

Electronic Supplementary Information

Comparison study on the influences of the central metal ions in palladium(II)- and gadolinium(III)-porphyrins for phosphorescence-based oxygen sensing

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I. Structural characterization and the purity of Gd-HMME and Pd-HMME

The structures and purity of these metalloporphyrins were confirmed by mass spectrometry, UV-visible, and Fourier transform infrared (FTIR) spectroscopy.

Figure S1 shows the mass spectrum of Gd-HMME. The mass spectrum was recorded on liquid chromatography/mass spectra (LC/MS) analyzing system (Thermo Finnigan Surveyor LCQ DECA XP plus, USA). The $[M+H]^+$ peak of Gd-HMME appears at about 803.27, which corresponds to the signal of Cl-Gd-HMME.

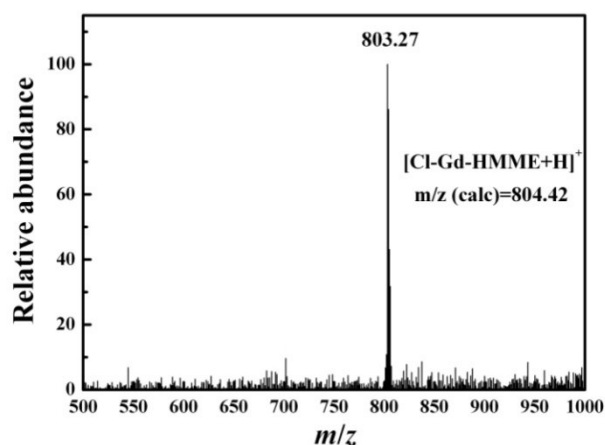


Figure S1. Mass spectrum of Gd-HMME (positive mode). $[Cl-Gd-HMME+H]^+$: Gd-HMME molecule with a chloride ion and proton.

The structure of Gd-HMME was also confirmed by FTIR spectroscopy (Fig. S2). The FTIR spectra (KBr pellets) were recorded on a Varian Excalibur HE 3100 spectrometer. The typical N–H vibration (about 3311 cm^{-1}) for porphyrin free base disappeared in the FTIR spectrum of Gd-HMME.

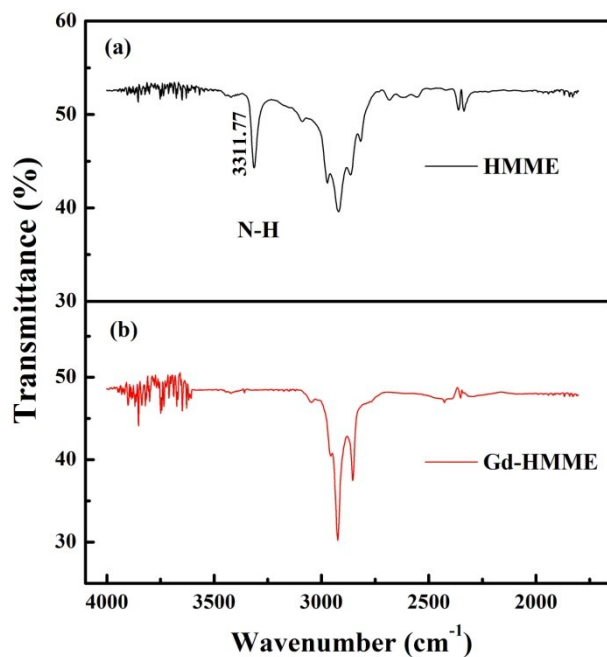


Figure S2. FTIR spectra of HMME and Gd-HMME.

The absorption spectra of HMME and Gd-HMME are shown in Fig. S3(a) and (b). It can be seen that HMME has four absorption Q bands while Gd-HMME has two Q bands (Pd-HMME also has two Q bands). This certifies the success of our synthesis.

