

Peer Review File

Microsecond Triplet Emission from Organic Chromophore-Transition Metal Dichalcogenide Hybrids via Through-Space Spin Orbit Proximity Effect



Open Access This file is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. In the cases where the authors are anonymous, such as is the case for the reports of anonymous peer reviewers, author attribution should be to 'Anonymous Referee' followed by a clear attribution to the source work. The images or other third party material in this file are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

Reviewer #1 (Remarks to the Author):

In this work, the authors introduced a novel triplet emitter design strategy by building heterostructures of DDT with various transition metal dichalcogenides (TMDs), e.g., MoS₂, MoSe₂, WS₂, and WSe₂, and observed the TMDs-induced photophysical variations in DDT. DDT on TMDs emits bright green phosphorescence with a few tens of microsecond lifetimes at room temperature (RT). And the key structural features of TMDs and POPs were also been identified: 2H-lattice structures with heavy transition metal atoms in TMDs and aromatic carbonyl with an ortho hydroxy in POPs. The relaxation decays of POPs exhibiting slow phosphorescence can be largely improved through the through-space spin-orbit proximity effect of TMDs. The authors also explained the interaction between the POPs and the TMDs in a detailed analysis, however, the study of the luminescent properties of the system is still lacking. Some puzzling questions remain as following.

1. For scanning tunneling microscopy analysis, it is recommended to supplement the STM diagram of the control group MoS₂ without DDT.
2. Why is the maximum emission wavelength (470 nm) of DDT in Figure 1f red-shifted by almost 20 nm from that in Figure 1g (451 nm)?
3. How does the lifetime of DDT/MoS₂ change at 77K compared to the DDT? And to illustrate the lifetime of DDT/MoS₂ at 77K should be provided.
4. In Figure 4d, the phosphorescence lifetimes for DDTs on MoS₂, MoSe₂, WS₂, and WSe₂ decrease sequentially, but the lifetime of DDT/MoS₂ in Figure 4e is the lowest instead. Is it just because of the experimental error? These results should be as uniform as possible.
5. The DDT/MoS₂ aqueous suspension has a noticeable green phosphorescence. Do the other DDT/TMDs have a similar luminescent behavior in solution and PL spectra for suspension? And corresponding photos should be added if possible.
6. For Br6A/MoS₂, why is the phosphorescence lifetime of the Br6A crystal on MoS₂ (87 μ s) shorter than that of the Br6A overhang part (1.4 ms)?
7. In supporting information, the experiments show that "The crystal structures of DDT rely on the presence of MoS₂. SC-XRD analysis is performed to establish the crystal structure deformation of DDT via strong vdW interaction with MoS₂....." Therefore, the authors should explore whether the change of DDT crystal structure caused by MoS₂ is another major cause of ultrafast RTP emission.
8. In Figures S1 and S2, the scale bar need to be marked.

Reviewer #2 (Remarks to the Author):

Obtaining rapid and efficient phosphorescence from spin-triplet excited states in purely organic emitters is an interesting fundamental research problem to address and may have applications in OLEDs. In their work, authors explore the ability of TMDs to enable fast and efficient phosphorescence in heterostructures with small molecule organic semiconductor crystals, which appears to be achieved through a variation of the external heavy atom effect. Whilst the results are interesting, I have significant concerns about the interpretations the authors have made about their data, in particular the EPR. Furthermore, the external heavy atom effect is already well known and demonstrating it again here is not particularly novel. TMDs are a very 'trendy' research field at the moment, which, in my opinion, can make routine demonstrations of established concepts appear more impactful than they really are. Therefore, I would recommend that the authors revisit the interpretation of some of their experimental data, before resubmitting to a more specialised journal. Below, I have provided some comments that I hope will assist the authors with revising their manuscript.

1. In Fig. 3a, the authors show some Raman data for DDT and DDT on MoS₂, noting that a peak around 1350 cm⁻¹ is shifted in the MoS₂ sample. About this observation, they state:

'As for DDT, the peak at 1350 cm⁻¹ represents the vibration modes of aromatic carbonyl groups. Intriguingly in DDT/MoS₂, only this peak related to the carbonyl groups of DDT is shifted toward a lower frequency at 1330 cm⁻¹, while no shift is observed in other Raman modes. The red-shifted Raman mode of carbonyl groups indicates energy loss of phonons and an altered electronic

structure of carbonyl groups of DDT on MoS₂, indicating a strong interaction between the carbonyl of DDT and MoS₂.

This interpretation is incorrect: carbonyl stretches are almost always located between 1650-1750 cm⁻¹, which is nowhere near the 1350 cm⁻¹ mode referred to by the authors. 1350 cm⁻¹ is around the 'fingerprint' region of a molecule, which is likely related to C-C or C-O (single bond) stretches. Thus, a shift in a mode at 1350 cm⁻¹ is not related to a carbonyl ground and therefore does not provide experimental evidence that the carbonyl groups are specifically interacting with MoS₂.

2. For the Raman measurements, is the laser focused at the interface between DDT and MoS₂ or in the bulk DDT like in the PL measurements of Fig. 2? Given the differences seen in the PL spectra at each position, this is an important point to clarify.

3. In Figs. 3b-d, the authors show the EPR spectra of DDT, MoS₂, and the DDT/MoS₂ heterostructure. There are many issues with this data and the interpretation, which I will list below.

First, the authors state that the measurement is the 'X-band EPR spectra'. However, they do not state if this is light induced EPR (L-EPR) or dark EPR. This is very important to clarify, as right now I am struggling to see how the data of the DDT/MoS₂ heterostructure fits in with the interpretations of the manuscript.

If we presume that the measurement is L-EPR, then there are the following issues. The biggest one is that if the SOC is as large as the authors claim it is from the EPR data and the T₁ and T₂ relaxation times are as fast as a few ns, it should not be possible to even measure a L-EPR spectrum. Typically, triplet states in purely organic materials are not measurable in L-EPR as the spin polarisation decays too fast, not even considering the situation described by the authors with much larger SOC and faster spin relaxations. Thus, only very long-lived spin-polarised states like (trapped) polarons are normally visible in L-EPR (10.1021/jp511021v).

However, if for the sake of discussion, we take the assignment of the signal in the DDT/MoS₂ to be the triplet exciton on DDT, then there are still problems in the interpretation. The authors claim that the signal centred around 160 mT is the half field transition of the triplet exciton. However, this does not look like a half field transition as it is far too broad (~75 mT). Instead, the authors should consider whether they may instead have a very large Zero Field Splitting D-parameter in DDT/MoS₂ and what they are seeing is not the half field transition, but rather the low field Z-transition ($m_s = \pm 1$), with the central peaks around 280 mT representing the X and Y transitions ($m_s = \pm 1$). To check this, the authors should extend the magnetic field sweep range to higher fields to see if they find another Z transition or not. The authors could also check whether the broad transition could be the half field from the relation in Equation 1 of the following paper: 10.1021/ja00360a005.

If it instead transpires that the measurement is instead dark EPR, then the measurements shown would suggest that DDT/MoS₂ has a spin-triplet ground state, as spin-singlet states are not visible in EPR spectroscopy as they are not paramagnetic. If the DDT has a triplet ground state in the heterostructure with MoS₂, then the authors would need to reconsider the interpretations of the entire paper.

4. Regardless of all the above discussion, the authors should attempt to simulate their EPR spectra to obtain important information about the paramagnetic species present (e.g. ZFS parameters, accurate g-values, etc).

5. As with many TMD studies, I also have concerns about the reproducibility of the authors' findings. In this case, they are drop casting a DDT solution onto an MoS₂ flake. The flake itself will

have a lot of variation in its size, shape and surface morphology, and there is also the potential for differences in the DDT crystal formation from drop casting, as this sample formation method is difficult to control. Therefore, I would be keen to see that data reproduced on at least a couple of other samples to confirm that their observations are robust.

6. The experimental details section contains very little information, which makes it difficult to understand the EPR spectrum presented, as discussed above. The authors should greatly increase the detail of the experimental section to allow the reader to better understand (and reproduce, if necessary) their experimental results.

Reviewer #3 (Remarks to the Author):

In the manuscript "Ultrafast Microsecond Organic Triplet Emitters via Spin Orbit Proximity Effect by Hybridizing Organic Chromophores on Transition Metal Dichalcogenides", the authors report on a study of a series of organic phosphors exhibiting enhanced triplet emission rates in proximity to prototypical transition metal dichalcogenides. Their study combines time-resolved optical spectroscopy, Raman spectroscopy, paramagnetic resonance spectroscopy, structural analysis by STM and XRD, and engineering of the chemical structures with modeling of the crystal structures and DFT calculations.

In my opinion, the scientific topic and experimentally broad study design in general suffices the criteria of relevance, noteworthiness and broad interest for publication in Nature Communications. Before recommending the manuscript for publication though, I would like the authors to address the following points.

The authors should better explain or narrow down their claim of a "novel strategy, termed 'through-space spin-orbit proximity effect'" (page 16), as the basic phenomenon of externally enhancing spin-orbit coupling by proximate heavy atoms is known since the 1950s, see e.g. [Kasha, J. Chem. Phys. 20 (1), 71 (1951)], [McGlynn et al., J. Chem. Phys. 39, 675 (1963)], [McGlynn et al., J. Chem. Phys. 37, 1818 (1962)], [McGlynn et al., J. Phys. Chem. 66, 2499 (1962)].

The authors specifically claim that the "unique through-space spin-orbit proximity effect of TMD stems from the broken inversion symmetry", that the "broken inversion symmetry of MoS₂ provokes the valence-band-edge state to split the d orbitals [...] this might destabilize the energy states and electron spin movements of DDT" (page 11) and that the "broken inversion symmetry with strong SOC and spin splits destabilizes the dipole moment in (n, n*) of DDT" (page 13). In their study, the specific role of the broken inversion symmetry in enhancing of SOC in DDT is not experimentally distinguished from the basic effect of SOC induced by close proximity of the carbonyl groups to the heavy Mo atom. The relevance of the broken inversion symmetry should be better worked out as this seems central to their claim of relevance.

Additional remarks:

1. On page 7, the authors omit discussion of other modifications of the Raman spectra upon aggregation of DDT on the MoS₂ surface, specifically around 650-700cm⁻¹ and 250cm⁻¹. I would like to see these changes included in the discussion.

2. On page 10, it is not immediately clear how the shown crystal structure aligns with the MoS₂ surface.

3. On page 13 in the paragraph starting "Scheme 1a illustrates", the authors state "one of two carbonyl oxygens in DDT closely aligns on Mo atoms at K point" - what K-point do the authors refer to? This needs to be clarified.

4. On pages 15/16, the authors discuss the proximity effect of MoS₂ on Br6A. How are the stated lifetimes of 87μs and 1.4ms defined and determined? The associated figure S11 would indicate 1/e-lifetimes for emission from the pure Br6A of below 200μs.

5. The XRD analysis results are not corroborated by the original data - the results are simply stated in the supporting information and the main text.

6. Table S1: missing energy units (eV).

7. Figures S1, S2: Missing indication of scale bar lengths.

8. Figure S4: It would be helpful to indicate graphically how the STM alignment of DDT molecules correlates with the crystal structure presented in Fig. S6.

