Singlet oxygen is an emissive ligand†

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Unprecedented experimental evidence shows that gaseous singlet oxygen (1O2) acts as an emissive ligand following collisional photosensitization. This evidence was obtained by monitoring 1O2 phosphorescence intensity at \( \approx 1275–1280 \) nm and the excited state lifetime of singlet oxygen generated by known tetraphenylporphyrin photosensitizers, while varying the atmospheric environment.

Singlet oxygen (specifically \( O_2(1\Delta_g) \), hereafter \( ^1O_2 \)) is the first electronic excited state of the dioxygen molecule\(^1,3\) and has been known as a strong oxidizing agent for decades, with recent studies demonstrating a rich potential of applications in a wide variety of fields, including cancer therapy\(^4\) and antimicrobial activity.\(^5\) While \( ^1O_2 \) can be prepared in several ways, the most popular is photosensitization, a catalytic means of using ambient or supplied light, absorbed by an intermediate molecule, the photosensitizer (PS), whose triplet excited state (\( ^3PS^* \)) is quenched by ground state dioxygen (\( O_2(\Sigma_g^+) \)), hereafter \( ^3O_2 \).\(^6,8\) This Dexter-type energy transfer\(^9,10\) requires such proximity between \( ^3PS^* \) and \( ^3O_2 \) that a collision is all but implied. Photosensitization often readily occurs in solution from dissolved PS and \( ^3O_2 \) (homogeneous process) but also at the solid–gas interfaces. Crystallographic elucidations and computational analyses have also been conducted on the subject,\(^14\) establishing the possibility of a transient complexed state as the energy transfer takes place (eqn (1) or (4) in ref. 14) when zinc(II) porphine (ZnP) is used as photosensitizer. A kinetic study of the homogeneous process also suggests the existence of transient complexxes in freebase tetraphenylporphyrin and several other entirely organic photosensitizers.\(^14,15\)

\[
^3ZnP + ^1O_2 \rightarrow ^1(^3ZnP^3O_2) \rightarrow ^1(^3ZnP^1O_2) \rightarrow ^1(^3ZnP^1O_2) \\
\rightarrow ^3ZnP + ^1O_2  
\]

We herein report three pieces of evidence showing \( ^1O_2 \) phosphorescence from a coordinated species, \([ZnTPP] \leftrightarrow (^1O_2) \) formed following heterogeneous photosensitization, here at the solid–gas interface. This assessment was conducted with MTTP photosensitizers (\( M = 2H^+ (H_2TPP), Zn (ZnTPP), Pd (PdTTP); TPP = 5,10,15,20-tetraphenylporphyrin) \) while varying the composition of the atmosphere (air, pure \( O_2 \) (pure \( Ar \)), MeOH vapour) and monitoring the intensity and lifetime of the \( ^1O_2 \) phosphorescence band using the general set-up described in Fig. S2 (ESI†). Past and original DFT computations support these new findings.

**Preliminary tests:** first, \( ^1O_2 \) phosphorescence from dilute ZnTPP solutions in DCM and MeOH was recorded to demonstrate that both solvents allow \( ^1O_2 \) phosphorescence, and therefore must allow prior photosensitization (Fig. S1, ESI†). The emission band observed at \( \approx 1275 \) nm is consistent with those typically reported in the literature.\(^16\) The \( ^1O_2 \) excitation spectra appear like the absorption spectrum of ZnTPP, meaning that more singlet oxygen is produced as ZnTPP absorbs more photons, and in turn produces more populated excited states able to transfer energy to \( ^3O_2 \). This proves that ZnTPP is acting as the photosensitizer. It is noteworthy that the \( ^1O_2 \) emission signal is roughly 15× weaker in MeOH than in DCM, suggesting a significant level of static quenching in the former solvent: MeOH does not quench \( ^1O_2 \) itself, but rather hinders its generation, likely by coordinating the Zn(II) atom and generating steric hindering.

**Atmosphere cycling experiment:** the detailed description can be found in the ESI†. A sealed 10 × 10 mm quartz cuvette containing drop-cast ZnTPP was analysed by measuring \( ^1O_2 \) phosphorescence intensity in a pure oxygen atmosphere,
followed by argon, air, then methanol-saturated air, and finally methanol-saturated oxygen (Fig. 1). A fresh dry sample under pure O₂ produced the highest intensity. After purging the cuvette with argon, the signal significantly decreased but did not disappear completely. The cuvette was then purged with air, and the signal intensity increased. Following this, the introduction of MeOH-saturated air resulted in a slow but complete disappearance of ¹O₂ phosphorescence. Finally, purging with MeOH-saturated O₂ vapour, a very slight signal increase was noted, however considering noise levels, it cannot be confidently attributed to signal resurgence.