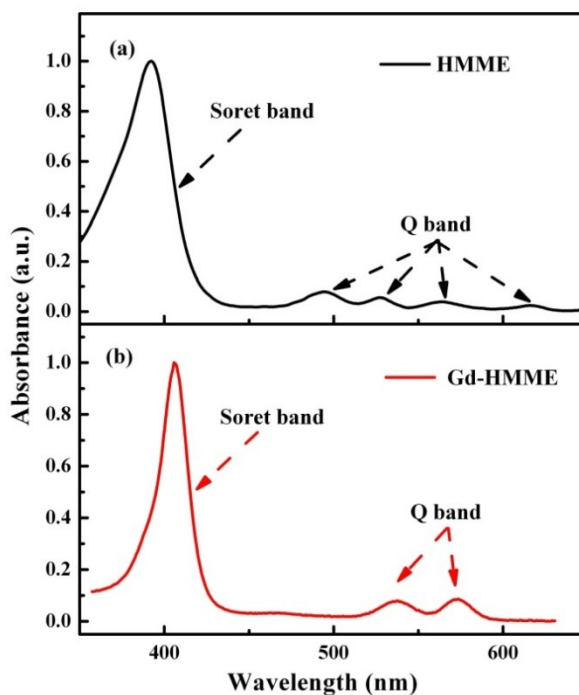


Figure S3. Typical normalized UV-visible absorption spectra of HMME (a) and Gd-HMME (b) in methanol solutions.

Furthermore, in the process of the synthesis of Gd-HMME and Pd-HMME, excess

anhydrous GdCl_3 and PdCl_2 were used. The absorption features of HMME were not found in the absorption spectrum of the corresponding metalloporphyrins. Therefore, we believe almost all HMME molecules were transferred to metalloporphyrins.

II. The measurements for the lifetime of phosphorescence

To determine the lifetime of phosphorescence, decay profile was measured. A square wave was given to a diode laser controller (Thorlabs ITC510) to control a diode laser centered at 405 nm (Thorlabs TCLDM9). Photoluminescence signals were recorded by a grating spectrometer (Zolix Omni- λ 300) and amplified by a photomultiplier tube (Zolix PMTH-S1-R212) with a high voltage power supply (Zolix HVC1800). The time-resolved signal was averaged with a digital phosphor oscilloscope (Tektronix DPO5054) and the decay curve was sent to a personal computer for lifetime determination. The lifetime evaluation was performed by fitting the decay curve to an exponential function using adjustable parameters.

III. Measurement of absolute phosphorescence quantum yields on filter paper

The phosphorescence quantum yields (QYs) of Pd- and Gd-HMME on filter paper were measured using an integrating sphere and an absolute method described in a previous work.^{S1} The integrating sphere used in this work was the Labsphere 3.3 inch reflective sphere with a reflectivity of more than 99%. A halogen standard lamp was used to calibrate the measuring system. A 405 nm laser diode was used as the excitation source. The absolute quantum yield of phosphorescence can be defined by Equation S1.

$$\Phi_p = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} \quad (\text{S1})$$