9. Table S3: undefined acronyms EDA, COVP, PCT.

Response Letter

Journal: Nature Communications

Manuscript ID: NCOMMS-23-53080-T

Title: Ultrafast Microsecond Organic Triplet Emitters via Spin Orbit Proximity Effect by Hybridizing Organic Chromophores on Transition Metal Dichalcogenides

Response to the Reviewers' Comments

The authors would like to express our sincere gratitude to the reviewers for their valuable feedback on our manuscript. We have carefully reviewed each comment and revised the manuscript accordingly. We hope that the revised manuscript meets the expectations of the reviewers. To enhance readability, the reviewers' comments and the authors' responses have been color-coded in black and blue, respectively. In the revised manuscript, revised parts are highlighted in yellow.

Reviewer #1 (Remarks to the Author):

In this work, the authors introduced a novel triplet emitter design strategy by building heterostructures of DDT with various transition metal dichalcogenides (TMDs), e.g., MoS₂, MoSe₂, WS₂, and WSe₂, and observed the TMDs-induced photophysical variations in DDT. DDT on TMDs emits bright green phosphorescence with a few tens of microsecond lifetimes at room temperature (RT). And the key structural features of TMDs and POPs were also been identified: 2H-lattice structures with heavy transition metal atoms in TMDs and aromatic carbonyl with an ortho hydroxy in POPs. The relaxation decays of POPs exhibiting slow phosphorescence can be largely improved through the through-space spin-orbit proximity effect of TMDs. The authors also explained the interaction between the POPs and the TMDs in a detailed analysis, however, the study of the luminescent properties of the system is still lacking. Some puzzling questions remain as following.

1. For scanning tunneling microscopy analysis, it is recommended to supplement the STM diagram of the control group MoS₂ without DDT.

Response:

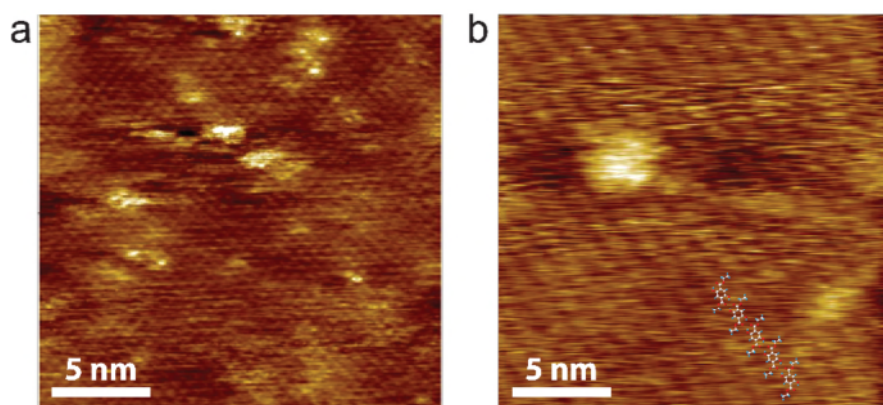


Figure R1-1. STM images of **a**, transferred MoS₂ and **b**, DDT alignment on the MoS₂. Revised Fig. S4.

As Reviewer#1 recommended, the STM of pristine MoS₂ (Figure R1-1a) and graphics of DDT assembly on the MoS₂ (Figure R1-1b) were added to the supplementary Figure for better understanding.

2. Why is the maximum emission wavelength (470 nm) of DDT in Figure 1f red-shifted by almost 20 nm from that in Figure 1g (451 nm)?

Response:

The emission characteristics of organic phosphors are widely recognized to be readily affected by the crystallinity in the solid state¹⁻³ and the dipole rearrangement derived from various factors⁴. The emission of DDT also demonstrates shifts depending on its crystallinity. E. Cho et al. reported that DDT, suspended in solvents and amorphous-like films, emits photoluminescence at a wavelength about 20 nm lower than DDT crystals.⁵ DDT shown in Figures 1f and g are the crystal and suspension states, respectively, and the difference between their emission wavelength is approximately 20 nm. This aligns closely with the study on the

emission variations of DDT by crystallinity⁵.

3. How does the lifetime of DDT/MoS₂ change at 77K compared to the DDT? And to illustrate the lifetime of DDT/ MoS₂ at 77K should be provided.

Response:

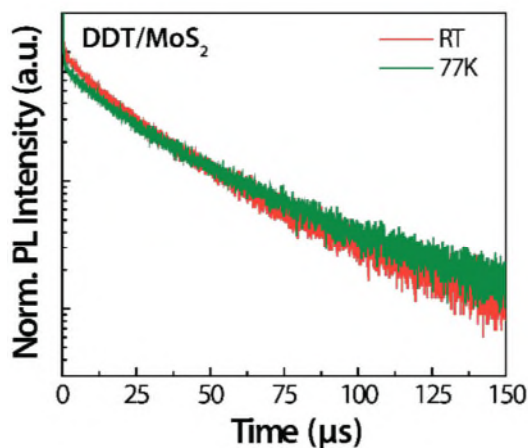


Figure R1-2. TRPL spectra of the DDT/MoS₂ aqueous suspension at RT and 77 K.

At room temperatures (Figures 1i and j), MoS₂ promotes suspended DDT molecules to activate triplet emissions via the through-space spin-orbit proximity effect when in proximity. It contributes to three orders of magnitude higher SOC coefficient in the hybrid system compared to intrinsic DDT features, despite the presence of vibrational dissipation that hinders radiative recombination.

Next, we conducted emission decay measurements on a DDT/MoS₂ aqueous suspension at 77 K for comparison with pristine DDT. Figure R1-2 shows the lifetime decay curves of DDT/MoS₂ at room temperature (orange) and 77 K (green). As expected, the phosphorescent decay in the DDT/MoS₂ hybrid remains almost unchanged and similar regardless of the temperature conditions under 517 nm incident light. This indicates that the through-space spin-orbit proximity effect of MoS₂ dictates photophysical dynamics in the system. The phosphorescent lifetime of DDT/MoS₂ at 77 K is observed to be 27.98 μs, exhibiting no significant variations compared to the 23.22 μs lifetime of DDT/MoS₂ at RT. This subtle change might be attributed to the complete deactivation of non-radiative energy loss since the thermal energy is nearly zero at low temperatures.^{6,7} These results and corresponding descriptions were included in the manuscript.

4. In Figure 4d, the phosphorescence lifetimes for DDTs on MoS₂, MoSe₂, WS₂, and WSe₂ decrease sequentially, but the lifetime of DDT/MoS₂ in Figure 4e is the lowest instead. Is it just because of the experimental error? These results should be as uniform as possible.

Response:

We apologize for the confusion. As suspected by Reviewer#1, individual DDT/TMDs exhibit subtle variations in lifetimes due to several reasons: proximity to the TMD surfaces, crystallinity, and minor variation in measurement setups. Figure 4d presents lifetimes extracted from various DDT/TMDs samples shown in Figure 4b, and the emission decays depicted in

Figure 4e represent average values obtained from 10 different samples. For clarity and accuracy, we revised the corresponding descriptions in the manuscript.

In Figure 4c, it is evident that DDT on 2H-TMDs containing heavy atoms emits consistent phosphorescence around 518 nm, whereas DDT on TiS_2 generates blue fluorescence at 466 nm. In addition, the lifetime decays of DDT/TMDs are significantly differentiated into two regimes: microseconds and nanoseconds (Figure 4d). In heavy metal-mediated 2H-TMDs, the lifetimes of DDT are 16.7, 14.2, 13.6, and 13.2 μs for MoS_2 , MoSe_2 , WS_2 , and WSe_2 heterostructures, respectively. This aligns with the results of the RTP obtained from the DDT/ MoS_2 interface (Figures 1j and 2b). On the contrary, the emission decay of DDT/ TiS_2 occurs within approximately 5 ns. Figure 4e presents statistical results of average emission decays extracted from 10 DDT/TMDs samples. The lifetimes of DDT crystals are 20.1 ± 1.3 , 21.7 ± 2.4 , 23.2 ± 1.2 , and 17.6 ± 1.1 μs in combinations with MoS_2 , MoSe_2 , WS_2 , and WSe_2 while DDT/ TiS_2 shows nanosecond fluorescence up to 5.35 ± 0.4 ns. It is clearly shown that heavy transition metal atoms with 2H-honeycomb structures in TMDs are inevitable to enable the microsecond RTP of DDT.

5. The DDT/ MoS_2 aqueous suspension has a noticeable green phosphorescence. Do the other DDT/TMDs have a similar luminescent behavior in solution and PL spectra for suspension? And corresponding photos should be added if possible.

Response:



Figure R1-3. Photo of DDT/TMD suspensions under a UV lamp.

We employed chemical exfoliation techniques on TiS_2 , MoSe_2 , WS_2 , and WSe_2 flakes, and followed by reprecipitating DDT solution to produce dispersed DDT/TMD suspensions. As illustrated below, all TMDs except TiS_2 emit bright green phosphorescence. Consistent with the solution drop casting results, TiS_2 exhibits a blue emission from the suspension, closely matching the intrinsic emission of a DDT suspension (Figure 1g inset). This information was incorporated into the Supporting Information.

6. For Br6A/ MoS_2 , why is the phosphorescence lifetime of the Br6A crystal on MoS_2 (87 μs) shorter than that of the Br6A overhang part (1.4 ms)?

Response:

The Br6A system was introduced to investigate the potential for enhancing SOC in materials already possessing valid intersystem crossing routes through the through-space spin-orbit proximity effects. As elaborated in the manuscript, Br6A represents a purely organic phosphor with an ultra-long decay of room temperature phosphorescence in millisecond regimes⁸. The

millisecond-scale phosphorescence of Br6A implies that despite accessible ISC routes, the SOC efficiency is relatively insufficient to facilitate rapid transitions, resulting in slow triplet emission. Additionally, close-packing of Br6A is crucial to prohibit collisional quenching at room temperature.

In this context, we hypothesized that if MoS₂ could induce a spin-orbit proximity effect to Br6A due to its strong SOC with broken inversion symmetry, electrons in Br6A would be facilitated to couple with external orbitals, enabling faster phosphorescent lifetimes as evidence of SOC enhancement. Experimentally, it is evident that the fluorescence portion of Br6A emission is significantly reduced in combination with MoS₂ (Figure S12c). This suggests enhanced SOC efficiency related to triplet-mediated transitions in the Br6A system. Consequently, the lifetime of Br6A/MoS₂ is nearly 16 times faster than pristine Br6A. This finding well aligns with the results observed from DDT/MoS₂. Therefore, the through-space spin-orbit proximity effect of 2H-TMDs with heavy atoms successfully enhances SOC in phosphors possessing feasible ISC routes with relatively weak SOC.

7. In supporting information, the experiments show that “The crystal structures of DDT rely on the presence of MoS₂. SC-XRD analysis is performed to establish the crystal structure deformation of DDT via strong vdW interaction with MoS₂.” Therefore, the authors should explore whether the change of DDT crystal structure caused by MoS₂ is another major cause of ultrafast RTP emission.

