Electronic Supplementary Information for

Lifetime and diffusion distance of singlet oxygen

under atmospheric conditions

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I. Supplementary Methods

Supplementary Method 1 | Derivation of eqns (3) and (4)

In this method, we derive eqns (3) and (4) in the main text from the reaction-diffusion equations given in eqns (1) and (2). The Laplace transform of eqn (1) is given by

$$s\hat{R}(x,s) = D\partial_x^2\hat{R}(x,s) - \gamma\hat{R}(x,s) + \delta(x)\frac{P_0}{s} - \delta(x-L)\hat{\alpha}(s), \tag{S1-1}$$

where $\alpha(t) = \kappa C(L,t)R(L,t)$. In terms of the Green′s function, defined by $\hat{G}(x,s\,|\,x_0) = [s - D\partial_x^2]^{-1}\delta(x-x_0)$, we obtain the analytic expression of $\hat{R}(x,s)$ from eqn (S1-1) as follows:

$$\hat{R}(x,s) = \frac{P_0}{s}\hat{G}(x,s+\gamma\,|\,0) - \hat{G}(x,s+\gamma\,|\,L)\hat{\alpha}(s). \tag{S1-2}$$

Here, this Green′s function, $\hat{G}(x,s\,|\,x_0)$, satisfies the same boundary conditions as $\hat{R}(x,s)$, which are the reflecting boundary conditions, $\partial_x\hat{G}(x,s\,|\,x_0)\big|_{x=0} = \partial_x\hat{G}(x,s\,|\,x_0)\big|_{x=L} = 0$. Noting that $dC(L,t)/dt = -\alpha(t)$ from eqn (2) and assuming that the concentration of DPBF is in excess, i.e., $C(L,t) \cong C_0$, we represent $\hat{\alpha}(s)$ as

$$s\hat{C}(L,s) - C_0 = -\hat{\alpha}(s) \cong -\kappa C_0\hat{R}(L,s), \tag{S1-3}$$

with C_0 denoting the initial density of DPBF on the glass surface. Substituting eqn (S1-3) into eqn (S1-2), we obtain

$$\hat{R}(x,s) = \frac{P_0}{s}\hat{G}(x,s+\gamma\,|\,0) - \kappa C_0\hat{R}(L,s)\hat{G}(x,s+\gamma\,|\,L). \tag{S1-4}$$

Substituting L in place of x in eqn (S1-4) and solving the resulting equation for $\hat{R}(L,s)$, we obtain the formal expression of $\hat{R}(L,s)$ as

$$\hat{R}(L,s)=\frac{P_0\hat{G}(L,s+\gamma\,|\,0)}{s\left[1+\kappa C_0\hat{G}(L,s+\gamma\,|\,L)\right]}. \tag{S1-5}$$

By definition, this Green′s function satisfies $\left[s-D\partial_x^2\right]\hat{G}(x,s\,|\,x_0)=\delta(x-x_0)$ with the reflecting boundary conditions $\partial_x\hat{G}(x,s\,|\,x_0)\Big|_{x=0}=\partial_x\hat{G}(x,s\,|\,x_0)\Big|_{x=L}=0$. The analytic expression of this Green′s function can be obtained as

$$\hat{G}(x,s\,|\,x_0)=\frac{1}{2Dz}\frac{e^{z[2L-(x_0+x)]}+e^{z(x_0+x)}+e^{z(2L-|x-x_0|)}+e^{z|x-x_0|}}{e^{2zL}-1}, \tag{S1-6}$$

where $z=\sqrt{s/D}$.

Substituting eqn (S1-6) into eqn (S1-5), we obtain the following analytic expression of $\hat{R}(L,s)$:

$$\hat{R}(L,s)=\frac{1}{s}\frac{P_0\,\mathrm{csch}(z'L)}{Dz'+C_0\kappa\coth(z'L)}, \tag{S1-7}$$

where $z'=\sqrt{(s+\gamma)/D}$. By solving eqn (2) in the main text, we can easily arrive at the analytic expression of $C(L,t)/C_0$ in terms of $R(L,t)$,

$$C(L,t)/C_0=\exp\left[-\int_0^t d\tau\kappa R(L,\tau)\right]. \tag{S1-8}$$

To extract the lifetime of singlet oxygen from the experimental results shown in Fig. 2 using our theoretical model, we first extract the value of P_0/C_0 from the experimental data

obtained for the case where $L = 0$. The small L limit expression of eqn (S1-8) is given by

$$\lim_{l \to 0} C(L,t) = C_0 \exp\left[-\frac{P_0}{C_0} t \right]. \tag{S1-9}$$

Given the extracted value of P_0/C_0 ($\cong 3.99 \times 10^{-3}$ min^{-1}), we can represent eqn (S1-8) using two unknown parameters κC_0 and γ, as the value of D was previously reported. To determine the optimal values of the adjustable parameters, we perform the numerical inverse Laplace transform of eqn (S1-7) using the Stehfest algorithm[1], substitute the result into eqn (S1-8), and find the parameter values that best explain the experimental data shown in Fig. 2.

