nature portfolio

Peer Review File

Modulation of triplet quantum coherence by guest-induced structural changes in a flexible metal-organic framework

Editorial Note: This manuscript has been previously reviewed at another journal. This document only contains reviewer comments and rebuttal letters for versions considered at Nature Communications.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The present manuscript prepared by Akio Yamauchi et al. investigates the use of photoexcited triplets qubit generated in qubit-MOF platform for quantum sensing application. The chosen qubit-MOF architecture is based on introducing DAT into the well known metal-organic platform MIL-53. In the next step, authors added different guest analytes to qubit-MOF and observed the coherence time (T1 and T2) of the photoexcited qubit. Due to the presence of different analytes in MOF pore, MOF itself undergoes molecular changes which will impact the coherence of triplet qubit. As molecular qubits have fragile coherence, owing to inevitable interaction with the environment, they used these coherences in their favor for quantum sensing application. The main findings are presented in Fig.2., where the change in the volume of MOF due to the guest analyte vs coherence time (T2).

Recently, molecular spin-qubit has gained huge interest from the scientific community, because their properties can be easily tuned and manipulated. Overall, the present work is solid, and the manuscript is well written and also presents a new scheme of using photoexcited triplet qubit for quantum sensing application. Also, authors have satisfactory replied to concerns raised by reviewer #1 & reviewer #2 with additional explanation and evidence. Thus I support the publication in nature communication with no further reviewing round.

However, I just have a little curiosity if authors could clarify in their manuscript.

1- Due to the introduction of guest analyte, there is rearrangement of molecular geometry, which can change the electronic properties such as dipole. Is there any correlation between guest analyte they added and host qubit-MOF?

2- As authors operate at room temperature, there will be an abundance of activated optical and acoustic phonon density of states. Can they comment on which type of phonon are critical to coherences (T1 and T2)?

3- If we read 1- and 2- together, can we draw a general conclusion for enhanced quantum sensing applications, like charge-lattice correlation?

Reviewer #2 (Remarks to the Author):

In this manuscript, the authors infiltrated photoexcited triplet molecules (DAT) into a metal-organic framework (MIL-53) and investigated the influence of adsorbed organic guests on the electron spin decoherence time (T2) of DAT. They observed that some adsorbents, such as tetrahydrofuran and pyridine, significantly improves T2. Such improvement shows positive correlation with the guest accessible pore volume of MIL-53. This is an interesting spin dynamic study exploring the interplay between infiltrated triplets, porous materials, and adsorbed guest molecules. The authors have addressed some concerns raised by previous reviewers. Nonetheless, the theme of this manuscript, "quantum chemical sensing", is plausible and stretched, and the mechanism of coherence variation is not clear. Thus, I cannot support publishing this manuscript on Nat. Commun. and suggest the authors to tweak the theme towards the structure-property relationship of spin coherence in this MOF-triplet system. Please find my detailed comments below.

Major comments:

1. Although this work harnesses the quantum coherence to detect molecules such that it may be qualified remotely as a prototypical demonstration of quantum sensing, it fails to establish "chemical sensing". A chemical sensor should be able to analyze chemicals qualitatively and quantitatively, and its sensitivity, precision, and selectivity (or better, specificity) should be evaluated. This work does not discuss quantitative analysis nor its associated sensitivity or precision. It vaguely demonstrates qualitative analysis with low selectivity. As shown in Fig. 2b, isopropanol and deuterated toluene give similar T2. So do tetrahydrofuran and pyridine. At least with this system itself, one cannot distinguish these pairs of organic molecules. Putting together, it is a stretch to call this MOF-triplet system as a chemical sensor. I suggest the authors to address at least sensitivity and selectivity:

a) Sensitivity: This can be acquired by controlling the amount of analytes loaded into the MOF and

examine its influence on T2.
b) Selectivity: The authors should determine the selectivity for different functional groups (e.g. alcohol vs. ketone) and then for different molecules with the same functional group (e.g. ethanol vs isopropanol).

2. The authors should articulate the advantage of relaxometric sensing in terms of sensitivity, precision, and specificity, especially compared with well-established optical, electrochemical, and chemiresistive sensing strategies.

3. As pointed out by a previous reviewer, another paper on MOF-based quantum sensing (J. Am. Chem. Soc. 2022, 144, 19008) has already demonstrated quantitative ionic sensing with specificity (and somewhat low sensitivity) based on hyperfine spectroscopy. That paper also shows relaxometric responses of the MOF to organic molecules at room temperature, where tetrahydrofuran improves both spin relaxation time (T1) and T2 of embedded organic radicals. The authors counter-argued that the previous paper on J. Am. Chem. Soc. cannot distinguish molecules containing the same nuclear spin, but their system can. As discussed in the last comment, this argument is not supported by their experimental data. There is another relevant paper published last year, which uses infiltrated paramagnetic molecules in MOFs to quantitatively analyze gaseous molecules with CW EPR (Nat. Commun. 2023, 14, 4922). These reports undermine the novelty of this work.

4. The structure-property relationship of spin coherence in this MOF-triplet system is not clear. The authors attributed the coherence improvement to pore filling, which is not sufficiently insightful. On one hand, decoherence is ultimately caused by spin-spin coupling and/or spin-phonon coupling. How does pore filling influence these two types of interactions? On the other hand, the authors did not explain why different molecules exhibit different pore filling. Given a new organic molecule, how does one predict if it would improve or reduce T2?

5. Related to the last comment, there are many factors affecting T2, such as nuclear spins, flip-flop caused by motion, tumbling, and spin relaxation. The authors should elaborate which factor is the most relevant.
a) Nuclear spin: The authors introduced analytes into the MOF through several different methods (Page 11). This may cause different loading of analytes, so the density of nuclear species and their distances to the triplet cannot be compared. Therefore, the authors should determine the loading of guest molecules.
b) Motion: This may be revealed by comparing the influence on T2 from different analytes with methyl groups.
c) Tumbling: This may be revealed by studying the influence of solvent viscosity on T2.
d) Spin relaxation: This may be essential as T2 of organic radicals is usually limited by T1 at room temperature.

Minor comments:
6. In P2, line 59, the authors claimed that achieving microsecond-scale room-temperature T2 is challenging for molecular qubits. This is not true. There are tens of organic radicals, especially triphenylmethyl radicals and nitroxide radicals and their derivatives, that exhibit T2 exceeding 1 microsecond or even 10 microseconds at room temperature. See examples in J. Magn. Reason. 2001, 152, 16. These radicals have rarely been called "molecular qubits" possibly due to historical reasons, but they indeed behave as qubits.