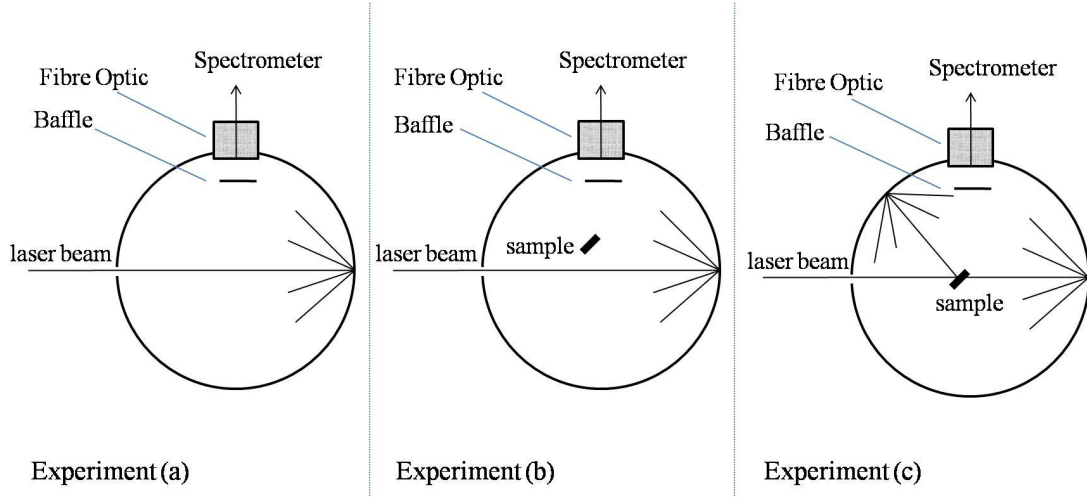


Figure S4. Diagram illustrating the three configurations of the sphere required for the efficiency measurement: a) the sphere is empty; b) the sample is in place and the laser beam is directed onto the sphere wall; c) the sample is in place and the laser beam is directed onto the sample.^{S1}

The measurement procedure for the quantum efficiency can be described as follows: L_a , L_b , and L_c are the photon numbers detected for the excited sources in experiments (a), (b), and (c), respectively, as shown in Figure S4. P_b and P_c are the photon numbers detected in experiments (b) and (c), as shown in Figure S4. A donates the sample absorption rate to the laser. μ is the fraction of the laser light scattered from the sphere wall absorbed by the sample. We can therefore write Equations S2 and S3.

$$L_b = L_a(1 - \mu) \quad (\text{S2})$$

$$L_c = L_b(1 - \mu)(1 - A) \quad (\text{S3})$$

From these equations, we obtain an expression for the absorption coefficient, A (Eq. S4).

$$A = 1 - \frac{L_c}{L_b} \quad (\text{S4})$$

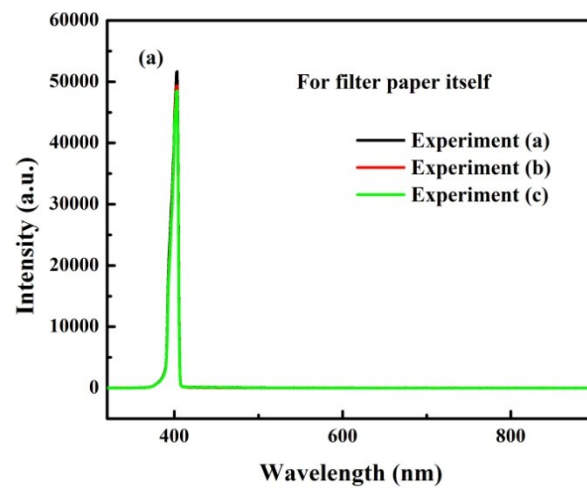
In experiment (c), the contribution of scattered laser light to the measurement spectra can be given as: $(1-A)(L_b+P_b)$. The contribution of the absorption of collimated laser light to the profile measured can be given as: $\Phi_p L_a A$. The total intensity of experiment

(c) can be described by Equation S5.

$$L_c + P_c = (1 - A)(L_b + P_b) + \Phi_p L_a A \quad (\text{S5})$$

Then, we find Equation S6.