**Analysis:** We know from X-ray structures of metalated porphyrins that MeOH and, in two reported cases, presumably triplet O₂ can bind lone, heavily distorted and sterically hindered zinc porphyrins. PCN-224-Fe(II)-O₂, with the framework itself generating steric hindering, has also been reported. Knowing this, there is a compelling case to be made that the behavior described by Fig. 1 is that of a coordination complex: the observation of a residual signal in the argon atmosphere after any gaseous O₂ is carried away, followed by its disappearance when MeOH is present, indicates the presence of a relatively stable intermediate. As any gaseous O₂ would be carried away upon successive argon purges, the remaining option for ¹O₂ persisting in the cuvette is the existence of this intermediate, the most likely form of which is coordinated [ZnTPP-O₂]. Methanol, whilst known to be a weak ligand, is stronger than O₂. Its introduction in the cell allows it to slowly replace any coordinated O₂, thus preventing its subsequent photosensitization, explaining the slow and complete disappearance of ¹O₂ phosphorescence over 5–10 min (Fig. 2).

**Excited state lifetime measurements:** Two other pieces of evidence are obtained upon changing the metallic site (M = 2H⁺, Zn(II), Pd(II)): first, when comparing ZnTPP and H₂TPP, a significant decrease in signal intensity is observed, and the position of the ¹O₂ emission band changes from 1280 to 1275 nm respectively (Fig. 3A). This shift suggests a change in the environment of ¹O₂, which can be explained by the coordinated vs. non-coordinated variants of ¹O₂.

Second, the presence of a metal results in a significant increase in one of the lifetime components (Fig. 3B and Table 1). All three porphyrins show a component in the roughly 10 μs range, and another at 5 μs, 218 μs, and 74 μs for H₂-, Zn-, and PdTPP respectively. The microsecond values are perfectly coherent with known and documented values recorded from solution and solid-state samples, and are still well within the theoretically predicted and experimentally observed purely gas-phase maxima going to full second (direct from EPR and calculated from diffusion distance). The changes in band position and lifetime duration can be explained by the change in ¹O₂’s interfacial environment (metal coordination vs. H-bonding). This further supports the ¹O₂ ligand explanation.

While the nature of the [ZnTPP-¹O₂] emissive compound is now convincingly proven, two questions remain: first, our experiments cannot determine whether coordination occurs...
before photosensitization (ligand is $^3$O$_2$, eqn (2)) which we call early coordination, or after photosensitization (ligand is $^1$O$_2$, eqn (3)) which we designate late coordination. Note that these possibilities are not mutually exclusive. Second, emissive lifetimes do not follow the trend expected of the heavy-atom effect: the long ZnTPP lifetime, while minor, is roughly 3× that of PdTPP.

$$\text{PS} \xrightarrow{^3\text{O}_2} \left[ \text{PS} + ^3\text{O}_2 \right] \xrightarrow{\text{hv}} \left[ ^1\text{PS}^* + ^3\text{O}_2 \right]$$

$$\xrightarrow{\text{ISC}} \left[ ^1\text{PS}^* + ^3\text{O}_2 \right] \xrightarrow{\text{EnT}} \left[ \text{PS} + ^1\text{O}_2 \right]$$

$$\text{PS} \xrightarrow{\text{hv}} ^1\text{PS}^* \xrightarrow{\text{ISC}} ^3\text{PS}^* \xrightarrow{^3\text{O}_2} \text{PS} + ^1\text{O}_2 \rightarrow \left[ \text{PS} + ^1\text{O}_2 \right]$$

Rusidy et al.$^{14}$ painted part of the picture in 2012 with their computations simulating the transition state of the photosensitization process. They determined that early coordination is plausible on zinc porphine, leading to a coordinated transition state and a stronger coordination bond following energy transfer, summed-up by eqn (1) and Fig. S2 (ESI†). They determined that the pre-energy transfer [$^7\text{ZnP}^* + ^3\text{O}_2$] Zn–O bond length was 2.948 Å, while the post-energy transfer [$^7\text{ZnP}^* + ^3\text{O}_2$] Zn–O bond length had reduced to 2.411 Å. These distances are longer than the resolved Zn–O distances of O$_2$ (2.08 Å) and MeOH (2.12 Å) in the saddle-shaped and sterically hindered zinc porphyrins complexes reported by Zhou et al.$^{12}$ Table S1 (ESI†) summarizes relevant compounds in the literature.