7. The authors need to measure the T2 of DAT in the solvent listed in Figure 1c to demonstrate the benefit of infiltrating DAT into MIL-53.

8. The authors need to explain how they chose the analytes listed in Figure 1c.

9. In P4, line 138, why was the standard curve in Figure S2 tested at different conditions from Ref. 44? Additionally, the authors should add the value of D-MIL-53⊃DAT to Figure S2.

10. In P6, line 193, the authors need to add UV-vis spectrum of MIL-53 to reveal the contribution of DAT.

11. In P6, line 206, the authors need to clearly label the data points in Figure S8. This figure is difficult to understand.

Reviewer #3 (Remarks to the Author):

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

Reviewer #1 (Comments for the Author):

The present manuscript prepared by Akio Yamauchi et al. investigates the use of photoexcited triplets qubit generated in qubit-MOF platform for quantum sensing application. The chosen qubit-MOF architecture is based on introducing DAT into the well known metal-organic platform MIL-53. In the next step, authors added different guest analytes to qubit-MOF and observed the coherence time (T1 and T2) of the photoexcited qubit. Due to the presence of different analytes in MOF pore, MOF itself undergoes molecular changes which will impact the coherence of triplet qubit. As molecular qubits have fragile coherence, owing to inevitable interaction with the environment, they used these coherences in their favor for quantum sensing application. The main findings are presented in Fig.2., where the change in the volume of MOF due to the guest analyte vs coherence time (T2).

Recently, molecular spin-qubit has gained huge interest from the scientific community, because their properties can be easily tuned and manipulated. Overall, the present work is solid, and the manuscript is well written and also presents a new scheme of using photoexcited triplet qubit for quantum sensing application. Also, authors have satisfactory replied to concerns raised by reviewer #1 & reviewer #2 with additional explanation and evidence. Thus I support the publication in nature communication with no further reviewing round.

Response: We appreciate that you highly evaluated our work and found suitable for publication in *Nature Communications*.

However, I just have a little curiosity if authors could clarify in their manuscript.

1- Due to the introduction of guest analyte, there is rearrangement of molecular geometry, which can change the electronic properties such as dipole. Is there any correlation between guest analyte they added and host qubit-MOF?

Response: Thank you for your insightful comments. The UV-vis absorption spectra showed no significant change before and after the guest introduction (Fig. S5). We also plotted the T_2 of D-MIL-53⊃[DAT + guest] samples against the dielectric constants of the guests (Fig. S6), but we did not find any correlation. Therefore, we conclude that the electronic interaction between DAT and the guest molecules does not have significant role in our systems.

2- As authors operate at room temperature, there will be an abundance of activated optical and acoustic phonon density of states. Can they comment on which type of phonon are critical to coherences (T1 and T2)?

Response: Thank you for your comments. T_2 was much longer than T_1, so the relaxation would be mainly caused by the fluctuations of interspin interactions such as zero-field splitting or hyperfine coupling rather than interaction with the lattice (and the phonon).

Action: we added the description and table S3 in SI.

3- If we read 1- and 2- together, can we draw a general conclusion for enhanced quantum sensing applications, like charge-lattice correlation?

Response: Thank you for your suggestion. From the results, it is indicated that the mobility of DAT qubit is most important. If we can construct the system that induce more change in the qubit mobility, by introducing the interacting point to the specific analytes or alternating the size of the pore, it will bring larger T_2 difference and improve the sensitivity.

Reviewer #2 (Remarks to the Author):

In this manuscript, the authors infiltrated photoexcited triplet molecules (DAT) into a metal-organic framework (MIL-53) and investigated the influence of adsorbed organic guests on the electron spin decoherence time (T2) of DAT. They observed that some adsorbents, such as tetrahydrofuran and pyridine, significantly improves T2. Such improvement shows positive correlation with the guest accessible pore volume of MIL-53. This is an interesting spin dynamic study exploring the interplay between infiltrated triplets, porous materials, and adsorbed guest molecules. The authors have addressed some concerns raised by previous reviewers. Nonetheless, the theme of this manuscript, “quantum chemical sensing”, is plausible and stretched, and the mechanism of coherence variation is not clear. Thus, I cannot support publishing this manuscript on Nat. Commun. and suggest the authors to tweak the theme towards the structure-property relationship of spin coherence in this MOF-triplet system. Please find my detailed comments below.

Response: We appreciate your comments. Following your suggestion, we tweaked the theme to “guest-responsive quantum coherence toward future quantum chemical sensing”, and not to claim this work itself to “quantum chemical sensing”. However, we’d like to emphasize that while previous molecular quantum sensing relies on direct spin-spin interaction like hyperfine coupling, our strategy is utilization of the changes in molecular mobilities brought by the guest molecules. Previously, molecular motions have been just considered as obstacle since they can be a harsh relaxation source especially at room temperature, but we showed that they can be even useful for creating the response of quantum coherence. This is a significance of our work and lays the new foundation for future quantum sensing.

Action: we removed the word “quantum chemical sensing” from the title and modified it as “Modulation of triplet quantum coherence by guest-induced structural changes in a flexible metal-organic framework”. We also modified the description throughout the manuscript, such as line 25 in page 2, line 75 in page 3, line 99-101 in page 3, and line 308 in page 9.

Major comments:

1. Although this work harnesses the quantum coherence to detect molecules such that it may be qualified remotely as a prototypical demonstration of quantum sensing, it fails to establish “chemical sensing”. A chemical sensor should be able to analyze chemicals qualitatively and quantitatively, and its sensitivity, precision, and selectivity (or better, specificity) should be evaluated. This work does not discuss quantitative analysis nor its associated sensitivity or precision. It vaguely demonstrates qualitative analysis with low selectivity. As shown in Fig. 2b, isopropanol and deuterated toluene give similar T2. So do tetrahydrofuran and pyridine. At least with this system itself, one cannot distinguish these pairs of organic molecules. Putting together, it is a stretch to call this MOF-triplet system as a chemical sensor. I suggest the authors to address at least sensitivity and selectivity:

a) Sensitivity: This can be acquired by controlling the amount of analytes loaded into the MOF and examine its influence on T2.

b) Selectivity: The authors should determine the selectivity for different functional groups (e.g. alcohol vs. ketone) and then for different molecules with the same functional group (e.g. ethanol vs isopropanol).