$$\Phi_p = \frac{P_c - (1 - A)P_b}{L_a A} \quad (\text{S6})$$



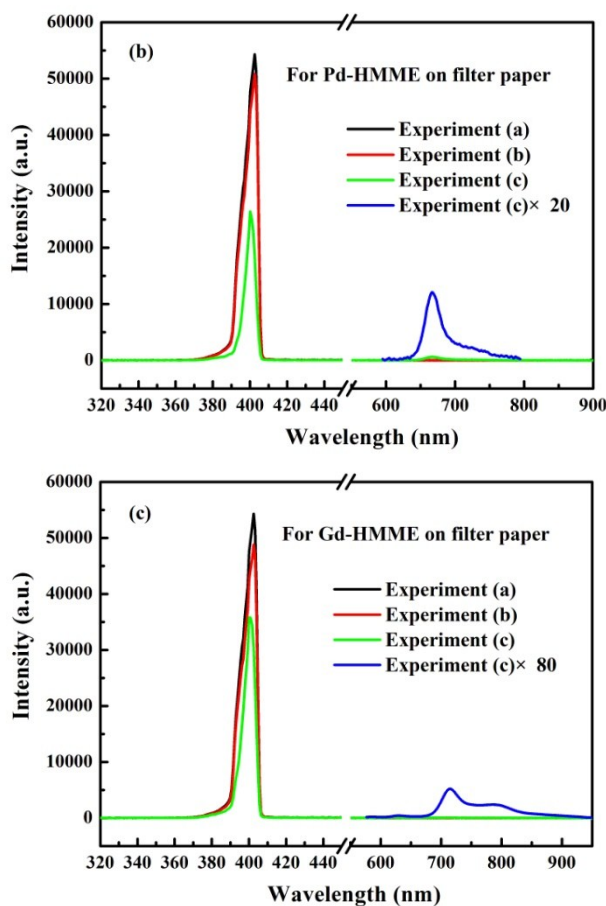


Figure S5. (a) Three spectra for filter paper itself obtained in experiments (a), (b), and (c). The three spectra of Pd- (b) and Gd-HMME (c) obtained in experiments (a), (b), and (c).

The analysis above was applied to measure the absolute phosphorescence QYs of Pd- and Gd-HMME on filter paper. Firstly, to determine whether the filter paper had an influence on the measurement, we recorded the three spectra for filter paper itself in experiments (a), (b), and (c), which are shown in Figure S5(a). One can see that the three spectra for filter paper were almost the same. Thus, the influence of filter paper on the measurement for Pd- and Gd-HMME can be ignored. Then, the three spectra for Pd- and Gd-HMME were recorded. Figures S5(b) and S5(c) show the three spectra of Pd- and Gd-HMME obtained in experiments (a), (b), and (c). Based on these spectra and Eq. S6, the absolute phosphorescence quantum yields of Pd- and Gd-HMME on filter paper were determined to be 8.3% and 3.2% respectively. The QY for Gd-HMME

obtained based on the absolute method is comparable to that for Gd-HMME based on the relative method described in our previous work.^{S2}

Using the same method, the absolute phosphorescence QYs of Pd- and Gd-DVDMS were determined to be 11.1% and 3.6% respectively.

IV. Chemical structure of DVDMS

Figure S6 shows the chemical structure of DVDMS.^{S3}

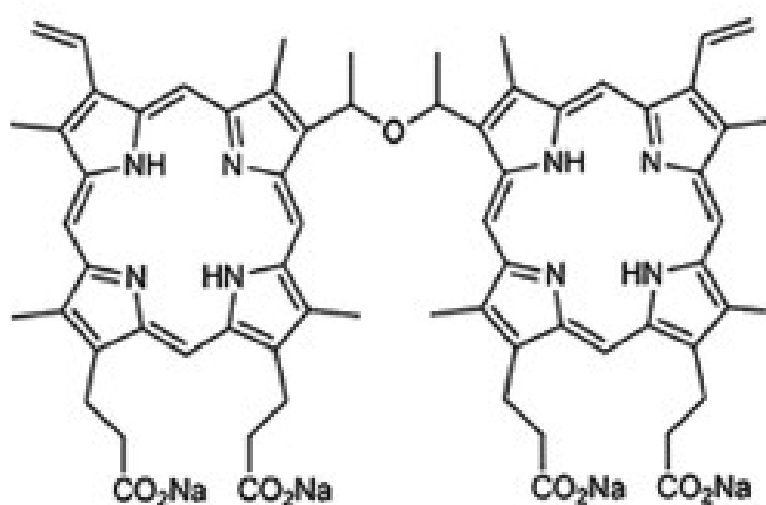


Figure S6. Chemical structure of DVDMS.