We have attempted to imitate Rusidy’s computations using undistorted ZnTPP. Our calculated intermolecular interactions between optimized geometries of $^7\text{ZnP}^* + ^3\text{O}_2$ (S$_0 + T_0$, both ground states), $^7\text{ZnP}^* + ^3\text{O}_2$ (T$_1 + T_0$, before energy transfer), and $^1\text{ZnTPP} + ^1\text{O}_2^*$ (S$_0 + T_0$, after energy transfer), hereafter identified [$^7\text{ZnP}^* + ^3\text{O}_2$]. They resulted in Zn–O distances of 3.05 Å, 3.08 Å, and 2.36 Å respectively. The first two distances are in good agreement with Rusidy’s 2.948 Å for triplet oxygen, which indicate very weak, if any interaction between the porphyrins and $^3$O$_2$, and 2.36 Å also compares well with Rusidy’s 2.411 Å between porphyrin and $^1$O$_2$, indicating weak coordination. $^1\text{ZnTPP} + ^1\text{MeOH}$ (S$_0 + S_1$) was optimized as well (hereafter [$^1\text{ZnTPP} + ^1\text{MeOH}$]), resulting in a Zn–O distance of 2.30 Å (comparable to the 2.12 Å Zhou et al.$^{12}$ and the 2.07 Å Zhang et al.$^{13}$ obtained by X-ray), meaning that the ZnTPP–MeOH bond is slightly stronger than the ZnTPP–$^3$O$_2$ bond. This suggests that while both early and late coordination are plausible, late coordination seems more likely.

The calculated $\Delta E$ (Fig. 4) between $^7\text{ZnP}^* + ^3\text{O}_2$ and $^7\text{ZnP}^* + ^3\text{O}_2$ is 1.58 eV, corresponding to a 0–0 transition at 785 nm, which compares well to experimental results,$^{20}$ at 77 K in toluene, which record the transition at 770 nm. After energy transfer, the forming of the [$^7\text{ZnP}^* + ^3\text{O}_2^*$] complex’s Zn–O bond seems indeed a downhill process by 0.17 eV, or 16.4 kJ mol$^{-1}$, which is in the magnitude of H-bonding strength.

As to the second question of why the $^1$O$_2$ phosphorescence lifetime does not follow the trend expected of the heavy atom effect, hypotheses remain mostly speculative. The fact that the Zn–O distance is anticipated to be long may decrease the effect of spin–orbit coupling. It is also possible that we see both the coordination (or H-bonding for H$_2$TPP) component of the lifetime (variable) and non-interaction component ($\approx$ 10 µs) of $^1$O$_2$. Finally, the limited number of points (fastest binning is 1 µs due to hardware limitations) undoubtedly influences the quality of the fit, and by extension the exact values.

### Table 1

<table>
<thead>
<tr>
<th>H$_2$TPP</th>
<th>ZnTPP</th>
<th>PdTPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3 ± 0.9</td>
<td>10.0 ± 0.5</td>
<td>9.8 ± 0.5</td>
</tr>
<tr>
<td>9.6 ± 1.5</td>
<td>218 ± 0.5 (minor)</td>
<td>73.8 ± 0.5</td>
</tr>
</tbody>
</table>

The uncertainties stem from the fitting model: the lower limit of binning was 1 µs, so very few points were available for H$_2$TPP, resulting in higher uncertainties. *The data presented in this table has already been published in ref. 16.

![Fig. 3](image-url) (A) Comparison of the $^1$O$_2$ phosphorescence signal intensity at the solid-state/gas interface of H$_2$TPP and ZnTPP samples (pure O$_2$). (B) Comparison of the normalized $^1$O$_2$ phosphorescence decays of H$_2$TPP, ZnTPP and PdTPP samples, pure O$_2$. *The data presented in subfigure B has already been published in ref. 16.
We have reported spectra showing the persistence of interfacial singlet oxygen (1O₂(g)) phosphorescence in an argon atmosphere, followed by signal extinction when methanol vapors are introduced in an air atmosphere. This behavior proves the existence of an emissive coordinated complex, either occurring (late coordination) or persisting (early coordination) after the heterogeneous photosensitization process, which is then broken by competition from the comparatively stronger MeOH ligand. Rare crystal structures and excited-state lifetime measurements support the existence of this complex, and while DFT seem to point toward the late coordination being more likely, the current level of experimental evidence cannot distinguish between the early and late coordination hypotheses. EPR measurements might help in this regard, as it could enable one to distinguish between non-coordinating and coordinating 1O₂ and 3O₂. If future experiments determine that the reported behavior is not unique to Zn, a better understanding of 1O₂(g)’s interactions with metal-containing molecules could enable some of control over its diffusion distance, and by extension, over its action radius. The action of MeOH also demonstrates that it is possible to disable singlet oxygen production in an environment where the presence of oxygen and light are otherwise favorable to photosensitization. Finally, O₂’s loss of molecular symmetry when acting as a ligand is certain to break the degeneracy of its π orbitals, leading to new electronic behaviours which may in time prove useful.

P. Asselin: conceptualization, formulating methodology performing experiments, data treatment, analysis of results, literature review, writing and proofreading manuscript; A. Schlachter: formulating methodology, performing experiments, analysis of results, proofreading manuscript; P. D. Harvey: conceptualization, analysis of results, literature review, writing and proofreading manuscript, funding acquisition, overall supervision of the work.

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Data availability
The data supporting this article has been included as part of the ESI.† The data presented in Fig. 4B and Table 1 is reused from Schlachter et al. https://doi.org/10.1002/adfm.202404111.

Conflicts of interest
There are no conflicts to declare.

Notes and references
† Safety: see ESI for safety details.