Response: We appreciate your important comments. As mentioned above, we have reconsidered the main theme of this paper from chemical quantum sensing to guest-responsive quantum coherence in accordance with your suggestion. It is extremely important to first establish the response mechanism that will serve as the basis for future quantum sensing. We have shown in this study that not only the previous direct spin-spin interactions but also the mobility of the qubit is an important parameter. This is expected to make it possible to indirectly distinguish analytes that could not be distinguished by direct interactions alone. We agree with your point that sensitivity and selectivity should be clarified in order to claim quantum sensing, but the main focus of this paper has shifted from quantum sensing to more fundamental quantum coherence response, and these points are now beyond the scope of this paper. Our current experimental setup does not allow us to control the amount of analytes, but it is very important to make such a setup in the future to measure the dependence of T_2 on the guest amount. MOFs modified with various substituents have been reported, and using these MOFs would improve the selectivity of guest uptake. Even if a single material does not give sufficient selectivity, selective analyte detection will be possible in the future by arraying many combinations of MOFs and qubits and recognizing the pattern of response obtained.

2. The authors should articulate the advantage of relaxometric sensing in terms of sensitivity, precision, and specificity, especially compared with well-established optical, electrochemical, and chemiresistive sensing strategies.

Response: We appreciate your important remarks. As reported in the past quantum sensing of Li ions with inferior detection limits compared to optical and electrochemical sensing (L. Sun et al., *J. Am. Chem. Soc.* **2022**, *144*, 19008), improving the sensitivity of quantum sensing is an important issue for the entire field. We used relaxometry to study the effect of guest adsorption on quantum coherence, but in principle other sensing protocols using more advanced pulse sequences could also be applied. In particular, a dramatic improvement in sensitivity can be expected by using visible light detection instead of microwaves. Recently, optically detected magnetic resonance (ODMR) using pentacene doped in dense molecular crystals has been reported (A. Mena et al., arXiv:2402.07572; H. Singh et al, arXiv:2402.13898). On the other hand, our system uses photoexcited triplets as qubits, which are highly compatible with ODMR. Although beyond the scope of this report, the sensitivity is expected to be greatly improved by using ODMR detection.

Action: we added the description in page 10, line 327-329.

3. As pointed out by a previous reviewer, another paper on MOF-based quantum sensing (J. Am. Chem. Soc. 2022, 144, 19008) has already demonstrated quantitative ionic sensing with specificity (and somewhat low sensitivity) based on hyperfine spectroscopy. That paper also shows relaxometric responses of the MOF to organic molecules at room temperature, where tetrahydrofuran improves both spin relaxation time (T1) and T2 of embedded organic radicals. The authors counter-argued that the previous paper on J. Am. Chem. Soc. cannot distinguish molecules containing the same nuclear spin, but their system can. As discussed in the last comment, this argument is not supported by their experimental data. There is another relevant paper published last year, which uses infiltrated paramagnetic molecules in MOFs to quantitatively analyze gaseous molecules with CW EPR (Nat. Commun. 2023, 14, 4922). These reports undermine the novelty of this work.

Response: In the paper on MOF-based quantum sensing of Li ions (*J. Am. Chem. Soc.* **2022**, *144*, 19008), the authors stated that the identification of nuclear species is possible, but they did not mention whether the identification of chemicals consisted of same nuclear species is possible. For Li^+ sensing, the strength of hyperfine coupling of ^7Li are almost same for $LiClO_4$-THF, LiCl-THF, and LiBr-THF (Fig. S24), and they cannot distinguish these chemicals from hyperfine coupling. The ESEEM peak ratio of $^7Li/^1H$ are different for each chemical, but they cannot determine the species without information of concentration. It is true that the solvent

THF lengthened the memory time T_m of the radicals in MOF as you point out in the Supporting Information of the JACS paper, but the authors did not relate that phenomenon to quantum sensing that distinguishes THF from other solvents. In other words, the response of different coherence times to various molecules is a novel point made by our paper. In addition, the system in the JACS paper was not designed to respond to guest molecules, so the rate of change of T_m with THF was small, 132% from 153 ns to 202 ns. On the other hand, our system using the flexible MOF was designed to focus on the response to guest molecules, and the introduction of THF resulted in a 600% change in T_2 from 0.1 μs to 0.6 μs, and a large 1000% change from 0.1 μs to 1.0 μs for FU and BQ. Our report provides a clear demonstration of the new concept of indirect guest molecule detection through changes in qubit mobility, which is both novel and advantageous.

As for another paper you mentioned (*Nat. Commun.* **2023**, *14*, 4922), we'd like to note that our manuscript was first made public in *ChemRxiv* (DOI: 10.26434/chemrxiv-2022-4hnsj) and submitted to *Nat. Chem.* in August 2022, and then transferred to *Nat. Commun.* According to the spirit of *ChemRxiv* and other archive services, the priority and precedence of a discovery should be judged based on the first publication in archive systems. Our publication in *ChemRxiv* was done 1 year before the publication of the *Nat. Commun.* paper. In addition, according to the editors of *Nat. Commun.*, they will not consider any similar papers published independently in the meantime to compromise the novelty of the study. Therefore, the novelty of our finding should not be affected by that particular paper.

4. The structure-property relationship of spin coherence in this MOF-triplet system is not clear. The authors attributed the coherence improvement to pore filling, which is not sufficiently insightful. On one hand, decoherence is ultimately caused by spin-spin coupling and/or spin-phonon coupling. How does pore filling influence these two types of interactions? On the other hand, the authors did not explain why different molecules exhibit different pore filling. Given a new organic molecule, how does one predict if it would improve or reduce T2?