Response:

Recent studies on room temperature phosphorescence have addressed the influence of crystal structures of organic phosphors on their photophysical characteristics.^{1,9–11} For instance, Z. An et al. proposed that organic phosphor arrangements, such as j-aggregation and h-aggregation, can aid in stabilizing excited triplet states to realize ultralong phosphorescence with decay times of up to seconds.¹² Thus, it could seem plausible to speculate that the crystal distortion in DDT may also play a role in generating ultrafast RTP, as raised by Reviewer#1. We have also taken this possibility into consideration and explored it in the early stages of our research.

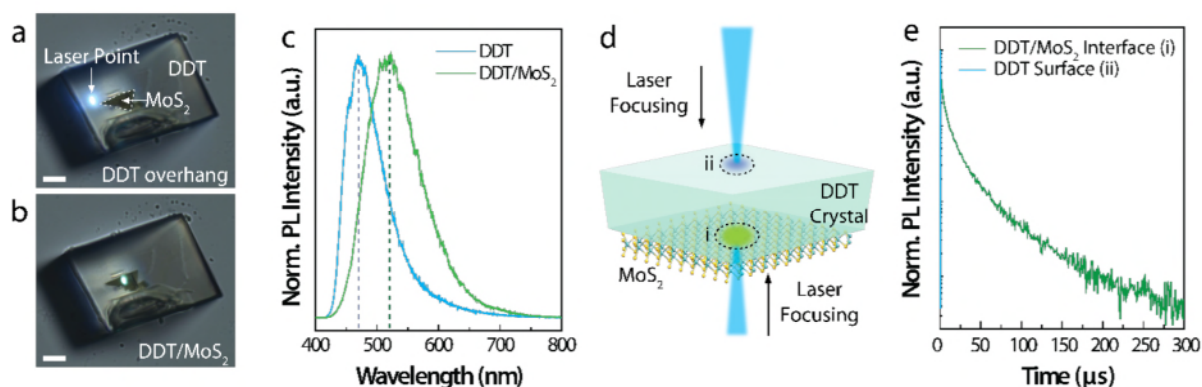


Figure R1-4. Optical images of **a**, DDT overhang and **b**, DDT/MoS₂ interface of a single DDT crystal on MoS₂ under 405 nm light irradiation. **c**, PL spectra of DDT overhang and DDT/MoS₂ interface. **d**, Scheme of DDT crystal with different focuses, and **e**, corresponding TRPL spectra obtained from different focuses in a single DDT crystal.

Multiple analyses were performed on DDT and MoS₂ heterostructures from various

perspectives to verify the driving force of ultrafast RTP at a DDT/MoS₂ interface. As addressed in Figures S4 and S6, DDT molecules initially assemble as layered-like planes on the MoS₂ basal plane and then form a densely packed crystal as a triclinic. The crystal structure of DDT in conjunction with MoS₂ differs from its intrinsic form. This indicates that MoS₂ definitely impacts intermolecular interactions among DDT molecules during crystallization, leading to the deformation of DDT assemblies. Despite the distorted lattice structures of DDT, individual DDT crystals site-selectively formed on MoS₂ are a single-crystalline nature, as depicted in Figures R4a and b. If the crystal deformation in the DDT/MoS₂ system promotes ultrafast RTP emissions, one would expect RTP generation throughout the crystal, regardless of its proximity to the MoS₂ interface. However, as evidenced throughout the entire paper and in Figure R1-4, RTP is exclusively observed at the interface with MoS₂, whereas other regions, both vertically and laterally distant from 2H-MoS₂, emit blue fluorescence even within a single DDT crystal. This implies that the deformed DDT crystal structure is not a major cause of RTP emission. Instead, the proximity of DDT to 2H-TMDs matters significantly when RTP emerges through the space-through spin-orbit proximity effect.

Moreover, the spacing of the distorted DDT alignment on MoS₂ is notably minimal compared to various potential alignments of DDT on MoS₂ (Figure S5). This suggests that DDT readily interacts with heavy Mo atoms, potentially boosting internal SOCs in this particular alignment. Note that the proximity to TMDs is a major prerequisite to ensure effective heavy atom involvement during the heavy atom effect on phosphors or weak SOC systems^{13,14}. The proximity between the Mo atoms of MoS₂ and the carbonyl oxygen of DDT is essential to enable efficient through-space spin-orbit proximity effect and subsequent RTP.

8. In Figures S1 and S2, the scale bar need to be marked.

Response:

The scale bars in both Figure S1 and S2 are 100 μm. The scale information was included in the captions.

References for Reviewer#1

1. Cai, S. *et al.* Enabling long-lived organic room temperature phosphorescence in polymers by subunit interlocking. *Nat. Commun.* **10**, 4247 (2019).
2. Zhang, T. *et al.* Pure Organic Persistent Room-Temperature Phosphorescence at both Crystalline and Amorphous States. *ChemPhysChem* **19**, 2389–2396 (2018).
3. Qian, L. *et al.* Crystallization-Induced Emission Enhancement in a Phosphorus-Containing Heterocyclic Luminogen. *J. Phys. Chem. B* **113**, 9098–9103 (2009).
4. Sudhakar, P. & Radhakrishnan, T. P. Stimuli responsive and reversible crystalline–amorphous transformation in a molecular solid: fluorescence switching and enhanced phosphorescence in the amorphous state. *J. Mater. Chem. C* **7**, 7083–7089 (2019).
5. Cho, E. *et al.* A Single-Benzene-Based Fluorophore: Optical Waveguiding in the Crystal Form. *Chempluschem* **84**, 1130–1134 (2019).
6. Sawicki, E. & Johnson, H. Characterization of aromatic compounds by low-

- temperature fluorescence and phosphorescence: Application to air pollution studies. *Microchem. J.* **8**, 85–101 (1964).
7. Kearns, D. R. & Case, W. A. Investigation of Singlet $\rightarrow$ Triplet Transitions by the Phosphorescence Excitation Method. III. Aromatic Ketones and Aldehydes. *J. Am. Chem. Soc.* **88**, 5087–5097 (1966).
 8. Bolton, O., Lee, K., Kim, H.-J., Lin, K. Y. & Kim, J. Activating efficient phosphorescence from purely organic materials by crystal design. *Nat. Chem.* **3**, 205–210 (2011).
 9. Arunkumar, S., Ghosh, D. & Kumar, G. R. Heavy main group element containing organometallic phosphorescent materials. *Results Chem.* **4**, 100399 (2022).
 10. Shao, W. & Kim, J. Metal-Free Organic Phosphors toward Fast and Efficient Room-Temperature Phosphorescence. *Acc. Chem. Res.* **55**, 1573–1585 (2022).
 11. Gu, L. *et al.* Colour-tunable ultra-long organic phosphorescence of a single-component molecular crystal. *Nat. Photonics* **13**, 406–411 (2019).
 12. An, Z. *et al.* Stabilizing triplet excited states for ultralong organic phosphorescence. *Nat. Mater.* **14**, 685–690 (2015).
 13. Gmitra, M. & Fabian, J. Graphene on transition-metal dichalcogenides: A platform for proximity spin-orbit physics and optospintronics. *Phys. Rev. B* **92**, 155403 (2015).
 14. Xiao, D., Liu, G.-B., Feng, W., Xu, X. & Yao, W. Coupled Spin and Valley Physics in Monolayers of MoS₂ and Other Group-VI Dichalcogenides. *Phys. Rev. Lett.* **108**, 196802 (2012).

Reviewer #2 (Remarks to the Author):

Obtaining rapid and efficient phosphorescence from spin-triplet excited states in purely organic emitters is an interesting fundamental research problem to address and may have applications in OLEDs. In their work, authors explore the ability of TMDs to enable fast and efficient phosphorescence in heterostructures with small molecule organic semiconductor crystals, which appears to be achieved through a variation of the external heavy atom effect. Whilst the results are interesting, I have significant concerns about the interpretations the authors have made about their data, in particular the EPR. Furthermore, the external heavy atom effect is already well known and demonstrating it again here is not particularly novel. TMDs are a very ‘trendy’ research field at the moment, which, in my opinion, can make routine demonstrations of established concepts appear more impactful than they really are. Therefore, I would recommend that the authors revisit the interpretation of some of their experimental data, before resubmitting to a more specialised journal. Below, I have provided some comments that I hope will assist the authors with revising their manuscript.

The comments from Reveiwer#2 are appreciated and provide valuable insights, particularly regarding EPR interpretation, which we have gained further understanding of during this revision. However, it is important to note that our study introduces a novel concept in developing triplet emitters that diverges from the traditional external heavy atom effect in organic chromophores.

As highlighted by Reviewer#2, the heavy atom effect (HAE) is a well-established concept known to enhance spin-orbit coupling, thereby exerting phosphorescent emission in organic chromophore systems. Additionally, recent emerging research has focused on the proximity spin-orbit effect, where transition metal dichalcogenides (TMDs) facilitate coupling with graphene and alter its spin dynamics by creating a layered hybrid of TMDs/graphene.

While both phenomena involve alterations in spin-orbit coupling (SOC) stemming from heavy atoms within molecular or hybrid systems, the specific materials used and their responses to SOC interference are distinct from each other. The reported proximity spin-orbit effect of transition metal dichalcogenides (TMDs) primarily impacts the electrical features and spin polarization of graphene, which is relevant to spintronic devices. To date, no study has reported that a hybrid structure of TMDs with other two-dimensional materials or organic chromophores can alter the optical properties of adjacent materials with weak SOC to induce phosphorescence at room temperatures.

External Heavy Atom Effect	Spin-orbit Proximity Effect	Through-space Spin-Orbit Proximity Effect
-----------------------------------	------------------------------------	--

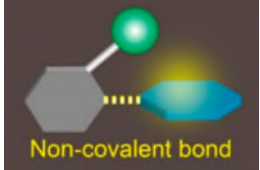
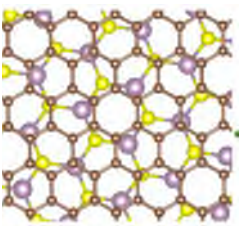
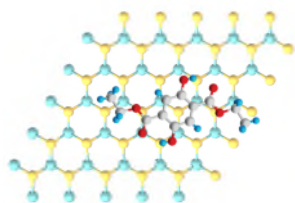
 1	 2	
Organic Chromophores/ Halogen atoms	Graphene/ Transition metal dichalcogenides	Organic Chromophores/ Transition metal dichalcogenides
Impacting photophysical properties	Impacting electrical properties and spin dynamics under magnetic fields	Impacting photophysical properties
ms to s		μ s
1,3,4	2,5–7	This Work

Table R2-1. Summary of representative differences between heavy atom effect, spin-orbit proximity effect, and this work.

The HAE, on the other hand, is mainly utilized to boost the emission efficiency of room temperature phosphors and demonstrate applications, such as organic light emitting diodes. Internal HAE occurs when an organic chromophore contains a heavy metal, such as halogen atoms or transition metal atoms, leading to intramolecular dipole relocation that enhances SOC as well as accelerates subsequent emissive decay. External HAE, which relies on similar kinetics yet two chromophores involved, contributes to the close-packing and arrangement of crystals subjected to both the atomic number of functionalized heavy atoms and intermolecular distances between the two chromophores.