V. Absorption and luminescence spectra of Pd- and Gd-DVDMS

Fig. S7(a) shows the absorption spectra of Pd- and Gd-DVDMS. It can be seen that there is also red shift in the absorption spectrum of Gd-DVDMS compared with that of Pd-DVDMS. The same phenomenon was also found in the luminescence spectra between Pd- and Gd-DVDMS, which is shown as Fig. S7(b).

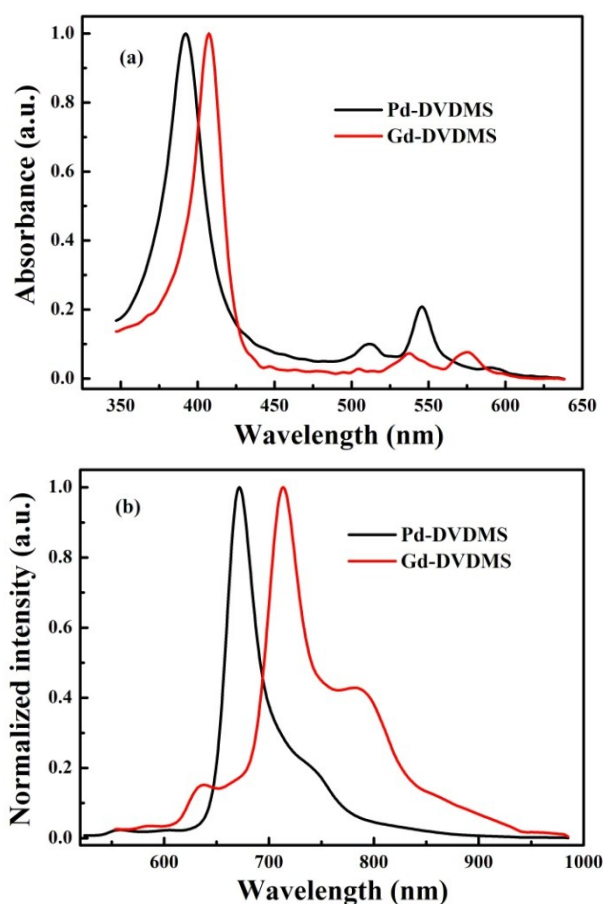


Figure S7. Absorption (a) and luminescence (b) spectra of Pd- and Gd-DVDMS.

VI. The decay time profiles in solution and the plots of phosphorescence decay time of Pd- and Gd-HMME against oxygen concentration

Figure S8 shows the phosphorescence decay time profiles of Pd- (a) and Gd-HMME (b) in solution in the presence of different concentrations of oxygen, as well as the plots of phosphorescence decay time of Pd- (c) and Gd-HMME (d) against oxygen concentration in solution. Figure S9 shows the phosphorescence decay time profiles of Pd- (a) and Gd-HMME (b) on filter paper in the presence of different concentrations of oxygen, as well as the plots of phosphorescence decay time of Pd- (c) and Gd-HMME (d) against oxygen concentration on filter paper.