Response: The relationship between T_2 and each relaxation factors is written as follows (*J. Am. Chem. Soc.* **2022**, *144*, 19008):

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_{ee}} + \frac{1}{T_{en}}$$

where T_{ee} and T_{en} were relaxation from dipolar interaction between electron spins and from hyperfine coupling between electron spin and surrounding nuclear spins, respectively. Since the T_1 of our systems were around one magnitude longer than T_2, the spin-lattice relaxation and spin-phonon coupling would not have major role in relaxation. Indeed, for D-MIL-53⊃DAT (denoted as empty), T_2 and T_1 were 0.144 μs and 1.450 μs, respectively. Thus, the value of ($1/T_2 - 1/2T_1$), which reflects the effect of spin-spin coupling, was calculated as 6.60 μs^{-1} (Table S3). This is significantly different from the value for D-MIL-53⊃[DAT+BQ] of 0.90 μs^{-1} (T_2 = 0.999 μs, T_1 = 5.132 μs). Therefore, the effect of spin-spin coupling terms should be main factor for spin-spin relaxation.

Triplet electron spin has the dipolar interaction in the composing two spins, so-called zero-field splitting (ZFS). Since ZFS is anisotropic to magnetic field and can be fluctuated by the molecular motions, the change in the pore density can affects the relaxation rate by the suppression of the motions through steric hindrance of guests.

For the third term (hyperfine interaction), there are two types of nuclear spins with large gyromagnetic ratio (^{1}H, ^{19}F) in the system: spins on the guest molecules and OH protons attached to aluminum metals (the MOF ligands were deuterated and the spin on ^{1}H of deuterated ligands can be negligible). We plotted T_2 the number of ^{1}H and ^{19}F spins from guest analytes inside a unit cell (Fig. S14). If the nuclear spins of guest molecules are dominant to the relaxation, the T_2 should be shorter with the increase of the number of nuclear spins, but such behavior was not observed. Note that some guests with methyl groups like toluene might be exceptional because methyl protons can have significant effect for relaxation (Fig. S11, *h*-toluene vs *d*-toluene). The hyperfine coupling between the OH proton and DAT should also exist. While the hyperfine interaction would not be the dominant factor, the degree of fluctuation of hyperfine interaction can be weakened when the molecular motion of DAT is suppressed by guests.

Thus, the fluctuations of anisotropic ZFS parameters and hyperfine interactions due on the molecular motion of DAT would mainly contribute to the decoherence process. We concluded that these fluctuations that facilitate the relaxation were suppressed by the guest molecules that fill the pore and restrict the motions of DAT qubit as discussed in the manuscript.

It has been well understood and documented why different molecules exhibit different pore filling in MIL-53 (for example, ref 39-41 in the main manuscript), and we avoid to repeat the same discussion in the current manuscript. It is possible to estimate the pore filling for a given new guest by general methods such as X-ray structural analysis and adsorption isotherm measurements, and it should be possible in principle to predict T_2 from the relationship between T_2 and guest occupied volume obtained in this study.

Action: we added the discussion in SI (page 18).

5. Related to the last comment, there are many factors affecting T2, such as nuclear spins, flip-flop caused by motion, tumbling, and spin relaxation. The authors should elaborate which factor is the most relevant.

Response: As we discussed above, the fluctuations of anisotropic ZFS parameters and hyperfine interactions due on the molecular motion of DAT would be dominant for the decoherence process. These fluctuations were suppressed by the guest molecules that fill the pore and restrict the motions of DAT qubit.

a) Nuclear spin: The authors introduced analytes into the MOF through several different methods (Page 11). This may cause different loading of analytes, so the density of nuclear species and their distances to the triplet cannot be compared. Therefore, the authors should determine the loading of guest molecules.

Response: We have quantified the loading amount of each guest analytes by TGA results and summarized in Table S2 (as n_{guest}) in the original manuscript. MIL-53 changes its structure during guest adsorption, so we defined guest occupancy inside the pore as guest occupied volume to discuss the density of guests. We also calculated the density of ^{1}H and ^{19}F nuclear spins of guests from the loading amount (Fig. S14). As mentioned above, if the nuclear spins of guest molecules are dominant to the relaxation, the T_2 should be shorter with the increase of the number of nuclear spins, but such behavior was not observed.

b) Motion: This may be revealed by comparing the influence on T2 from different analytes with methyl groups.

c) Tumbling: This may be revealed by studying the influence of solvent viscosity on T2.

Response: As discussed above, two types of motions are considered as relaxation factors: motion of highly mobile functional groups like methyl group and motion of DAT itself (the reviewer probably call this as tumbling). In the presence of methyl group (like *h*-toluene, acetonitrile), T_2 became very short, but it became longer by deuteration of guest molecules. This result suggests that methyl rotation can be a dominant factor when it exists.

On the other hand, in the absence of methyl group, the motions of qubit itself would be important. The anisotropic ZFS interaction and hyperfine interaction are fluctuated because the orientation of DAT and the distance between DAT and nucleus including OH protons are modulated by DAT motions. According to the MD simulation results, the mobility of DAT in D-MIL-53⊃[DAT+BQ], which showed long T_2 around 1 μs and high guest occupancy, was suppressed than other systems (Fig. S16). Furthermore, longer T_2 was observed for DAT in D-MIL-53⊃DAT (empty) at low temperature and for DAT in rigid terphenyl crystal (Fig. S18). In both systems, the molecular motion of DAT was largely restricted. Therefore, we concluded that the motion of DAT qubit is the dominant factor for spin-spin relaxation (in the absence of methyl groups).

Note that it would be difficult to discuss the effect of solvent viscosity on T_2, because host-guest interactions are important in small subnanometer channels such as MIL-53, and the molecular mobility inferred from bulk viscosity may not hold in the pore. Instead of viscosity as a measure of bulk, we consider that the local density of guest molecules (guest occupied volume) is a better measure in the pore.

d) Spin relaxation: This may be essential as T2 of organic radicals is usually limited by T1 at room temperature.

Response: Since the T_1 of our systems were around one magnitude longer than T_2, T_1 does not dominate the decoherence process. As described in above, the value of ($1/T_2 - 1/2T_1$) was 6.60 μs^{-1} for empty D-MIL-53⊃DAT (T_2 = 0.144 μs, T_1 = 1.450 μs), this is almost same as the inverse of T_2 (6.94 μs^{-1}). For D-MIL-53⊃[DAT+BQ] (T_2 = 0.999 μs, T_1 = 5.132 μs), the value of ($1/T_2 - 1/2T_1$) was 0.90 μs^{-1}, also close to the $1/T_2$ of 1.00 μs^{-1} (Table S3).

The contributions of spin–lattice relaxation in T_2 were less than 12.8 % for all systems, indicating the spin–spin relaxation is not limited by spin–lattice relaxation.

Action: we added Table S3 in SI.