However, there are substantial distinctions between the external HAE and the DDT/TMDs platform. In the external hybrid, the two chromophores are interconnected and closely packed within three-dimensional crystals, interacting with each other in all directions. In contrast, as separate crystals, DDT molecules form an interfacial contact on the surface of TMDs. Accordingly, the through-space spin-orbit effect is observable only in regions where DDT molecules are in close proximity to the TMDs. This suggests that triplet emitters consisting of TMDs/DDT hybrids have the potential to achieve the thicknesses as thin as a few nanometers. Most importantly, subsequent phosphorescent lifetimes exhibit distinctly different regimes: ultralong lifetimes of more than milliseconds for external HAE and microsecond for the through-space spin-orbit proximity effect.

For the above reasons, the through-space spin-orbit proximity effect elucidated in our study is distinct from and unique, compared to external HAE and spin-orbit proximity effects. This work addresses fundamental principles in depth and uncovers key features of chromophores and transition metal dichalcogenides in triplet emitter designs. We believe that our findings could enable fellow researchers to explore and expand this new species of fast and stable phosphorescence emitters.

1. In Fig. 3a, the authors show some Raman data for DDT and DDT on MoS₂, noting that a peak around 1350 cm⁻¹ is shifted in the MoS₂ sample. About this observation, they state:

‘As for DDT, the peak at 1350 cm⁻¹ represents the vibration modes of aromatic carbonyl groups. Intriguingly in DDT/MoS₂, only this peak related to the carbonyl groups of DDT is shifted toward a lower frequency at 1330 cm⁻¹, while no shift is observed in other Raman modes. The red-shifted Raman mode of carbonyl groups indicates energy loss of phonons and an altered electronic structure of carbonyl groups of DDT on MoS₂, indicating a strong interaction between the carbonyl of DDT and MoS₂.’

This interpretation is incorrect: carbonyl stretches are almost always located between 1650-1750 cm⁻¹, which is nowhere near the 1350 cm⁻¹ mode referred to by the authors. 1350 cm⁻¹ is around the ‘fingerprint’ region of a molecule, which is likely related to C-C or C-O (single bond) stretches. Thus, a shift in a mode at 1350 cm⁻¹ is not related to a carbonyl ground and therefore does not provide experimental evidence that the carbonyl groups are specifically interacting with MoS₂.

Response:

We appreciate the thorough reviews of the spectroscopic results and the considerate corrections provided by Reviewer#2. Despite undergoing numerous revisions during the preparation of the manuscript, it appears that some corrections were overlooked.

The Raman analysis was conducted on pristine DDT and DDT/MoS₂ with a CW laser. In DDT/MoS₂, peaks around 1350 and 1700 cm⁻¹ present clear blue shifts towards the lower frequency direction compared to pristine DDT (Figure R2-1). These two peaks most likely represent the stretch modes of C-O bond and the stretching mode of C=O bond in DDT, respectively.⁸⁻¹⁰ For clarification, we revised Figure 3a and the corresponding descriptions.

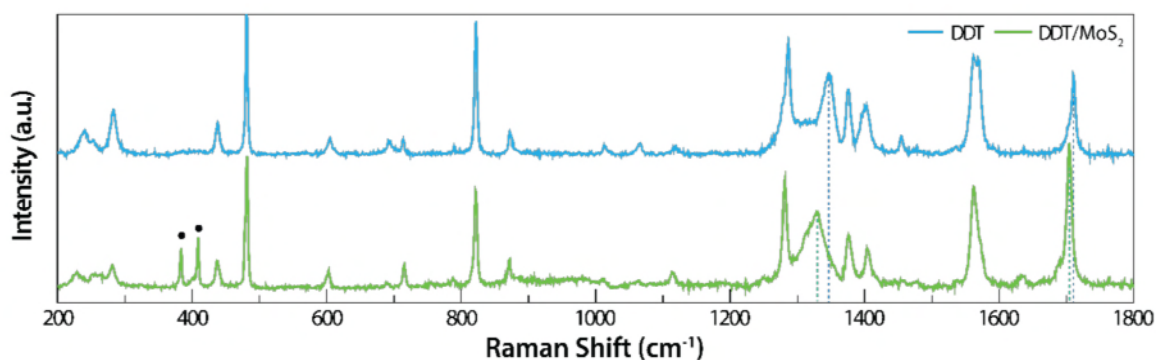


Figure R2-1. Revised Figure 3a. Raman spectra of pristine DDT and DDT/MoS₂.

2. For the Raman measurements, is the laser focused at the interface between DDT and MoS₂ or in the bulk DDT like in the PL measurements of Fig. 2? Given the differences seen in the PL spectra at each position, this is an important point to clarify.

Response:

We utilized a customized confocal microscope to acquire PL, TRPL, and Raman spectroscopic data. This setup enables precise adjustment of measurement conditions involving an optical

mirror and interchangeable detectors, such as the charge-coupled device (CCD) and the photomultiplier tube (PMT). The flexibility the setup provided allows fine measurements on various samples.

Raman analysis presented in Figure 3 was carried out on the DDT/MoS₂ hybrid sample shown in Figure 1. The Raman spectrum of DDT/MoS₂ (the blue in Figure R2-1) was obtained at the DDT/MoS₂ interface, while the DDT spectrum was measured with a focus on the DDT interface with the SiO₂ substrate. We provided the measurement information in the caption of Figure 3a.

3. In Figs. 3b-d, the authors show the EPR spectra of DDT, MoS₂, and the DDT/MoS₂ heterostructure. There are many issues with this data and the interpretation, which I will list below.

First, the authors state that the measurement is the 'X-band EPR spectra'. However, they do not state if this is light induced EPR (L-EPR) or dark EPR. This is very important to clarify, as right now I am struggling to see how the data of the DDT/MoS₂ heterostructure fits in with the interpretations of the manuscript.

If we presume that the measurement is L-EPR, then there are the following issues. The biggest one is that if the SOC is as large as the authors claim it is from the EPR data and the T1 and T2 relaxation times are as fast as a few ns, it should not be possible to even measure a L-EPR spectrum. Typically, triplet states in purely organic materials are not measurable in L-EPR as the spin polarisation decays too fast, not even considering the situation described by the authors with much larger SOC and faster spin relaxations. Thus, only very long-lived spin-polarised states like (trapped) polarons are normally visible in L-EPR (10.1021/jp511021v).

However, if for the sake of discussion, we take the assignment of the signal in the DDT/MoS₂ to be the triplet exciton on DDT, then there are still problems in the interpretation. The authors claim that the signal centred around 160 mT is the half field transition of the triplet exciton. However, this does not look like a half field transition as it is far too broad (~75 mT). Instead, the authors should consider whether they may instead have a very large Zero Field Splitting D-parameter in DDT/MoS₂ and what they are seeing is not the half field transition, but rather the low field Z-transition ($m_s = \pm 1$), with the central peaks around 280 mT representing the X and Y transitions ($m_s = \pm 1$). To check this, the authors should extend the magnetic field sweep range to higher fields to see if they find another Z transition or not. The authors could also check whether the broad transition could be the half field from the relation in Equation 1 of the following paper: 10.1021/ja00360a005.

If it instead transpires that the measurement is instead dark EPR, then the measurements shown would suggest that DDT/MoS₂ has a spin-triplet ground state, as spin-singlet states are not visible in EPR spectroscopy as they are not paramagnetic. If the DDT has a triplet ground state in the heterostructure with MoS₂, then the authors would need to reconsider the interpretations of the entire paper.

4. Regardless of all the above discussion, the authors should attempt to simulate their EPR spectra to obtain important information about the paramagnetic species present (e.g. ZFS parameters, accurate g-values, etc).

Response:

We appreciate the insightful comments on the EPR results and will address the corrections and related information point-by-point. First of all, the measurements were conducted under dark conditions. Thus, as clarified by Reviewer#2, the EPR signals observable at around 160 mT are possibly associated with a triplet ground state of DDT in the hybrid form (Figures 3b and d). This is highly intriguing since pristine DDT exhibits no detectable signals in that magnetic field range. The abrupt emergence of these EPR signals is likely due to the populated triplet characters in DDT that stems from the interaction with MoS₂. We hypothesized that, along with through-space spin-orbit proximity effect, sulfur vacancies of pristine MoS₂ may also play a part of roles in dominating the ground triplet characters of the hybrid DDT. To address this possibility, we modeled sulfur defects as a high-spin triplet state on the 2×2 MoS₂ surface where a sulfur was removed and the system was kept at neutral charge (Figure R2-2). The spin density on the defective MoS₂ should be exactly 2 for zero electronic interaction with DDT. With DDT present, however, the spin density on MoS₂ was 1.99 e⁻ and the spin density on DDT was 0.009 e⁻. This sharing of spin with DDT represents a significant electronic coupling and likely results in the amplified EPR spectrum. However, although some parameters were uncovered to contribute to the observed EPR reactions, we acknowledge that further research will still be necessary for a deeper and clear understanding.

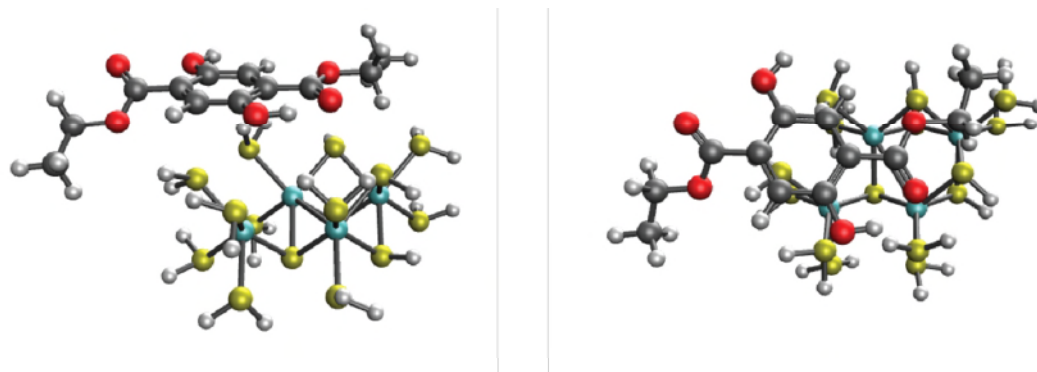


Figure R2-2. The hybrid system of DDT and defect MoS₂.

Next, the measured EPR signals were simulated by Easyspin software, as shown in Figure R2-3, to extract information about the paramagnetic species. The g_{xx} and g_{yy} values were 2.35, while g_{zz} was found to be 2.23. In addition, zero-field splitting (ZFS) D- and E-parameters were determined to be 2068.0 and 553.1 MHz, respectively. Interestingly, the prominent EPR signal near 160 mT could not adequately fit with the ZFS parameters, suggesting that it may not be relevant to the Z transition. Meanwhile, no other EPR signals were observable at higher magnetic fields up to 500 mT. This finding aligns well with the assumption that an EPR signal would not be detected around 450 mT unless the peak at 160 mT represents the Z transition.