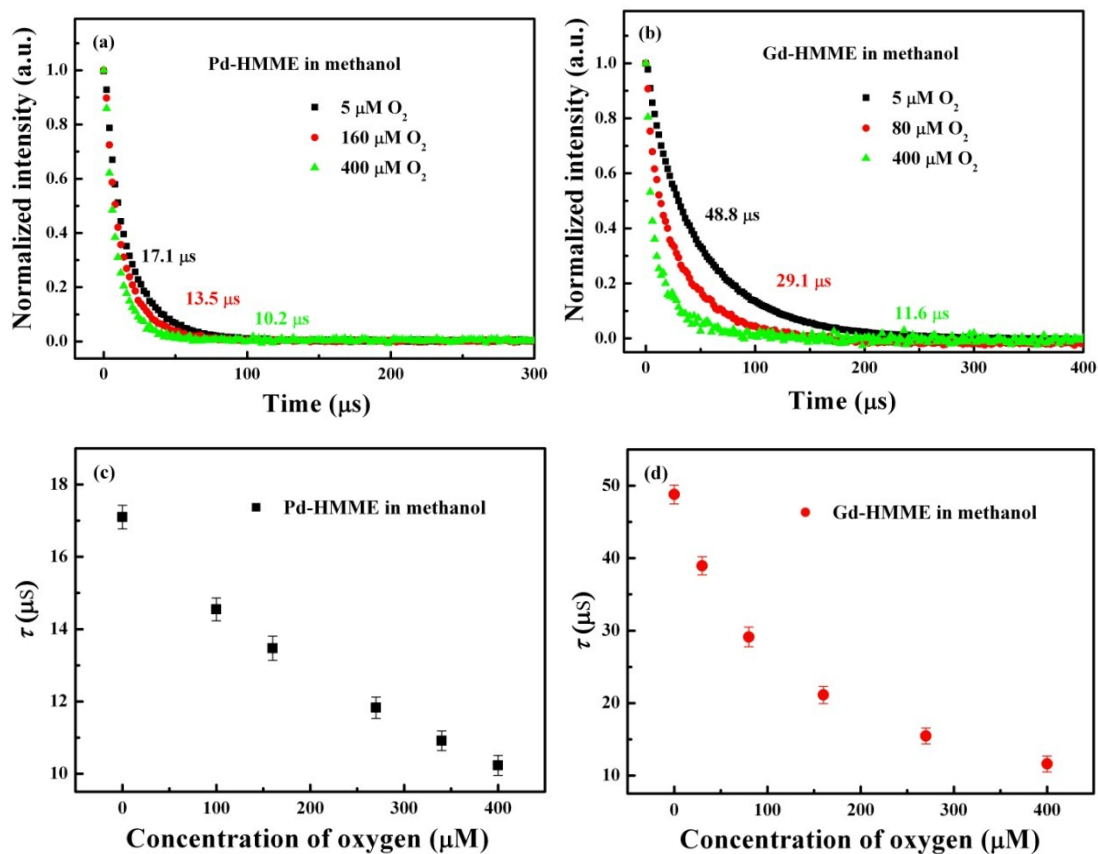


Figure S8. The decay time profiles of Pd- (a) and Gd-HMME (b) in solution in the presence of different concentrations of oxygen, and the plots of phosphorescence decay time of Pd- (c) and Gd-HMME (d) against oxygen concentration in solution.