Table S3. Relationship between T_2, T_1 and other relaxation factors. The value of $1/T_2 - 1/2T_1$ indicates the contribution of other relaxation processes than spin–lattice relaxation.

Guest	T_2 (μs)^a	T_1 (μs)^a	$1/T_2$ (μs^{-1})	$1/2T_1$ (μs^{-1})	$1/T_2 - 1/2T_1$ (μs^{-1})	Contribution of spin–lattice relaxation in T_2 (%)^b
Empty	0.144	1.450	6.94	0.345	6.60	4.97
H_2O	0.156	3.935	6.41	0.127	6.28	1.98
PrOH	0.290	2.133	3.45	0.234	3.21	6.80
Py	0.564	3.886	1.77	0.129	1.64	7.26
FU	1.020	3.999	0.98	0.125	0.86	12.8
BQ	0.999	5.132	1.00	0.097	0.90	9.73
THF	0.648	3.160	1.54	0.158	1.38	10.3
$CHCl_3$	0.101	1.128	9.90	0.443	9.46	4.48
EtAc	0.104	1.548	9.62	0.323	9.29	3.36
h-Tol	< 0.1	2.986	> 10	0.167	> 9.83	< 1.67
EtOH	< 0.1	1.047	> 10	0.478	> 9.52	< 4.78
AcNt	< 0.1	0.978	> 10	0.511	> 9.49	< 5.11

a: the values in lower magnetic field were used.

b: calculated from ($1/2T_1$) / ($1/T_2$) = T_2 / $2T_1$.

Minor comments:

6. In P2, line 59, the authors claimed that achieving microsecond-scale room-temperature T2 is challenging for molecular qubits. This is not true. There are tens of organic radicals, especially triphenylmethyl radicals and nitroxide radicals and their derivatives, that exhibit T2 exceeding 1 microsecond or even 10 microseconds at room temperature. See examples in J. Magn. Reason. 2001, 152, 16. These radicals have rarely been called “molecular qubits” possibly due to historical reasons, but they indeed behave as qubits.

Response: Thank you for your kind suggestion. Following your suggestion, we modified the description. We’d like to note that T_2 more than 1 μs is still rare for “spin-polarized” systems, and triplet spin polarization can be useful for the future sensitive optical detection using ODMR.

Action: we added the description in page 2, line 58-59.

7. The authors need to measure the T2 of DAT in the solvent listed in Figure 1c to demonstrate the benefit of infiltrating DAT into MIL-53.

Response: Thank you for your suggestion. It is well known that ESR measurements of photoexcited triplet states in solution are difficult (J. Fujisawa et al., *J. Am. Chem. Soc.* **1997**, *119*, 8736-8737). Measurement of T_2 would be impossible because the fluctuations in the ZFS interaction associated with molecular rotation induce pronounced spin relaxation, shortening T_1 to a few hundred ns. On the other hand, motional narrowing, as seen in solution, does not occur in MOFs, and thus the incorporation of DAT into the MOF nanopores effectively limits its rotation.

Action: we added the description in page 6, line 202-205.

8. The authors need to explain how they chose the analytes listed in Figure 1c.

Response: Thank you for pointing out. Based on previous reports on MIL-53, guest molecules were selected to cover as wide a range of MIL-53 unit cell volumes as possible. In addition, for liquid guests, we selected those with boiling points high enough not to be evacuated during sample preparation and not too high to be introduced by vapor diffusion. For solid guests, we chose those that could be introduced by sublimation.

Action: we added the description in page 4, line 140-144.

9. In P4, line 138, why was the standard curve in Figure S2 tested at different conditions from Ref. 44? Additionally, the authors should add the value of D-MIL-53⊃DAT to Figure S2.

Response: Thank you for your comment. We selected this condition to obtain more accurate plots. We considered that the higher concentration and shorter optical path length will reduce experimental error. We used the absorbance at 475 nm since this peak showed the strongest signal. We also added the value of D-MIL-53⊃DAT in the modified Figure S2.

Action: we added the data and caption in Fig. S2.

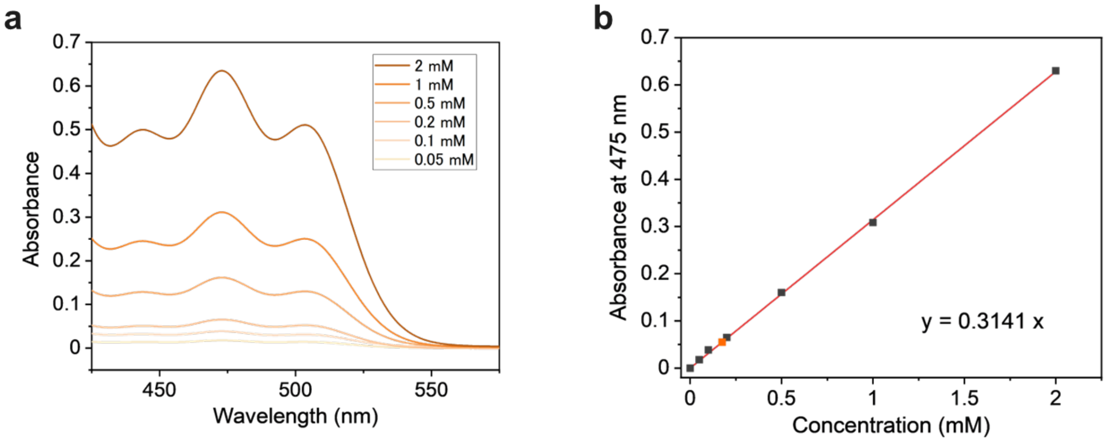

Fig. S2. **a**, UV-vis absorption spectra of a series of DAT standard dichloromethane solutions (0.05, 0.1, 0.2, 0.5, 1, 2 mM). **b**, The calibration line obtained from the absorbance of DAT dichloromethane solutions (0.05 mM, 0.1 mM, 0.2 mM, 0.5 mM, 1 mM and 2 mM) at 475 nm using 1 mm quartz cell. The absorbance at 475 nm was 0.055 when 20.0 mg of D-MIL-53⊃[DAT + H_2O] was digested to 4 mL dichloromethane solution (shown as orange dot). From the calibration curve, the concentration of DAT in the solution was calculated to be 0.175 mM.