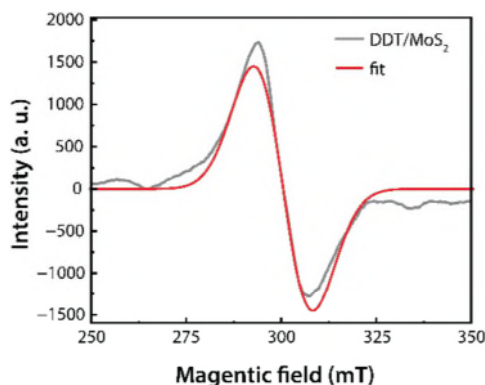


Figure R2-3. The least square-fit EPR spectrum

Furthermore, light EPR (L-EPR) was carried out on DDT/MoS₂ under 375 nm light irradiation (Figure R2-4) compared to dark EPR. No distinct EPR peaks possibly associated with excited triplet states of DDT appear while the intensity of EPR signals slightly diminishes across all magnetic fields. As pointed out by reviewer#2, the photo-excited spins are not detected from the EPR measurement due to the fast decay of the photo-excited spins from the excited states to the ground state in this platform.

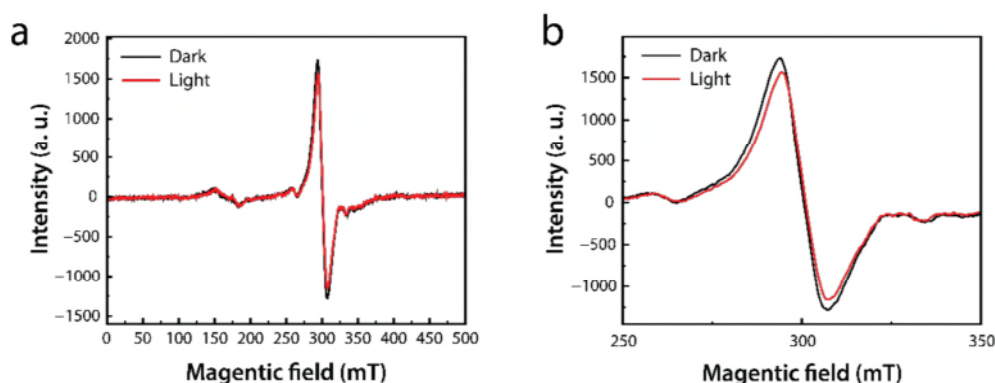


Figure R2-4. a, ERP spectra of DDT/MoS₂ under dark and light conditions. L-EPR utilized 375 nm light source for irradiation. **b,** The magnification of the EPR peak around 300 mT.

To ensure clarity in describing EPR results, all authors thoroughly reviewed the interpretations and made appropriate revisions to the manuscript.

5. As with many TMD studies, I also have concerns about the reproducibility of the authors' findings. In this case, they are drop casting a DDT solution onto an MoS₂ flake. The flake itself will have a lot of variation in its size, shape and surface morphology, and there is also the potential for differences in the DDT crystal formation from drop casting, as this sample formation method is difficult to control. Therefore, I would be keen to see that data reproduced on at least a couple of other samples to confirm that their observations are robust.

Response:

We couldn't agree more that reproducibility with reliable observations is crucial for determining a phenomenon and investigating its underlying mechanism. With full confidence, we were able to reproduce the RTP emission of DDT/2H-TMDs containing heavy atoms using the drop-cast method. It's worth revisiting the mechanism of DDT nucleation and crystal

growth on MoS₂. When dissolved in a solvent, DDT molecules migrate towards the MoS₂ surface and align in the most favorable coordination along the 2H lattices of TMDs, leading to a 2D-like self-assembly at the early stage of solution drop-casting. As long as the TMDs have periodic honeycomb structures with heavy atoms, DDT could undergo site-selective growth on these TMDs and interact with them in close proximity, thereby enhancing SOC and emitting subsequent RTP regardless of possible variations in size, shape, and thickness of TMD flakes.

We have verified the green phosphorescence of DDT/TMD heterostructures across diverse configurations involving bulk TMD flakes mechanically exfoliated (Figure R2-5a) and provided statistics of emission decay for individual complexes (Figures R2-5b and 5e) to offer readers a comprehensive understanding of reproducibility and sample-to-sample variations. In addition, we explored the potential for enhancing SOC of DDT with grown MoS₂ film. Experimentally, bilayer MoS₂ film was grown over a large area by the sulfurization of metal film¹¹ and patterned into a micro-scale square array. Then, a DDT solution was drop-cast onto the MoS₂ arrays to produce a DDT/MoS₂ heterostructure array. Figures R2-5c and d present optical and CCD emission images of the DDT/MoS₂ array. The emission decay of the DDT/MoS₂ array was investigated by fluorescence lifetime imaging microscopy (FLIM) on a microsecond scale, as shown in Figure R2-5e. The majority of emission decay is around 10 to 15 μ s throughout the array, aligning well with the results obtained from TMD flakes.

Therefore, we have observed that RTP reliably occurs across various DDT/TMD configurations, from flakes to grown films, using the solution drop casting method proposed in this study. However, we acknowledge that there is room for improvement in DDT crystallization and deposition. That would be a promising avenue for follow-up exploration to enable the applicability and compatibility of hybrid organic phosphors. The corresponding descriptions were provided in the revised manuscript and supporting information.

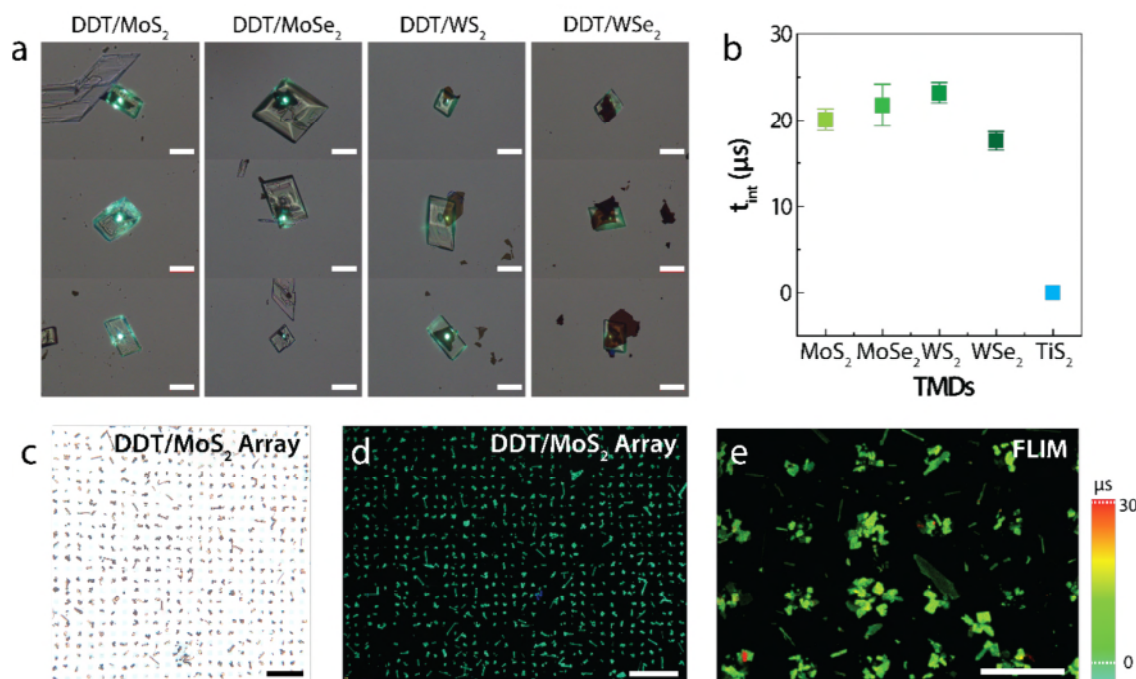


Figure R2-5. **a**, Optical images of DDT/TMDs with a laser focus at the TMD interfaces (scale bar = 20 μ m). **b**, Statistical results of average decay profiles in DDT/TMDs depicted in Figure

4e. **c**, Optical and **d**, CCD images of DDT/MoS₂ array (scale bar = 500 μm). Bilayer MoS₂ film was prepared by the sulfurization of Mo film¹¹. **e**, FILM image of DDT/MoS₂ arrays (scale bar = 100 μm). The color bar represents emission decay in a microsecond regime.

6. The experimental details section contains very little information, which makes it difficult to understand the EPR spectrum presented, as discussed above. The authors should greatly increase the detail of the experimental section to allow the reader to better understand (and reproduce, if necessary) their experimental results.

Response:

Detailed information on EPR measuring conditions was added in Materials and Methods.

References for Reviewer#2

1. Shi, H. *et al.* Highly Efficient Ultralong Organic Phosphorescence through Intramolecular-Space Heavy-Atom Effect. *J. Phys. Chem. Lett.* **10**, 595–600 (2019).
2. Li, Y. & Koshino, M. Twist-angle dependence of the proximity spin-orbit coupling in graphene on transition-metal dichalcogenides. *Phys. Rev. B* **99**, 075438 (2019).
3. Kenry, Chen, C. & Liu, B. Enhancing the performance of pure organic room-temperature phosphorescent luminophores. *Nat. Commun.* **10**, 2111 (2019).
4. Marian, C. M. Understanding and Controlling Intersystem Crossing in Molecules. *Annu. Rev. Phys. Chem.* **72**, 617–640 (2021).
5. Wang, Z. *et al.* Strong interface-induced spin–orbit interaction in graphene on WS₂. *Nat. Commun.* **6**, 8339 (2015).
6. Gmitra, M. & Fabian, J. Graphene on transition-metal dichalcogenides: A platform for proximity spin-orbit physics and optospintronics. *Phys. Rev. B* **92**, 155403 (2015).
7. Xiao, D., Liu, G.-B., Feng, W., Xu, X. & Yao, W. Coupled Spin and Valley Physics in Monolayers of MoS_2 and Other Group-VI Dichalcogenides. *Phys. Rev. Lett.* **108**, 196802 (2012).
8. Xu, W. *et al.* Local order and vibrational coupling of the C=O Stretching Mode of γ -Caprolactone in liquid binary mixtures. *Sci. Rep.* **7**, 12182 (2017).
9. Ma, H. *et al.* Hydrogen Bonding-Induced Morphology Dependence of Long-Lived Organic Room-Temperature Phosphorescence: A Computational Study. *J. Phys. Chem. Lett.* **10**, 6948–6954 (2019).
10. Ma, H. *et al.* Electrostatic Interaction-Induced Room-Temperature Phosphorescence in Pure Organic Molecules from QM/MM Calculations. *J. Phys. Chem. Lett.* **7**, 2893–2898 (2016).
11. Im, H. *et al.* Chaotic Organic Crystal Phosphorescent Patterns for Physical Unclonable Functions. *Adv. Mater.* **33**, 2102542 (2021).

Reviewer #3 (Remarks to the Author):

In the manuscript "Ultrafast Microsecond Organic Triplet Emitters via Spin Orbit Proximity Effect by Hybridizing Organic Chromophores on Transition Metal Dichalcogenides", the authors report on a study of a series of organic phosphors exhibiting enhanced triplet emission rates in proximity to prototypical transition metal dichalcogenides. Their study combines time-resolved optical spectroscopy, Raman spectroscopy, paramagnetic resonance spectroscopy, structural analysis by STM and XRD, and engineering of the chemical structures with modeling of the crystal structures and DFT calculations.