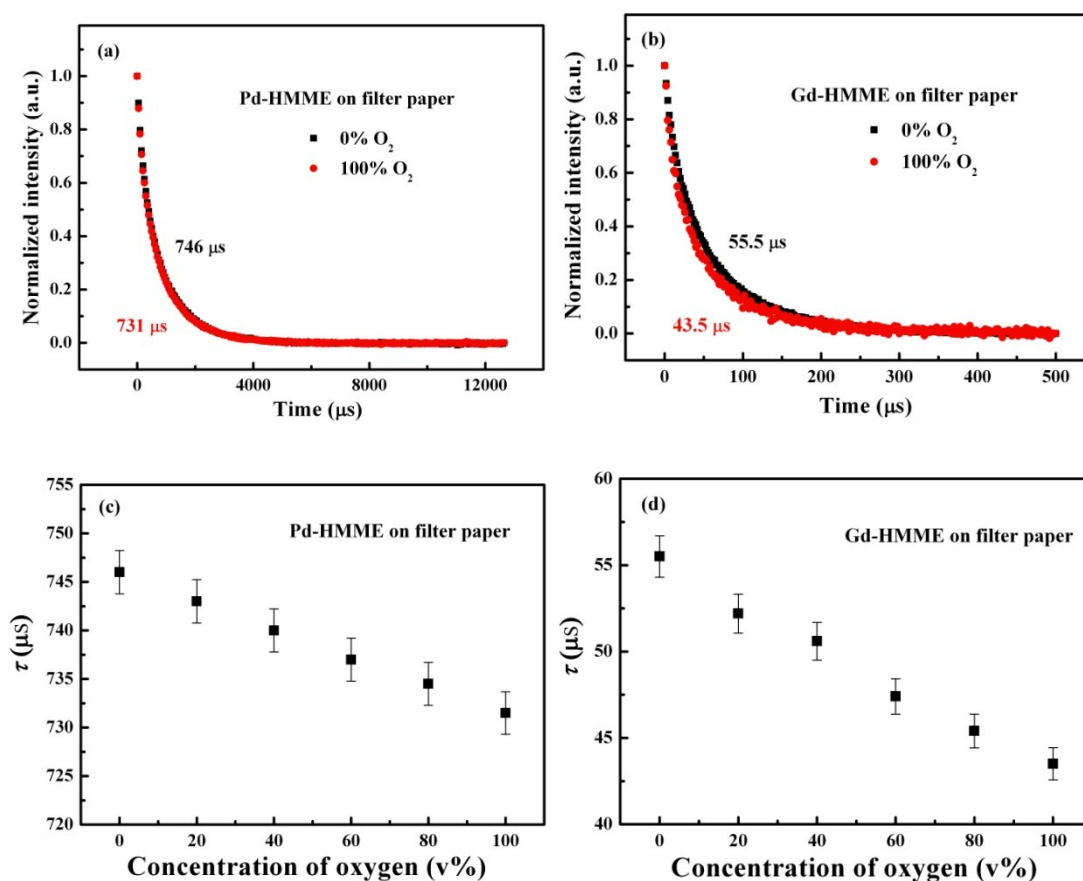


Figure S9. The decay time profiles of Pd- (a) and Gd-HMME (b) on filter paper in the presence of different concentrations of oxygen, and the plots of phosphorescence decay time of Pd- (c) and Gd-HMME (d) against oxygen concentration on filter paper.

VII. Measurement of singlet oxygen quantum yields

Singlet oxygen quantum yields (Φ_{Δ}) of metalloporphyrins were measured utilizing a biochemical trap, DPBF^{S4} based on a relative spectrophotometric method described by Wang et al.^{S5} DPBF can strongly absorb light around 410 nm but the reaction product of DPBF and $^1\text{O}_2$ (*o*-dibenzoylbenzene) does not absorb light at this wavelength.^{S6} To measure Φ_{Δ} of Pd-HMME, Gd-HMME was used as reference with a known Φ_{Δ} ($\Phi_{\Delta}^{\text{ref}} = 0.40^{\text{S5}}$). The absorption spectra of DPBF in the mixture with Pd-HMME (3.5 μM) and Gd-HMME (3.5 μM) under the excitation at different irradiation time were measured

to monitor the formation of $^1\text{O}_2$. The concentration of DPBF ($[\text{DPBF}]$) and irradiation time (t) follows the first-order kinetic equation^{S7},

$$\ln([\text{DPBF}]_0 / [\text{DPBF}]) = kt. \quad (1)$$

Here $[\text{DPBF}]_0$ is the initial concentration of DPBF. k is the degradation rate of DPBF.

In the relative method, the following equation was used,

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{ref}} \left(\frac{k}{A} \right) \left(\frac{A^{\text{ref}}}{k^{\text{ref}}} \right). \quad (2)$$

Where k^{ref} and k are the degradation rates of DPBF in mixture with Gd-HMME and Pd-HMME; A^{ref} and A are the absorption of excitation light (532 nm) by Gd-HMME and Pd-HMME. To obtain A , the product of absorptivity for Pd-HMME (Gd-HMME) and the normalized emission spectrum of the laser were integrated. Φ_{Δ} of Pd-HMME can be calculated based on k , A and $\Phi_{\Delta}^{\text{ref}}$.

Reference

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