10. In P6, line 193, the authors need to add UV-vis spectrum of MIL-53 to reveal the contribution of DAT.

Response: Thank you for your suggestion. We added the UV-vis spectrum of MIL-53. MIL-53 does not have the absorption in the visible range thus its absorption does not affect the results.

Action: we added the data in Fig. S4.

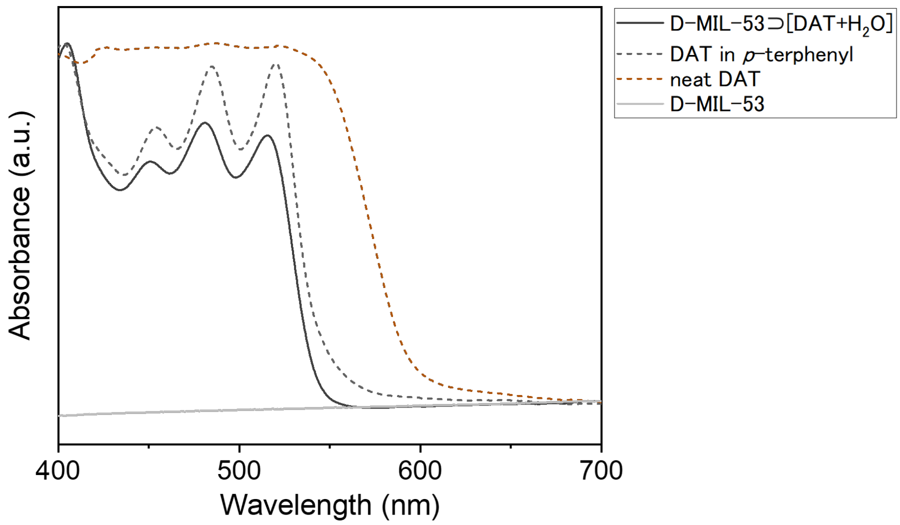

Fig. S4. UV-vis absorption spectra of D-MIL-53⊃DAT with H_2O (black line), 0.1 mol% DAT doped in *p*-terphenyl crystal (gray dot line), neat DAT (brown dot line), and D-MIL-53 (gray solid line).

11. In P6, line 206, the authors need to clearly label the data points in Figure S8. This figure is difficult to understand.

Response: Thank you for your kind suggestion. We added the label for Fig. S8, Fig. S12, Fig. S13, and Fig. S14. We also added the description for Fig. S14 to clarify which nuclear spins are considered.

Action: we added the label for Fig. S8, Fig. S12, Fig. S13, and Fig. S14.

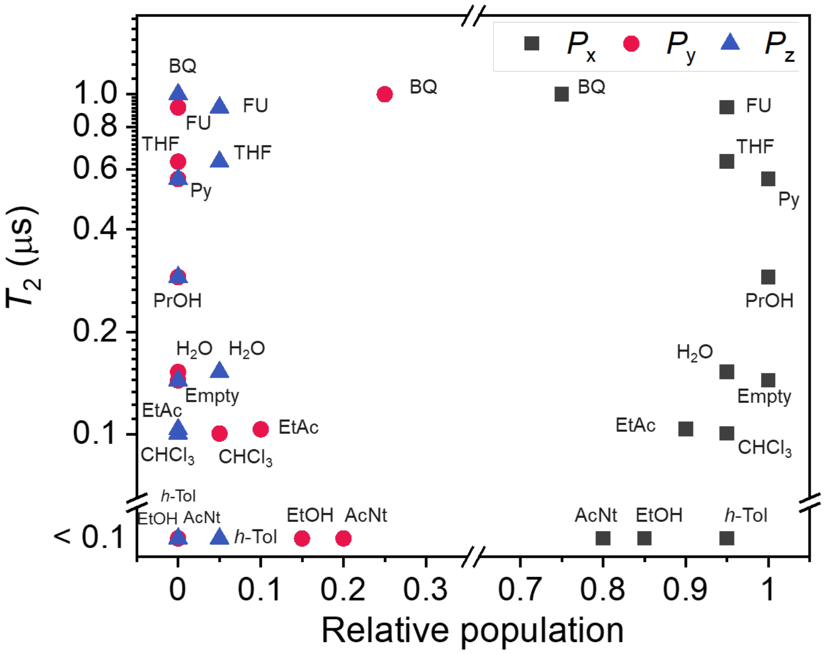

Fig. S8. Plot of T_2 against relative populations ($P_x : P_y : P_z$) of empty (D-MIL-53⊃DAT) and guest-filled (D-MIL-53⊃[DAT + guest]) samples.

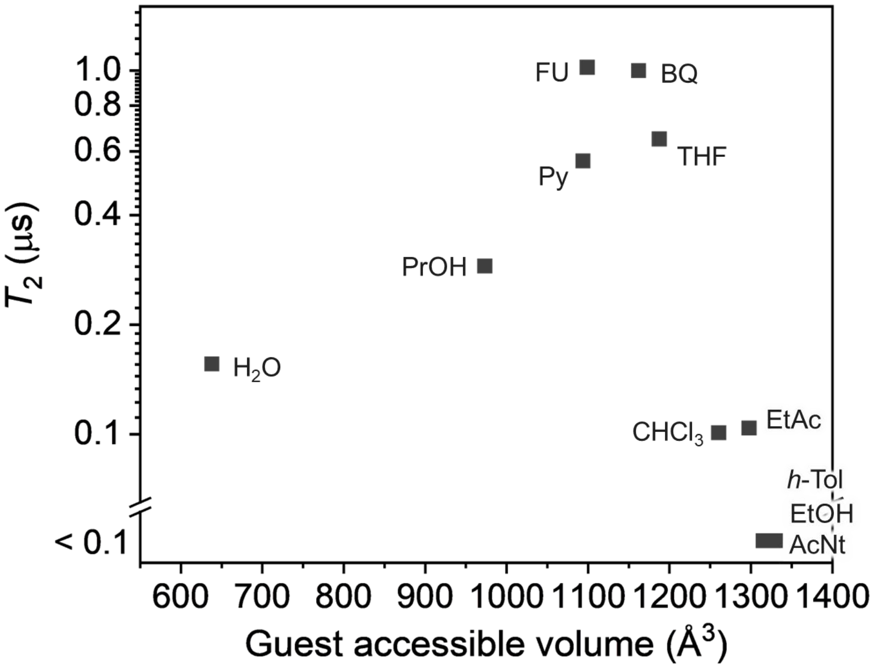

Fig. S12. Plot of T_2 against guest accessible pore volume (V_{pore}) of empty (D-MIL-53⊃DAT) and guest-filled (D-MIL-53⊃[DAT + guest]) samples.

