

## Electronic Supplementary Information

# Lutetium-containing sinoporphyrin sodium: A water-soluble photosensitizer with balanced fluorescence and phosphorescence for ratiometric oxygen sensing

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## I. The mass spectra of DVDMS and Gd-DVDMS

The mass spectra of the porphyrin (DVDMS) and the porphyrin coordinated to Gd(III) (Gd-DVDMS) were recorded and are shown in Fig. S1. The  $m/z$  peak of DVDMS appeared at about 1144.10, which corresponded to  $[\text{DVDMS}+5\text{H}-4\text{Na}]^+$ . Meanwhile, the  $m/z$  peak of Gd-DVDMS appeared at about 1521.54, which corresponded to  $[\text{2Gd}+\text{DVDMS}+2\text{H}-\text{Na}]^+$ . When the porphyrin is coordinated to Lu(III), the structure would be similar to that coordinated to Gd(III). Thus, the structure of Lu-DVDMS should be the same as that shown in Figure 1.

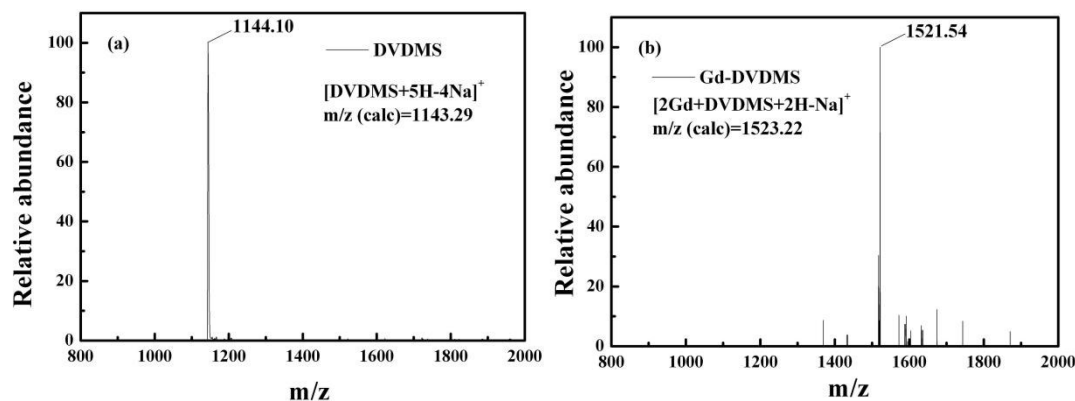


Figure S1. Mass spectroscopic data of DVDMS and Gd-DVDMS.

## II. Method of measuring 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- $\lambda$ 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. The purity of Lu-DVDMS**

The purity of Lu-DVDMS was examined by absorption spectral analysis. After dialysis, the only possible impurity is DVDMS. It has been demonstrated that DVDMS and Lu-DVDMS have different absorption properties in terms of Q bands. Due to the strong absorption at 506 and 630 nm, DVDMS can be detected from the absorption spectrum even at very low concentrations. The detection limit of DVDMS was lower than 0.1  $\mu\text{M}$  by absorption spectroscopy. At 10  $\mu\text{M}$ , the lack of the absorption features of DVDMS in the absorption spectrum of Lu-DVDMS solution indicates that the purity of Lu-DVDMS was no lower than 99%. This method was also used to examine the purity of other metalloporphyrins in previous works.<sup>1,2</sup>

### **IV. Water solubility of DVDMS and HMME**

Figure S2 shows the photographs of HMME (a) and DVDMS (b) at the same concentration (1 mg/mL) in PBS. It can be seen that the water solubility of DVDMS is much better than that of HMME.