Supplementary Method 2 | Reaction-diffusion equation accounts two relaxation pathway of DPBF

Here, we consider a more sophisticated model that accounts for the DPBF-induced non-radiative relaxation of singlet oxygen in addition to the non-radiative quenching of singlet oxygen by gas molecules in the air and the chemical reaction of singlet oxygen with DPBF at the detector. For this model, the reaction-diffusion equations are given by

$$\frac{\partial}{\partial t}R(x,t) = D\frac{\partial^2}{\partial x^2}R(x,t) - \gamma R(x,t) + \delta(x)P_0 - (\kappa+\kappa')\delta(x-L)C(L,t)R(L,t) \tag{S2-1}$$

$$\frac{d}{dt}C(L,t) = -\kappa C(L,t)R(L,t) \tag{S2-2}$$

where κ' denotes the rate constant associated with the DPBF-induced non-radiative deactivation of singlet oxygen. Other symbols have the same meanings as those in eqn (1). By solving eqn (S2-1) and (S2-2), we can obtain the analytic expression for the DPBF concentration at the detector, $C(L,t)$. $C(L,t)/C(L,0)$ $(\equiv C(t)/C_0)$ is given by

$$\frac{C(t)}{C_0} = \exp\left[-\kappa\int_0^t d\tau R(L,\tau)\right], \tag{S2-3}$$

where the singlet oxygen concentration, $R(L,t)$, at position $x = L$ being given by

$$\hat{R}(L,s) = \frac{1}{s}\frac{P_0\,\mathrm{csch}(z'L)}{Dz' + C_0(\kappa+\kappa')\coth(z'L)} \tag{S2-4}$$

in the Laplace domain. As in the main text, s denotes the Laplace variable and $z' = \sqrt{(s+\gamma)/D}$. In the small L limit, eqn (S2-4) reduces to

$$\lim_{L\to 0}\frac{C(t)}{C_0} = \exp\left[-\frac{P_0}{C_0}\frac{\kappa}{\kappa+\kappa'}t\right] \tag{S2-5}$$

By analyzing our experimental data obtained for $L = 0$ using eqn (S2-5) , we can extract the value of $P_0\kappa \big/ \left[C_0 \left(\kappa + \kappa' \right) \right]$, which is found to be $3.99 \times 10^{-3}\ \mathrm{min}^{-1}$. With this information at hand, we can quantitatively explain the experimental data shown in Fig. 2 obtained for various values of L, using eqn (S2-3) with two adjustable parameters, γ and $P_0\kappa$. The optimized values of these parameters are $\gamma = 0.341 \mathrm{sec}^{-1}$ and $\kappa P_0 = 1.51 \times 10^{-6}\ \mathrm{cm}/\mathrm{sec}^2$. The lifetime of singlet oxygen is estimated by $\gamma^{-1} \cong 2.94$ sec, which is in good agreement (within 5%) with the singlet oxygen lifetime, 2.80 sec, extracted by our analysis using the simpler model.