In my opinion, the scientific topic and experimentally broad study design in general suffices the criteria of relevance, noteworthiness and broad interest for publication in Nature Communications. Before recommending the manuscript for publication though, I would like the authors to address the following points.

The authors should better explain or narrow down their claim of a "novel strategy, termed 'through-space spin-orbit proximity effect'" (page 16), as the basic phenomenon of externally enhancing spin-orbit coupling by proximate heavy atoms is known since the 1950s, see e.g. [Kasha, J. Chem. Phys. 20 (1), 71 (1951)], [McGlynn et al., J. Chem. Phys. 39, 675 (1963)], [McGlynn et al., J. Chem. Phys. 37, 1818 (1962)], [McGlynn et al., J. Phys. Chem. 66, 2499 (1962)].

The authors specifically claim that the "unique through-space spin-orbit proximity effect of TMD stems from the broken inversion symmetry", that the "broken inversion symmetry of MoS₂ provokes the valence-band-edge state to split the d orbitals [...] this might destabilize the energy states and electron spin movements of DDT" (page 11) and that the "broken inversion symmetry with strong SOC and spin splits destabilizes the dipole moment in (n, π^*) of DDT" (page 13). In their study, the specific role of the broken inversion symmetry in enhancing of SOC in DDT is not experimentally distinguished from the basic effect of SOC induced by close proximity of the carbonyl groups to the heavy Mo atom. The relevance of the broken inversion symmetry should be better worked out as this seems central to their claim of relevance.

We apologize for the confusion. This paper utilized the term "broken inversion symmetry" to describe the honeycomb lattice arrangement of MoS₂ and other 2H-TMDs. This broken inversion symmetry, along with heavy transition metal atoms in TMDs, plays an essential role in interacting with DDT, particularly in the context of geometric alignments and orbital couplings. Firstly, it would be worth noting that general 2H-TMDs exhibit strong SOC originating from a heavy transition metal with broken inversion symmetry so that they could be considered a promising platform to enhance SOC of adjacent other 2D materials by spin-orbit interaction at the interface.¹ Some recent studies defined this phenomenon as proximity spin-orbit coupling.²⁻⁴

Secondly, various analyses, including STM, SC-XRD, and computational studies, were conducted to interpret the mechanism of the through-space spin-orbit proximity effect and the roles of each component in this complex platform. We discovered that DDT aligns at a particular coordinate along the MoS₂ lattice plane due to its geometric feature and the *vdW* forces. When coupled with MoS₂, carbonyl oxygens of DDT are favorably located at the Mo

atom, and the spacing between them is in the most proximity, along with the minimum total energy. This creates favorable conditions for maximizing the heavy atom effect of the transition metals in DDTs, possibly leading to SOC enhancement and RTP emission at the interface. It was confirmed with the computational study that this particular DDT/MoS₂ configuration induces effective charge transfers from carbonyl oxygen towards molybdenum and relocates (n, π^*) states of pristine DDT to the lower energy levels than (π, π^*) states, providing a new accessible ISC route from S₁ to T₂ and remarkably boosting SOC from T₁ to S₀ with hundreds larger than pristine. We found this phenomenon highly relevant to the proximity effect of TMDs, where their lattice structure with heavy metals is a key to introducing an interfacial spin coupling.

Moreover, extended studies on the interaction between other TMDs and DDT derivatives were carried out by varying the transition metals of TMDs or the position of hydroxyl groups of DDT derivatives. It was speculated that RTP could be promoted only when 2H-TMDs with heavy transition metals, such as Mo and W, and DDT derivatives consisting of a carbonyl group alongside an ortho-hydroxyl group stack in proximity. Thus, we believe that employing the term “broken inversion symmetry” is appropriate for describing one of the prerequisites in RTP promotion and elucidating the role of TMDs in the comprehensive dynamics of this system.

Additional remarks:

1. On page 7, the authors omit discussion of other modifications of the Raman spectra upon aggregation of DDT on the MoS₂ surface, specifically around 650-700cm⁻¹ and 250cm⁻¹. I would like to see these changes included in the discussion.

Response:

The main takeaway of Raman results shown in Figure 3a is the blue-shifts in Raman modes at around 1350 and 1700 cm⁻¹, corresponding to C-O and C=O bonds of DDT, indicating the prominent interfere of carbonyl and hydroxy groups in DDT molecules with MoS₂. As addressed by Reviewer#3, other peaks associated with other bonds in DDT also show the peak shift towards a lower frequency regime in corporation with MoS₂. However, the degree of variations is limited compared to the peaks of C-O and C=O bonds. We would keep the description as it is to highlight the major variations between pristine DDT and DDT/MoS₂.

2. On page 10, it is not immediately clear how the shown crystal structure aligns with the MoS₂ surface.

Response:

We included schematics of detailed parameters utilized for computational studies in a new Figure S6 as shown below for better visualization. Relevant descriptions were revised in the main text as well.

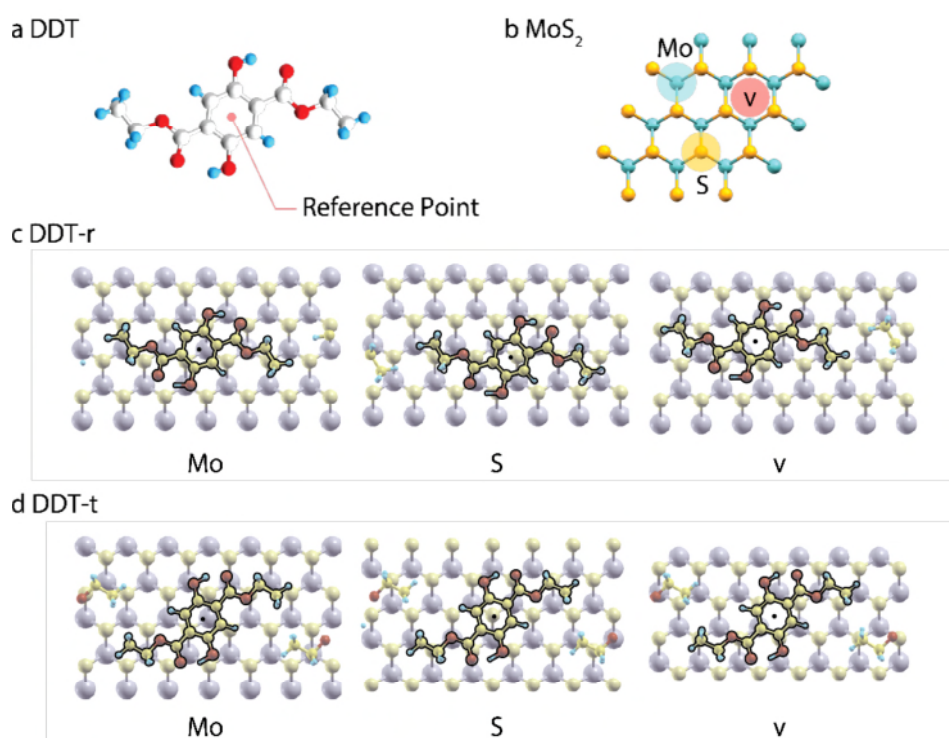


Fig. S6 | Potential DDT alignments on the MoS₂ basal plane. **a**, The reference point of DDT and **b**, possible sites for the reference point of DDT on the MoS₂ plane. DDT aligning on **c**, 4×4 and **d**, 4×5 matrices of MoS₂ unit cells. We assumed that DDT locates its phenyl center at a particular site, such as on Mo atom, S atom, or vacancy.

Furthermore, we conducted computational analysis based on the STM results to validate the alignment of DDT on the MoS₂ basal plane and to compute the total energy required for the formation of a stable heterostructure. This calculation could provide insight into the most stable alignment of DDT/MoS₂, allowing for an in-depth investigation into the detailed mechanism behind the through-space spin-orbit proximity effect of MoS₂ on DDT. Assumptions regarding the relative coordinates of DDT/MoS₂ are as follows; Firstly, the center of the phenyl ring of DDT serves as the reference point for DDT (Figure S6a). Secondly, three potential binding sites on the MoS₂ basal plane were defined for the reference point of DDT to occupy: Mo atom, S atom, or the void of the MoS₂ honeycomb structure, as shown in Scheme 1a and Figure S5b. Lastly, potential coordinates of DDT on MoS₂ were selected as periodic self-assemblies on 4×4 and 4×5 MoS₂ unit cells, denoted as DDT-r and DDT-t, respectively (Figures S6c and d). The alignments were obtained from the single-crystal XRD results of pristine DDT and DDT/MoS₂. Intriguingly, the crystal structure of DDT undergoes deformation from orthorhombic (symmetric alignment) to triclinic (asymmetric alignment) when coupled with MoS₂ during the crystallization process. Detailed crystallographic information and relevant descriptions are shown in Figure S7.

3. On page 13 in the paragraph starting "Scheme 1a illustrates", the authors state "one of two carbonyl oxygens in DDT closely aligns on Mo atoms at K point" - what K-point do the authors refer to? This needs to be clarified.

Response:

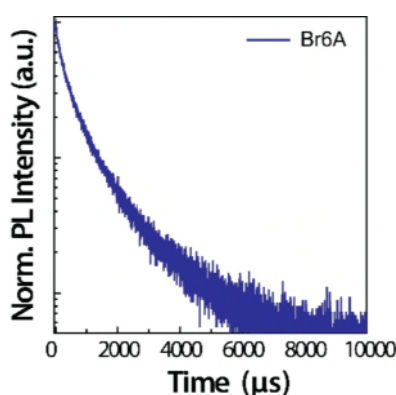
Sorry for the confusion and we revised the related descriptions for clarity.

4. On pages 15/16, the authors discuss the proximity effect of MoS₂ on Br6A. How are the stated lifetimes of 87uS and 1.4ms defined and determined? The associated figure S11 would indicate 1/e -lifetimes for emission from the pure Br6A of below 200us.

Response:

We calculated the emission lifetime of all samples, including Br6A and Br6A/MoS₂, utilizing the standard intensity average equation, which is as follows.

$$\tau_{int} = \frac{\sum_{i=1}^n \alpha_i \tau_i^2}{\sum_{i=1}^n \alpha_i \tau_i}$$



<i>i</i>	α_i	$\tau_i / \mu s$
1	0.09546	302.10845
2	0.19265	815.99584
3	0.0471	2373.38455

Figure R3-1. The lifetime decay curve of Br6A overhang and corresponding fitting components of α_i and τ_i ($i = 1, 2$, and 3).

TRPL spectra of Br6A overhang and Br6A/DDT were initially plotted within a limited time axis to highlight the microsecond phosphorescence arising from the enhanced SOC of Br6A with MoS₂. However, it could mislead readers about lifetimes, so we replotted the spectra in a wider time range up to 10,000 μs as provided in the revised supporting information (Figure S13).

5. The XRD analysis results are not corroborated by the original data - the results are simply stated in the supporting information and the main text.

