of individual molecules and can be rationalized with a double tunneling barrier. At the same time, observation of a Kondo resoance is observed for some particular charging configurations. While the study reports potentially interesting new insigths into acenes and ways to intrinsically decouple specific molecules, I feel that some of the points are discussed in a rather qualitative way and that overall status of the report is somewhat premature for publication. My main concerns are listed below.

We appreciate the constructive criticism of the referee and answer below to each of his listed concerns.

- Chemical functionalization with three-dimensional moieties has been used in the past with the aim of decoupling the main part of the molecules (see e.g. Moresco and Gourdon in PNAS, 2005 [DOI: 10.1073/pnas.0500915102]). However, efficiency of the approach for large molecules is very limited due to their flexibility so that decoupling can be rahter poor. Hence, a somewhat refined discussion with respect to the validity of the described decoupling approach would be adapted.

We follow the referee's suggestion and add the following discussion to the manuscript text, which includes also her/his outlined reference:

"The chemical addition of bulky side groups to the molecular structure of interest, which can act as molecule-substrate spacers and thereby reduce their coupling strength, has also been proved successful.[24–26] The efficiency of this self-decoupling strategy is generally poor due to the flexibility of the carbon backbones, which allows them coming close to the substrate by molecular deformations.[24] Nevertheless, it has been sufficient e.g. to regain the functionality of molecular switches that is otherwise quenched by the stronger interaction with the substrate.[27]"

- The authors show a DFT-based geometry of the surface-adsorbed molecule where the additional hydrogens point away from the surface. How is this rationalized? The opposite configuration with hydrogens pointing towards the surface seems to be equally accessible.

In the gas phase the hydrogenated heptacene is fully symmetric, formed by a completely planar C backbone where only the hydrogens at the hydrogenated sites protrude, one above and another below the plane. After deposition, the symmetry is broken, and the hydrogens pointing towards the surface are repelled by steric repulsion, causing the non-planarity of the molecule shown in figure 2e. The degree of the non-planar distortion depends on the particular adsorption site. The one shown in Fig.2e is the lowest in energy that we have found and further agrees with our experimental findings.

To make this clear in the manuscript we have amended the text as follows:

"Here, the key to rationalizing this surprising finding is the presence of the hydrogenated sp^3 C atoms of dihydroheptacene. According to density functional theory calculations, in the gas-phase the molecule presents a completely planar C backbone in which the two H atoms bound to each of the sp^3 C atoms protrude to either side of the plane. Upon adsorption on Ag(001) the symmetry is broken and the hydrogen atoms pointing towards the surface are repelled by steric repulsion. This causes a non-planarity of the molecule as shown in Fig. 2e, which in turn sufficiently reduces its electronic coupling from the substrate to generate the double barrier in the tunneling process."

- A more detailed comparison between the model system pentacene and the hydrogenated heptacene would be welcome in order to better understand why the later is decoupled from the surface and the former not. The two additional hydrogens seem to only affectthe adosrption height one side of the molecule. Is the other side remaining at the same height as pentacene? In this case, an efficient decoupling would be very surprising.

The C atoms of the "functionalized pentacene" nearest to the hydrogenated ring are indeed 0.14 Å further from the surface than the analog pentacene atoms. On the far side, however, the heights are the same within the limitations of DFT (unable to account for van der Waals interactions in all local and semilocal functionals), emphasizing again the good comparison between pentacene and the pentacene-segment of the functionalized heptacene. Nevertheless, the overwhelming experimental evidence (appearance of charging peaks, a Kondo peak, vibronic signature...) of a more decoupled pentacene segment shows that obviously the pentacene fragment is not a pentacene molecule. Our interpretation is that the electronic structure over the pentacene fragment is affected by the different hybridization with the ending group of the molecule. As a consequence the molecular orbitals have different weights on the pentacene fragment and the interaction with the substrate is reduced. Like in our reply to Referee 2, and the last question of Referee 3, let us emphasize once again that we are claiming a reduced coupling to the substrate as compared to pure pentacene and not a total decoupling.

- The authors emphasize the great varability of the properties of different molecules, which is assigned to varying substrate properties. Does it mean that the substrate is not clean? Can molecules be manipulated to similar orientations and lattice sites so that the show exactly the same properties?

The fact that we observe such variability for different molecules is not related to a dirty sample, which is clean by STM standards (no undesired adsorbates on hundreds of square nm) prior to deposition. There are, however, always surface and subsurface defects (the nature of which we don´t know and is beyond the scope of this paper) that affect and modulate the electric field lines. Some of them are observed as darker spots on the Ag(001) surface. In addition, even just the different supramolecular environment affects the electronic properties of molecules, and consequently the electric fields as the tip comes near. The result is that after molecule manipulation experiments we always had different charging peaks even if the molecules maintained a similar adsorption geometry and orientation. That can also be inferred from Fig. 2i: All the dihydroheptacene molecules are oriented along two equivalent orientations but all show different charging peaks depending on their position on the substrate and supramolecular environment.