II. Supplementary Figures

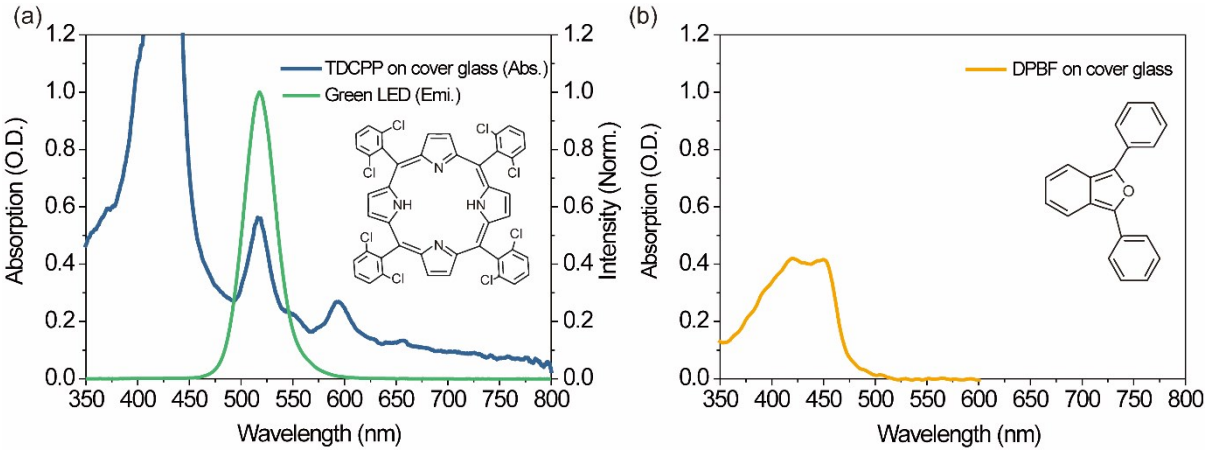

Fig. S1. Steady-state UV absorption spectrum of (a) meso-tetra (o-dichlorophenyl) porphine (TDCPP) and (b) 1,3-diphenylisobenzofuran (DPBF). 512 nm Q band of the TDCPP overlaps with the emission spectrum of the green LED. Singlet oxygen can be generated by photo-activated TDCPP by illuminating the green LED. DPBF has an absorption band of 415 nm.

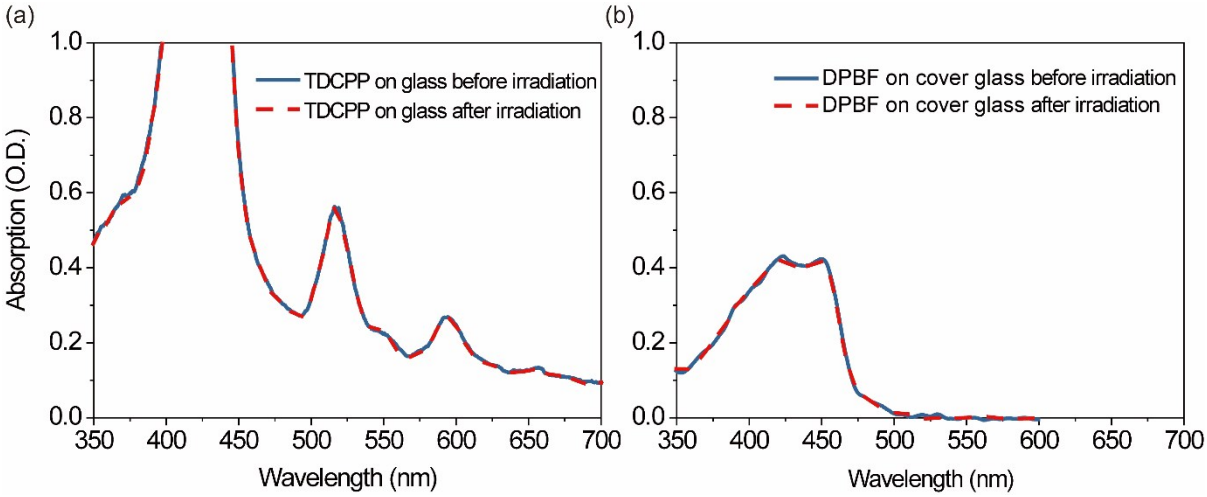

Fig. S2. Photodecomposition test of (a) TDCPP and (b) DPBF on the cover glass. Both TDCPP and DPBF do not decompose when separately exposed to green LED irradiation for 2 hours.

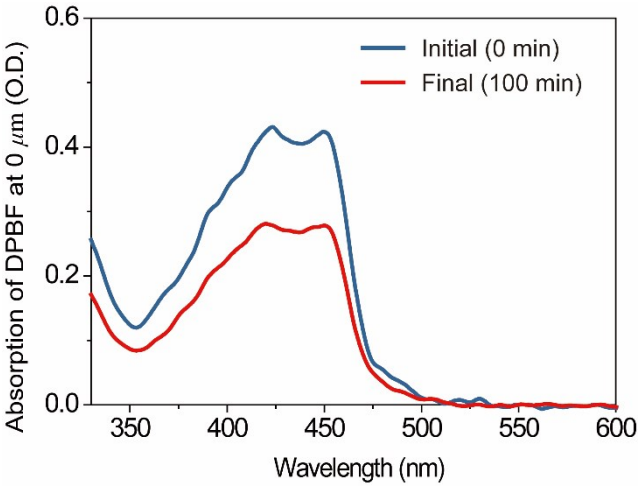

Fig. S3. Absorption spectrum of 1,3-diphenylisobenzofuran (DPBF) before (0 min) and after (100 min) reaction with singlet oxygen. The peak of 415 nm diminishes as DPBF′s bimolecular reaction with singlet oxygen continues.

III. Supplementary Reference

1. H. Stehfest, *Commun. ACM*, 1970, **13**, 47-49.