Response:

The descriptions of SC-XRD results of pristine DDT and DDT/MoS₂ were precisely addressed in the revised manuscript and supporting information.

6. Table S1: missing energy units (eV).

Response:

We included energy units in the table S1 as below.

Mo (eV)	S (eV)	v (eV)
---------	--------	--------

DDT-r	-22741.81915	-22741.79323	-22741.72179
DDT-t	-22741.70536	-22741.83982	-22741.73384

7. Figures S1, S2: Missing indication of scale bar lengths.

Response:

The scale bars in both Figure S1 and S2 are 100 μm . The information was included in the revised captions.

8. Figure S4: It would be helpful to indicate graphically how the STM alignment of DDT molecules correlates with the crystal structure presented in Fig. S6.

Response:

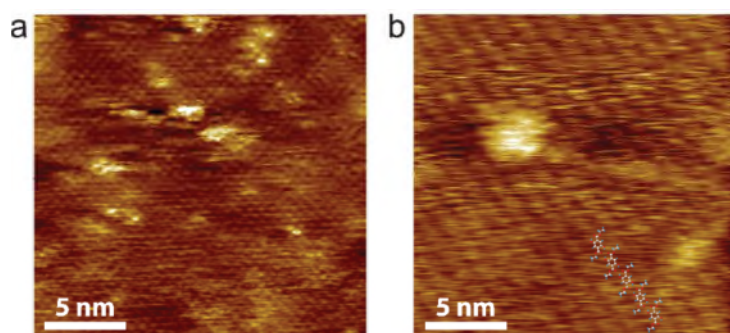


Figure R3-2. STM images of a, transferred MoS₂ and DDT alignment on the MoS₂. Revised Fig. S5.

As Reviewer#3 recommended, graphics of DDT assembly on the MoS₂ were included in the STM result for better understanding. Under a significant interference with MoS₂, DDT packing transitions from orthorhombic to triclinic and forms the heterojunctions with MoS₂ in proximity, allowing carbonyl oxygens of DDT molecules to align on the Mo atom. This is well shown in the STM image at the early stage after drop-casting the DDT DMF solution onto the MoS₂ basal plane.

9. Table S3: undefined acronyms EDA, COVP, PCT.

Response:

We added the full name of the following two acronyms: energy decomposition analysis (EDA) and complementary occupied-virtual pairs (COVP). As it is redundant with the rest of that entry we just deleted “PCT” from the table.

References for Reviewer #3

1. Xiao, D., Liu, G.-B., Feng, W., Xu, X. & Yao, W. Coupled Spin and Valley Physics in Monolayers of MoS₂ and Other Group-VI Dichalcogenides. *Phys. Rev. Lett.* **108**, 196802 (2012).

Response Letter

2. Avsar, A. *et al.* Spin–orbit proximity effect in graphene. *Nat. Commun.* **5**, 4875 (2014).
3. Wang, Z. *et al.* Strong interface-induced spin–orbit interaction in graphene on WS₂. *Nat. Commun.* **6**, 8339 (2015).
4. Gmitra, M. & Fabian, J. Graphene on transition-metal dichalcogenides: A platform for proximity spin-orbit physics and optospintronics. *Phys. Rev. B* **92**, 155403 (2015).

Reviewer #1 (Remarks to the Author):

In the manuscript entitled "Microsecond Triplet Emission from Organic Chromophore-Transition Metal Dichalcogenide Hybrids via Through-Space Spin-Orbit Proximity Effect", the authors have explored a novel triplet emitter design strategy by building heterostructures of DDT with various transition metal dichalcogenides (TMDs) to realize ultrafast and efficient phosphorescence, and conducted an exhaustive experiment and explanation to answer the queries raised by the reviewers. The manuscript has enough novelty and the authors have reasonably addressed all the queries raised. Hence the manuscript is suitable to publish in Nature Communications.

Reviewer #2 (Remarks to the Author):

The authors have provided a detailed response to the issues raised by the reviewers, which is appreciated. As a result, many of the technical concerns have now been addressed and the manuscript is more robust. I am not fully convinced by the authors' distinction between the external heavy atom effect and what they are observing in their system, however, I have one more pressing concern that must be addressed before the article can be considered for publication.

The authors' clarifications about the cwEPR measurement being in the dark have confirmed that the signal they are observing is from a ground state with spin-triplet character in DDT/MoS₂. This is a very interesting finding which calls into question the authors' interpretation of their results. If DDT/MoS₂ has a triplet ground state and the excited state also has spin-triplet character, then they are not observing phosphorescence (a process that, by definition, involves a spin flip), but rather a fully spin-allowed triplet-to-triplet radiative transition. Albeit one with a low oscillator strength given the long radiative lifetime. What comment do the authors have on this?

If the authors disagree with this interpretation, a robust response must be provided to explain where the triplet ground state signature in the EPR comes from and how its existence can be consistent with the emission mechanism proposed in their paper. However, if they agree that the ground state of DDT/MoS₂ has dominant triplet character, an alternative photophysical scheme should be proposed and included in the manuscript to explain the processes occurring in DDT/MoS₂. In addition, a more detailed explanation (beyond the brief discussion provided in the response document) of how the proximity of DDT to MoS₂ results in the formation of a spin-triplet ground state should be provided, as this behaviour is highly unusual and must be understood fully before the manuscript can be considered for publication.

Reviewer #3 (Remarks to the Author):

Both myself and reviewer #2 shared concerns about the originality of the spin-orbit proximity effect at the heart of the reported results. In the rebuttal, the authors argue that their observations constitute a novel concept compared to previous reports on spin-orbit proximity effects such as those observed for graphene/TMD heterostructures or heavy-atom effects in molecular phosphorescence. The distinction is claimed to be "the specific materials and their responses to SOC", the "interfacial contact on the surface of TMDs" and the fact that phosphorescence is observed in the TMD hybrid. While I find this claim of distinction to be on the weak side, and feel that the work would be better suited for a more specialized journal, I would in principle support publication in the present state.

Journal: Nature Communications

Manuscript ID: NCOMMS-23-53080-T

Title: Ultrafast Microsecond Organic Triplet Emitters via Spin Orbit Proximity Effect by Hybridizing Organic Chromophores on Transition Metal Dichalcogenides

Response to the Reviewers' Comments

All authors appreciate the positive comments and valuable feedback on our revised manuscript. We have considered the comments regarding the photophysical mechanism of the DDT/MoS₂ hybrid systems for further revision and will incorporate them into the revised manuscript accordingly. To enhance readability, the reviewers' comments and the authors' responses have been color-coded in black and blue, respectively. In the revised manuscript, revised parts are highlighted in yellow.

Reviewer Comments

Reviewer #1 (Remarks to the Author):

In the manuscript entitled "Microsecond Triplet Emission from Organic Chromophore-Transition Metal Dichalcogenide Hybrids via Through-Space Spin-Orbit Proximity Effect", the authors have explored a novel triplet emitter design strategy by building heterostructures of DDT with various transition metal dichalcogenides (TMDs) to realize ultrafast and efficient phosphorescence, and conducted an exhaustive experiment and explanation to answer the queries raised by the reviewers. The manuscript has enough novelty and the authors have reasonably addressed all the queries raised. Hence the manuscript is suitable to publish in Nature Communications.

Reviewer #3 (Remarks to the Author):

Both myself and reviewer #2 shared concerns about the originality of the spin-orbit proximity effect at the heart of the reported results. In the rebuttal, the authors argue that their observations constitute a novel concept compared to previous reports on spin-orbit proximity effects such as those observed for graphene/TMD heterostructures or heavy-atom effects in molecular phosphorescence. The distinction is claimed to be "the specific materials and their responses to SOC", the "interfacial contact on the surface of TMDs" and the fact that phosphorescence is observed in the TMD hybrid. While I find this claim of distinction to be on the weak side, and feel that the work would be better suited for a more specialized journal, I would in principle support publication in the present state.

Reviewer #2 (Remarks to the Author):

The authors have provided a detailed response to the issues raised by the reviewers, which is appreciated. As a result, many of the technical concerns have now been addressed and the manuscript is more robust. I am not fully convinced by the authors' distinction between the external heavy atom effect and what they are observing in their system, however, I have one more pressing concern that must be addressed before the article can be considered for publication.

The authors' clarifications about the cwEPR measurement being in the dark have confirmed that the signal they are observing is from a ground state with spin-triplet character in

DDT/MoS₂. This is a very interesting finding which calls into question the authors' interpretation of their results. If DDT/MoS₂ has a triplet ground state and the excited state also has spin-triplet character, then they are not observing phosphorescence (a process that, by definition, involves a spin flip), but rather a fully spin-allowed triplet-to-triplet radiative transition. Albeit one with a low oscillator strength given the long radiative lifetime. What comment do the authors have on this?

If the authors disagree with this interpretation, a robust response must be provided to explain where the triplet ground state signature in the EPR comes from and how its existence can be consistent with the emission mechanism proposed in their paper. However, if they agree that the ground state of DDT/MoS₂ has dominant triplet character, an alternative photophysical scheme should be proposed and included in the manuscript to explain the processes occurring in DDT/MoS₂. In addition, a more detailed explanation (beyond the brief discussion provided in the response document) of how the proximity of DDT to MoS₂ results in the formation of a spin-triplet ground state should be provided, as this behaviour is highly unusual and must be understood fully before the manuscript can be considered for publication.

Response:

First of all, all the authors sincerely appreciate the insightful comments provided by the Reviewer#2. These comments have enabled us to conduct further studies and refine our understanding of the photophysical dynamics of this finding.

DDT is an organic fluorophore that emits a blue light at room temperatures. Under vibration-dissipation-free conditions, it emerges green phosphorescence at 517 nm while maintaining its fluorescence. The corresponding lifetime is approximately 4 ms, indicating a weak SOC of pristine DDT. This is consistent with studies on other purely organic phosphors that exhibit ultralong radiative decays due to their weak SOC and inefficient ISC stemming from the absence of heavy atoms.¹⁻³ Additionally, DDT is a neutral organic molecule with no unpaired electrons, resulting in a singlet ground state.

In recent, 2D materials are known to enhance the SOC of adjacent 2D materials with inherently limited SOC, such as graphene, and to influence their electrical and spin dynamics through constructing van der Waals interfaces.⁴⁻⁸ To the best of our knowledge, it has not been previously addressed the potential for 2D materials to boost radiative transitions through enhanced SOC in their heterostructures.

Here, we uncovered that DDT can generate room temperature phosphorescence with a microsecond-scale decay time when it forms a heterostructure with MoS₂ or other 2D materials containing heavy transition metals in their 2H honeycomb lattices. Initially, a DDT molecule exclusively aligns on the MoS₂ basal plane such that its phenyl center is positioned over a sulfur atom of MoS₂, while one of its carbonyl oxygens is oriented towards a Mo atom. This coordination leads to the formation of a DDT/MoS₂ heterostructure in close proximity, facilitating intermolecular charge transfer and subsequent electron spin couplings. The significant interaction between the *d* orbitals of MoS₂ and the *p* orbitals of carbonyl oxygen of DDT lowers the energy bandgap in the (*n*, π^*) transition of DDT and reorders its excited states. Consequently, a feasible ISC route (*S*₁-*T*₂) emerges, and the SOC of *T*₁ to *S*₀ transition are significantly enhanced up to 62.3 cm⁻¹. We have termed this phenomenon the through-space spin-orbit proximity effect of MoS₂. This interpretation aligns well with the results, where only DDT derivatives possessing a hydroxyl group at an ortho position—enabling efficient electron

migration towards the carbonyl oxygen—exhibit room temperature phosphorescence through coupling with MoS₂.