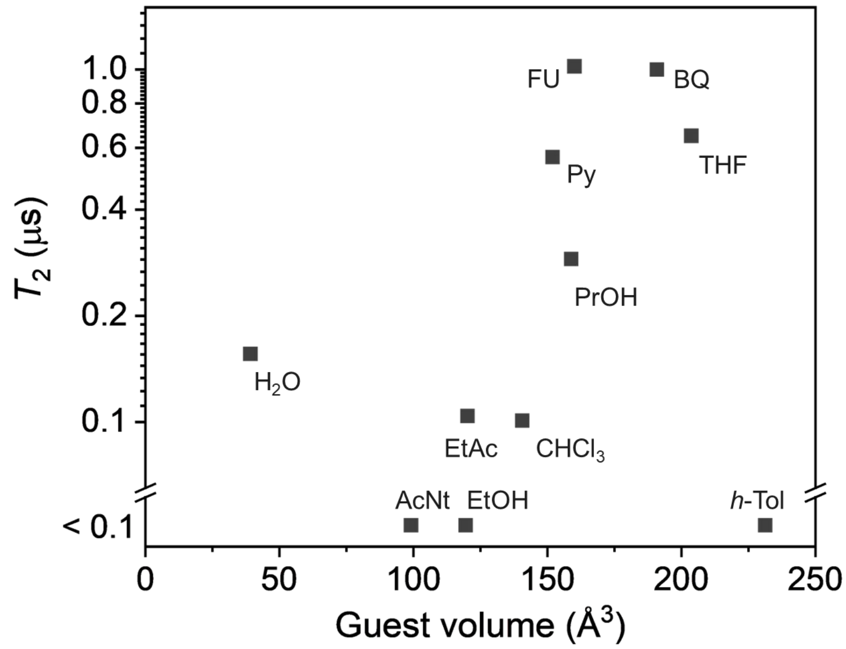

Fig. S13. Plot of T_2 against their guest volume (V_{guest}) of empty (D-MIL-53⊃DAT) and guest-filled (D-MIL-53⊃[DAT + guest]) samples.

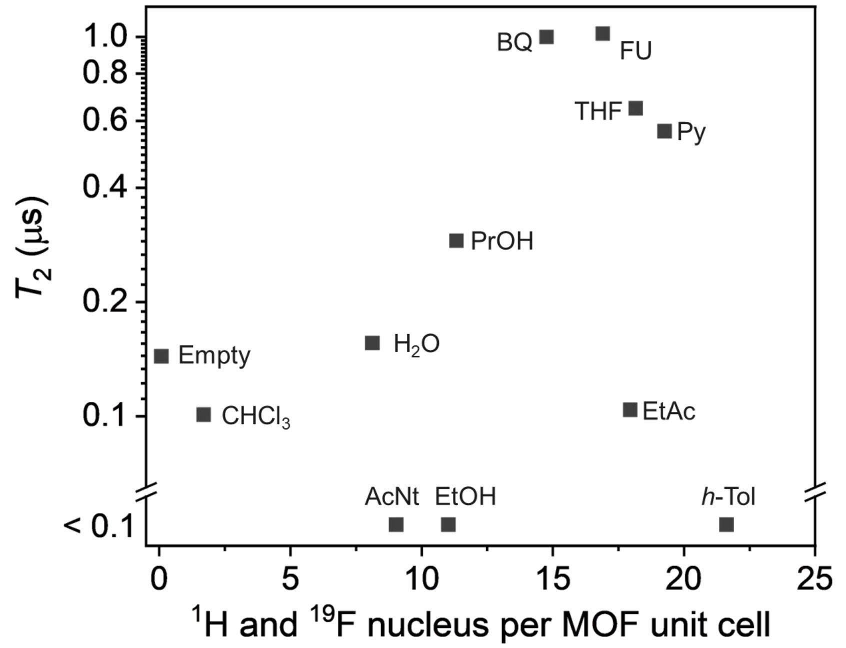

Fig. S14. Plot of T_2 against the number of ^{1}H and ^{19}F spins from guest analytes of empty (D-MIL-53⊃DAT) and guest-filled (D-MIL-53⊃[DAT + guest]) samples in a unit cell.

Reviewer #3 (Remarks to the Author):

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

Response: We’d appreciate your time and efforts for reviewing our manuscript.

REVIEWER COMMENTS

Reviewer #2 (Remarks to the Author):

In this revised manuscript, the authors have changed the title, added some data analysis, and addressed some of the reviewers' comments. Nonetheless, the manuscript still shows several flaws that render its current form disqualified for publishing on Nature Communications.

1. The authors have changed the theme of this manuscript to guest-induced changes in the decoherence time of organic triplets. This is much more reasonable than the previous concept of "quantum chemical sensing". However, the abstract and the introduction still focus on quantum sensing, which makes the reading experience disjointed. I suggest the authors to rewrite the introduction such that, in addition to discussing quantum sensing, it highlights more fundamental sides of coherence modulation in molecular systems. For instance, what are known mechanisms and strategies for coherence modulation? How would guests influence triplet coherence in principle? How would coherence modulation reveal host-guest interaction? Without introducing these key background, it would be difficult for readers to follow the theme of this manuscript.

2. The authors propose that the "mobility" or "motion" of the triplet plays a key role in guest-induced coherence modulation. However, the phenomenon that they described is indeed the "molecular tumbling": they attributed the main decoherence source to "the fluctuations of anisotropic ZFS parameters and hyperfine interactions" (Page 18 of the supplementary information), which is a signature of relaxation caused by molecular tumbling. I do not see the need to reinvent the terminology for triplets trapped in MOFs.

3. In the response to my 4th comment and in the Page 18 of the Supplementary Information, the authors state that "the effect of spin-spin coupling terms should be main factor of spin-spin relaxation". Nonetheless, in Page 5 Lines 166-167, they claim that "interactions between electron spins could be ignored". Which one is correct?

4. According to the Table S3 in the Supplementary Information, there seems a positive relationship between T1 and T2 (H2O is an exception). This is an interesting phenomenon, which may indicate that T2 is affected by spin-lattice relaxation. The authors should explain this relationship.