A similar (uncontrolled) variability of charging peaks has been reported for example in ref. 42 with TCNQ molecules on Au(111), all sharing the same supramolecular environment in a well-defined monolayer structure, as a function of the position on the substrate surface.

In response to the referee we have clarified this issue in the text as follows:

"However, not only the tip matters for the charging resonance appearance, but also inhomogeneities in the sample. The tunneling barrier and the electric field within the tunneling junction is also affected by the polarizability of a molecule´s surroundings (neighboring molecules, surface and subsurface defects…).[42–46] Therefore, even with the same tip, molecules sharing the same structure may display different charging peaks.[42] A conductance map measured at -80 mV on a variety of hydrogenated heptacene derivatives[11] displays, on each of

the “functionalized pentacene” molecules, charging rings with different shapes and sizes that are even centered on different molecular positions (Fig. 2i). Similar changes are found for a same molecule after tip-manipulation to another epitaxially equivalent substrate position. Fig. 2j shows STS data acquired with the same tip on equivalent positions of different “functionalized pentacene” molecules. The inset shows the dI/dV spectra, revealing charging resonances at very different bias values. Associated I vs. z curves taken at the same positions reveal the expected linear behavior when the current is plotted logarithmically, and notably different slopes (Fig. 2j). The slopes correlate with the effective barrier at the tunneling junction, which is typically associated with an average of tip and sample workfunction.[47] The tip being the same, once can conclude that the change in the effective barrier relates to local inhomogeneities in the substrate[42] and/or local supramolecular environment,[43–46] resulting in this particular case in a 0.51 eV larger effective tunneling barrier and 0.4 V lower charging bias threshold for the molecule associated with the red curves.”

- Oberservation of a Kondo resonance and the claim of efficient decoupling seems to be contradictory. Decoupling from the substrate implies that Kondo screening should not be effective anymore. This needs further discussion.

We agree with the referee in the apparent contradiction, since a certain molecule-substrate coupling is required for the Kondo resonance to appear, related to the screening of the molecular spin by the substrate electrons. However, whilst an exceedingly strong decoupling would indeed cause the Kondo resonance to disappear, the same applies if the coupling becomes too strong. A strong coupling scenario would broaden the molecular levels and decrease correlations, quenching the spin from the singly charged molecule. Those are the two limits represented by the case of pentacene on Ag(001) with and without a decoupling (MgO) layer. The dihydroheptacene case demonstrates a weaker molecule-substrate coupling than the pristine pentacene analogue, but (as expected) a stronger coupling than with the insulating MgO layer.

Following the referee’s suggestion, this has now been discussed in the text as follows:

“For that reason, whenever the zero bias point coincides with a molecule in its charged state (occupied LUMO), an additional zero bias resonance appears in the spectra (Fig. 2c-d), but not if the molecule at zero bias is in its neutral state (Fig. 2b-c). As opposed to the charging resonances, this zero bias resonance does not shift for varying tip heights (Fig. S2b) and is a manifestation of the Kondo effect associated with the spin 1/2 of the molecule as a single electron occupies its gas-phase LUMO.[41,42] This is confirmed by its anomalously fast broadening with temperature, whose width evolution is in agreement with a Kondo temperature of 73±2 K (Fig. S4). The presence of this Kondo resonance is further proof of the decoupling effect that the “pentacene functionalization” at C-2 and C-3 with sp^3 carbon atoms brings about. If that were not the case, a broader LUMO level and reduced electron correlations would cause an equal population of spin up and spin down LUMO orbitals,[36,37] resulting in no net spin and no Kondo peak, as occurs with pristine pentacene.[35] On the other hand, the Kondo resonance still implies a minor molecule-substrate coupling, since it relates to the screening of the molecular spin by the substrate electrons and would thus be absent for a more efficient decoupling as observed for pentacene on an insulating MgO buffer layer. We can thus conclude that on Ag(001) the “pentacene functionalization” by sp^3 carbon atoms results in sufficiently decoupled molecules to show charging resonances and stabilize a singly charged molecule with net spin 1/2, but with sufficient molecule-substrate interaction to

reveal a Kondo resonance. In other words, more decoupled than pristine pentacene on Ag(001) but, as could be expected, less than pentacene on a MgO bilayer on Ag(001).”

REVIEWERS' COMMENTS:

Reviewer #2 (Remarks to the Author):

The authors addressed each of my points and gave the satisfied reply. Concerning the decoupling, there is one interesting recent publication by Liu et al, which is not included: JPCL, 2019, 10, 15, 4297. Otherwise I do not see any needs for further necessary modifications.

Reviewer #3 (Remarks to the Author):

The new version of the manuscript addresses my concerns in a convincing way. Descprition of results and interpretation as well as references to related published work has been improved significantly.
Based on the new version, I can suggest publication in Communications Physics. There remain, however, a significant number of typing errors in an otherwise well written manuscript.