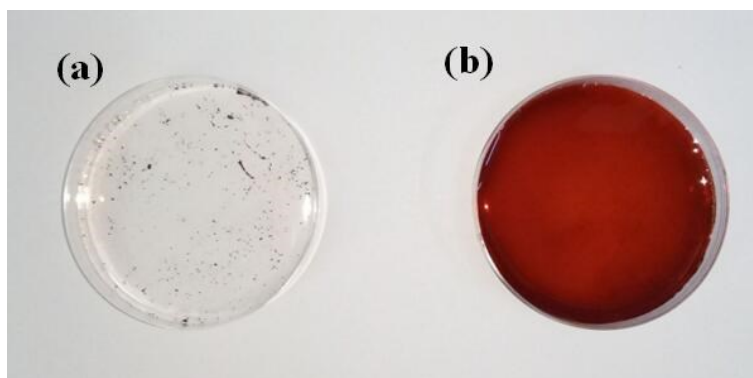


Figure S2 The photographs of HMME (a) and DVDMS (b) at the same concentration (1 mg/mL) in PBS.

## V. Singlet oxygen quantum yield of Lu-DVDMS

To determine the singlet oxygen quantum yield of Lu-DVDMS in an air-saturated solution, a relative spectrophotometric method<sup>3</sup> based on the following equation was used:

$$\frac{\Phi_{\Delta} A}{k} = \frac{\Phi_{\Delta}^r A^r}{k^r}. \quad (S1)$$

Here the superscript “r” stands for the reference reagent,  $k$  is the degradation rate of the singlet oxygen trapping reagent, and  $A$  is the absorption of excitation light by photosensitizers,<sup>3</sup> which is dependent on the concentration of the photosensitizer, extinction coefficient, and intensity of the incident light. The following equation describes this relationship:

$$A = \int I_{532}(\lambda) \times (1 - e^{-\varepsilon(\lambda)CL}) d\lambda. \quad (S2)$$

$I_{532}(\lambda)$  is the normalized emission spectrum of the 532 nm laser,  $\varepsilon(\lambda)$  is the absorption coefficient of each substance,  $C$  represents the concentration, and  $L$  is the light path length. To measure  $\Phi_{\Delta}$  of Lu-DVDMS, Gd-DVDMS was used as the reference with a  $\Phi_{\Delta}$  of 0.46 in air-saturated methanol.<sup>1</sup> DPBF was utilized as the singlet trapping reagent.<sup>5-9</sup> Three samples were prepared: (1) DPBF 15  $\mu$ M; (2) DPBF 15  $\mu$ M, Gd-DVDMS 2.50  $\mu$ M; (3) DPBF 15  $\mu$ M, Lu-DVDMS 2.5  $\mu$ M. Three milliliters of each sample was placed in a silica cuvette (1 cm length) and irradiated with a solid state-laser centered at 532 nm. The consumption of DPBF was monitored by UV-visible

absorption.

Figure S3 shows the absorption spectra of DPBF in the mixture with Gd-DVDMS (a) or Lu-DVDMS (b). The absorption of DPBF decreased with irradiation time in the mixture with Gd-DVDMS or Lu-DVDMS. It has been well demonstrated that the absorption spectrum of DPBF remains unchanged under the irradiation of a 532 nm laser.<sup>10</sup> The consumption of the singlet oxygen trapping reagent, DPBF, demonstrates the production of singlet oxygen.

The degradation rate of DPBF ( $k$ ) was determined using the decrease of the absorption peak at 410 nm over time. The value of the absorption peak was used to represent the concentration of DPBF ( $[DPBF]$ ), as the relationship between the concentration and absorbance of DPBF was linear in the studied range of concentrations.  $[DPBF]$  and irradiation time followed the first-order kinetic equation,<sup>11</sup>

$$\ln([DPBF]_0/[DPBF]) = kt. \quad (S3)$$

Here  $[DPBF]_0$  is the initial concentration of DPBF and  $t$  is the irradiation time. Figure S3(c) shows the time dependence of  $\ln([DPBF]_0/[DPBF])$  for DPBF in the mixture with Gd-DVDMS or Lu-DVDMS upon irradiation with a laser at 532 nm. The degradation rate  $k$  was determined by linear fitting of the experimental data.