However, there is another factor to consider in DDT/MoS₂ heterostructures: *Sulfur Vacancies* in MoS₂. Regardless of the sample preparation methods, MoS₂ contains intrinsic point and line defects, with sulfur vacancies being the most prevalent.⁹ Sulfur vacancies create localized defect states within the bandgap, leading to band hybridization and improved chemical reactivity. More intriguingly, anion-antisite defects in MoS₂ (and WS₂) introduce a magnetic moment and a paramagnetic triplet ground state.^{10,11} The triplet ground states derived from these defects in 2D materials are even preserved in a superlattice structure with other 2D materials.¹¹

The theory and corresponding calculations of the through-space spin-orbit proximity effect on DDT assume that MoS₂ is perfect in terms of lattice structure, without any defects on the basal plane, for the sake of simplification and capability limit of computational tools. Nevertheless, it is reasonable to expect actual MoS₂ samples to contain sulfur defects despite the relative defect concentration possibly varying by methods, such as CVD, PVD, and chemical exfoliation.¹⁰ Experimentally, we were able to observe these defects whose triplet ground states are evident in the dark-EPR results (Figure R1). Surprisingly, DDT/MoS₂ also exhibits significant EPR signals compared to that of pristine DDT. This possibly indicates that unpaired electrons stemming from sulfur defects transfer and hybridize with DDT, introducing triplet ground states into the DDT/MoS₂ heterostructure.

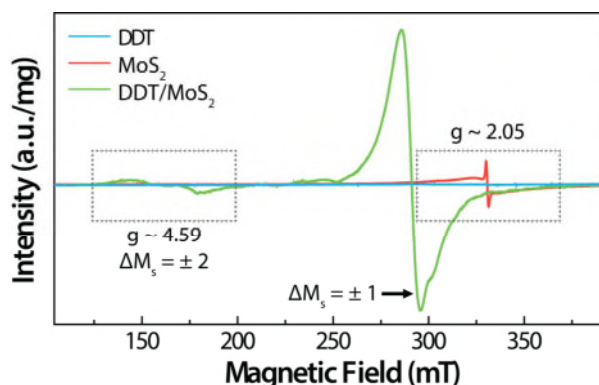


Figure R1. CW-EPR spectra of DDT, MoS₂, and DDT/MoS₂ in dark conditions.

To support this, a computational study was conducted in which sulfur defects were modeled as a high-spin triplet state on a 2×2 MoS₂ surface with a sulfur removed, and the system was kept at a neutral charge. In the absence of electronic interaction with DDT, the spin density on the defective MoS₂ should be exactly 2. However, with DDT present, the spin density on MoS₂ was 1.99 e⁻, and the spin density on DDT was 0.009 e⁻. This sharing of spin density with DDT indicates significant electronic coupling, likely promoting triplet ground states in the DDT/MoS₂ hybrid system. Thus, it is reasonable to infer that its emission undergoes an allowed transition, which is the most favorable route (Figure R2).

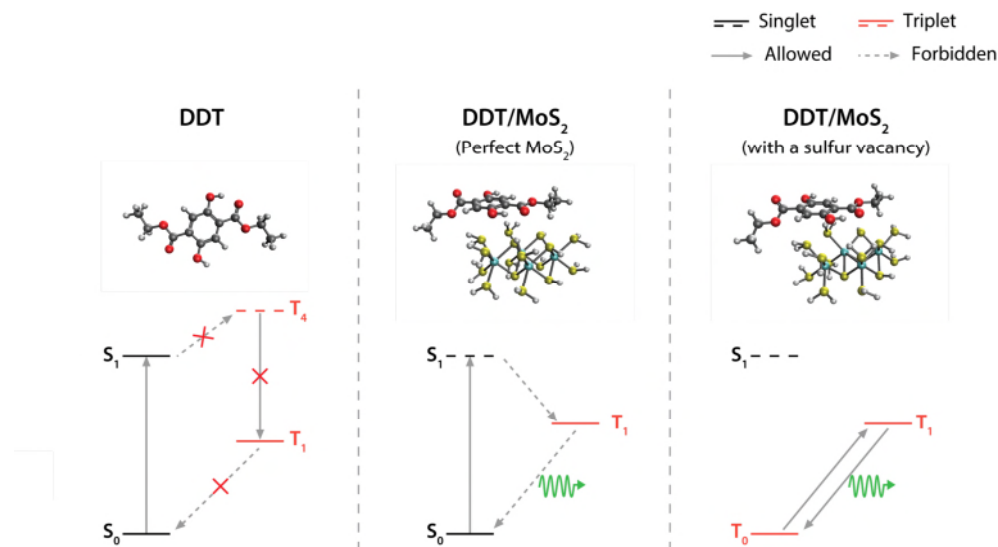


Figure R2. Energy band diagrams of DDT, DDT/perfect MoS₂, and DDT/MoS₂ containing a sulfur defect.

We attempted to compute the excited energy states of (n, π^*) and (π, π^*) transitions when the triplet ground states in this hybrid model were subjected to the introduction of a sulfur vacancy in the 2×2 MoS₂ basal plane. However, we encountered limitations with the TADFT software and were unable to proceed. We aim to explore this further in follow-up work, provided we identify software capable of performing these functions. We eagerly look forward to future opportunities to do so.

In conclusion, we believe that both factors collectively contribute to the enhanced SOC and promotion of microsecond RTP in the photophysical dynamics of the hybrid system, as the close proximity of DDT and MoS₂ facilitates intermolecular interaction at the interface. The dominance of either factor in dictating the entire radiative transitions likely depends on the concentration of sulfur defect on the MoS₂ basal plane. If allowed transitions are feasible, they would be the main features; however, the involvement of sulfur vacancies and the relative portion of antisite defects also play significant roles. It's worth noting that the MoS₂ samples used in our work were prepared by a liquid-exfoliation method^{12,13} that is recognized to create sufficiently low sulfur defects. As pointed out by Editor and Reviewer#2, we agree that addressing the influence of triplet ground states in DDT/MoS₂ is crucial for a solid, consistent interpretation of this unique phenomenon. The manuscript and supporting information have been revised accordingly, with the revisions highlighted in yellow.

References

1. Cai, S. *et al.* Enabling long-lived organic room temperature phosphorescence in polymers by subunit interlocking. *Nat. Commun.* **10**, 4247 (2019).
2. Kenry, Chen, C. & Liu, B. Enhancing the performance of pure organic room-temperature phosphorescent luminophores. *Nat. Commun.* **10**, 2111 (2019).
3. Shi, H. *et al.* Highly Efficient Ultralong Organic Phosphorescence through Intramolecular-Space Heavy-Atom Effect. *J. Phys. Chem. Lett.* **10**, 595–600 (2019).
4. Xiao, D., Liu, G.-B., Feng, W., Xu, X. & Yao, W. Coupled Spin and Valley Physics in Monolayers of MoS₂ and Other Group-VI Dichalcogenides. *Phys. Rev. Lett.* **108**, 196802 (2012).
5. Gmitra, M. & Fabian, J. Graphene on transition-metal dichalcogenides: A platform for proximity spin-orbit physics and optospintronics. *Phys. Rev. B* **92**, 155403 (2015).
6. Wang, Z. *et al.* Strong interface-induced spin–orbit interaction in graphene on WS₂. *Nat. Commun.* **6**, 8339 (2015).
7. Zhou, B. T., Taguchi, K., Kawaguchi, Y., Tanaka, Y. & Law, K. T. Spin-orbit coupling induced valley Hall effects in transition-metal dichalcogenides. *Commun. Phys.* **2**, 26 (2019).
8. Avsar, A. *et al.* Spin–orbit proximity effect in graphene. *Nat. Commun.* **5**, 4875 (2014).
9. Ouyang, Y., Zhou, Y., Zhang, Y., Li, Q. & Wang, J. Double-edged roles of intrinsic defects in two-dimensional MoS₂. *Trends Chem.* **4**, 451–463 (2022).
10. Hong, J. *et al.* Exploring atomic defects in molybdenum disulphide monolayers. *Nat. Commun.* **6**, 6293 (2015).
11. Tsai, J.-Y., Pan, J., Lin, H., Bansil, A. & Yan, Q. Antisite defect qubits in monolayer transition metal dichalcogenides. *Nat. Commun.* **13**, 492 (2022).
12. Eda, G. *et al.* Photoluminescence from Chemically Exfoliated MoS₂. *Nano Lett.* **11**, 5111–5116 (2011).
13. Kumar, R. R. *et al.* Sulfur Monovacancies in Liquid-Exfoliated MoS₂ Nanosheets for NO₂ Gas Sensing. *ACS Appl. Nano Mater.* **4**, 9459–9470 (2021).

Reviewer #2 (Remarks to the Author):

I appreciate the effort the authors have gone to in order to elucidate the spin-triplet ground state seen in the EPR measurements. I think that the hypothesis the authors have provided about sulphur vacancy defect sites on the TMD is interesting and reasonable, and I look forward to their future work on studying this in more detail. I would now be pleased to recommend acceptance of the manuscript.

One minor point:

About the origin of the triplet ground state, the authors say: 'However, it is clear that if sulfur vacancies are too prevalent, this spin-allowed transition would dominate the entire emission process, potentially leading to longer emissive decays.'

This statement is flawed, as if the spin-allowed triplet to triplet (T_1-T_0) radiative transition dominated, I would expect the emissive decay time to be faster than the formally spin-forbidden T_1-S_0 phosphorescence, even with significant SOC. I'd recommend to authors to remove this statement from the final version of the manuscript.

Response Letter

Journal: Nature Communications

Manuscript ID: NCOMMS-23-53080-T

Title: Ultrafast Microsecond Organic Triplet Emitters via Spin Orbit Proximity Effect by Hybridizing Organic Chromophores on Transition Metal Dichalcogenides

Response to the Reviewers' Comments

Reviewer #2 (Remarks to the Author):

I appreciate the effort the authors have gone to in order to elucidate the spin-triplet ground state seen in the EPR measurements. I think that the hypothesis the authors have provided about sulphur vacancy defect sites on the TMD is interesting and reasonable, and I look forward to their future work on studying this in more detail. I would now be pleased to recommend acceptance of the manuscript.

One minor point:

About the origin of the triplet ground state, the authors say: 'However, it is clear that if sulfur vacancies are too prevalent, this spin-allowed transition would dominate the entire emission process, potentially leading to longer emissive decays.'

This statement is flawed, as if the spin-allowed triplet to triplet (T1-T0) radiative transition dominated, I would expect the emissive decay time to be faster than the formally spin-forbidden T1-S0 phosphorescence, even with significant SOC. I'd recommend to authors to remove this statement from the final version of the manuscript.

Answer: We deleted the sentence as Reviewer 2 suggested.