5. In Figure S5, the UV-vis absorption spectrum of THF-treated material is different from others. Does it infer that THF causes changes in molecular structure of DAT?

Reviewer #3 (Remarks to the Author):

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

Reviewer #2 (Remarks to the Author):

In this revised manuscript, the authors have changed the title, added some data analysis, and addressed some of the reviewers' comments. Nonetheless, the manuscript still shows several flaws that render its current form disqualified for publishing on Nature Communications.

Response: We appreciate your positive comments and constructive suggestions. We appreciate this opportunity to further improve the quality of our manuscript. We have modified the manuscript accordingly to your comments.

1. The authors have changed the theme of this manuscript to guest-induced changes in the decoherence time of organic triplets. This is much more reasonable than the previous concept of "quantum chemical sensing". However, the abstract and the introduction still focus on quantum sensing, which makes the reading experience disjointed. I suggest the authors to rewrite the introduction such that, in addition to discussing quantum sensing, it highlights more fundamental sides of coherence modulation in molecular systems. For instance, what are known mechanisms and strategies for coherence modulation? How would guests influence triplet coherence in principle? How would coherence modulation reveal host-guest interaction? Without introducing these key background, it would be difficult for readers to follow the theme of this manuscript.

Response: We appreciate your important suggestion. We totally agree with your opinion and have modified the abstract and the introduction accordingly.

In general, the coherence time T_2 depends on several factors such as the motion of qubit itself and surrounding spins. The motion of the qubit changes the orientation of the molecule relative to the external magnetic field, and since the g factor is usually anisotropic, the interaction with the magnetic field is perturbed, causing relaxation. Other sources of relaxation are the surrounding electron and nuclear spins. In particular, nuclear motion in the surrounding molecules causes fluctuation in the local magnetic field, leading to relaxation. Relaxometry can be a powerful method to detect target analytes based on these mechanisms. However, since qubits exposed in the nanopores of MOFs and COFs can undergo significant relaxation from the motion of the qubit itself, it is necessary to design the environment around the qubit appropriately to have a sufficiently long T_2.

As with other paramagnetic qubits, the response of triplet qubits to target analytes based on hyperfine spectroscopy and relaxometry is expected. Characteristic of triplets is that they have an anisotropic and large (~GHz) zero-field splitting (ZFS) interaction, so that the molecular motion of the qubit causes a pronounced relaxation based on orientation change with respect to the magnetic field. Therefore, when target analytes are incorporated into the nanopores and the environment around the qubit changes, it is expected that the changes can be sensitively captured through relaxometry.

Action: we have added these explanations in line 21, 57-75, 88-94.

2. The authors propose that the "mobility" or "motion" of the triplet plays a key role in guest-induced coherence modulation. However, the phenomenon that they described is indeed the "molecular tumbling": they attributed the main decoherence source to "the fluctuations of anisotropic ZFS parameters and hyperfine interactions" (Page 18 of the supplementary information), which is a signature of relaxation caused by molecular tumbling. I do not see the need to reinvent the terminology for triplets trapped in MOFs.

Response: Thank you for your kind suggestion. As you pointed out, the fluctuation of anisotropic ZFS parameters were partly caused by the tumbling motion of DAT, so we modified the terminology where appropriate. In this system, however, not only the tumbling motion but also the translational motion of DAT can modify the hyperfine interactions and thus be the source of relaxation, and both of these motions are suppressed by the guest introduction. Therefore, we chose the term “motion” to cover the different type of modes.

Action: we modified the description in line 287 of the main text and page 18 of SI.

3. In the response to my 4th comment and in the Page 18 of the Supplementary Information, the authors state that "the effect of spin-spin coupling terms should be main factor of spin-spin relaxation". Nonetheless, in Page 5 Lines 166-167, they claim that "interactions between electron spins could be ignored". Which one is correct?

Response: Thank you for pointing this out. The wording was misleading and has been corrected. The spin–spin interaction of electron spins contains two types of interactions: (i) intramolecular interaction and (ii) intermolecular interaction. The former one is an interaction between electron spins within a single DAT triplet. Because DAT triplet contains two electron spins, these spins make anisotropic ZFS interaction each other. The latter one is an interaction between triplets in different DAT molecules, and we discussed about this interaction in page 5. We evaluated the effect of intermolecular spin–spin coupling by changing the laser power to lower concentration of DAT triplets, and the effect seemed small since there were no significant difference in T_2.

Action: we added the description in line 171 of the main text and page 18 of SI.

4. According to the Table S3 in the Supplementary Information, there seems a positive relationship between T1 and T2 (H2O is an exception). This is an interesting phenomenon, which may indicate that T2 is affected by spin-lattice relaxation. The authors should explain

this relationship.

Response: Thank you for your important remarks. It is known that spin dipolar interaction between electron spins can affect T_1 as well as T_2 (S. Yamauchi et al., *J. Phys. Chem. A* **2003**, *107*, 1478-1485). Since the ZFS interactions induce these relaxations, the relaxation times can be altered when the molecular motion is suppressed. Therefore, the molecular motion of DAT would affect both T_1 and T_2. Although T_1 and T_2 are correlated in this system probably due to the similar origins, T_1 is much longer than T_2 and contribution of spin–lattice relaxation to spin–spin relaxation is less than 12.8 % (Table S3), and therefore T_2 should not be limited by spin–lattice relaxation.

Action: we added the discussion in SI (page 18-19).

5. In Figure S5, the UV-vis absorption spectrum of THF-treated material is different from others. Does it infer that THF causes changes in molecular structure of DAT?

Response: Thank you for your suggestion. We assume that you are mentioning about the dark green spectrum, which is the spectrum with BQ (*p*-benzoquinone) as a guest, not THF. As mentioned in the main text (line 199-200) and the caption of Figure S5, the additional broad absorption is due to the absorption of BQ. There are no significant changes in *D* and *E* values obtained from time-resolved EPR (Table S1), which indicates no significant electronic interaction between DAT and BQ.

Reviewer #3 (Remarks to the Author):

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

Response: We'd appreciate your time and efforts for reviewing our manuscript.

REVIEWERS' COMMENTS

Reviewer #2 (Remarks to the Author):

The authors have addressed my previous comments to satisfaction. I support its acceptance.

Reviewer #3 (Remarks to the Author):

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