According to Eq. (S1), the  $\Phi_{\Delta}$  of Lu-DVDMS was calculated based on the degradation rates ( $k$ ) of DPBF in the mixture with Gd-DVDMS or Lu-DVDMS, the absorption of excitation light ( $A$ ) of Gd-DVDMS or Lu-DVDMS, as well as  $\Phi_{\Delta}^r$  of

Gd-DVDMS. Eq. (S2) was used to obtain  $A$  of Gd-DVDMS or Lu-DVDMS. The  $\Phi_{\Delta}$  of Lu-DVDMS was determined to be  $0.23 \pm 0.06$ .

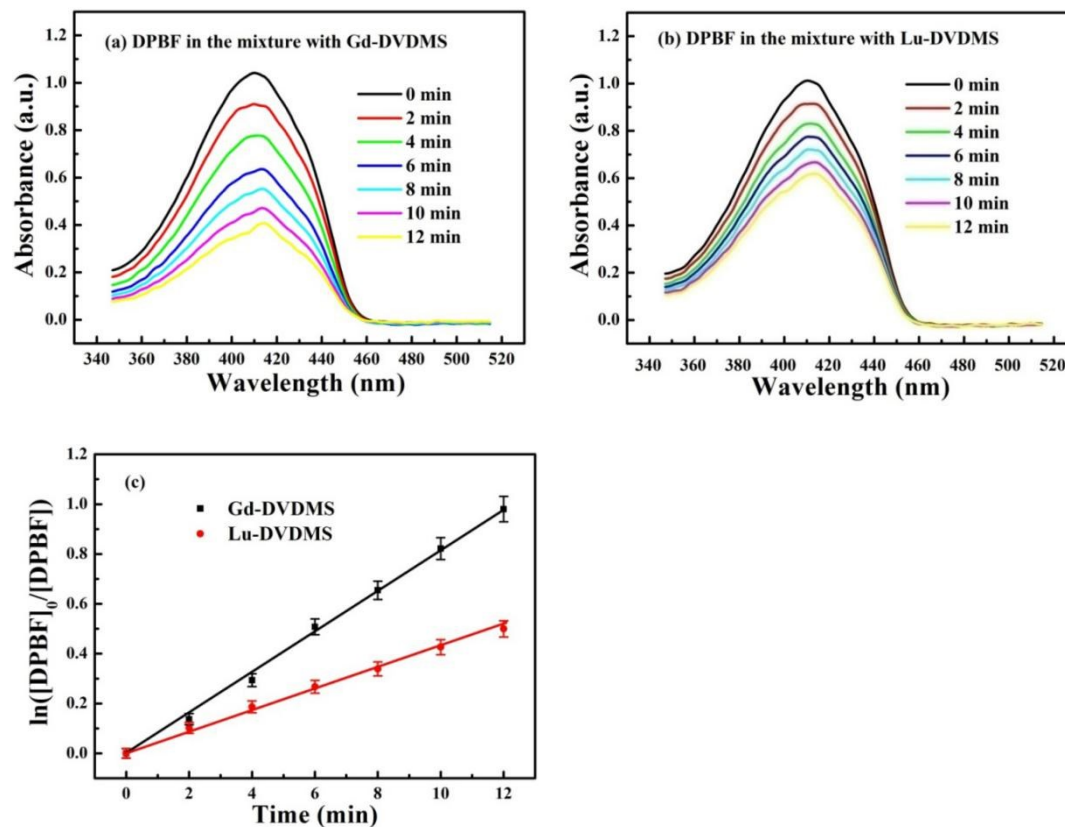


Figure S3. The absorption spectra of DPBF in the mixture with Gd-DVDMS (a) or Lu-DVDMS (b), (c) the time dependence of  $\ln([\text{DPBF}]_0/[\text{DPBF}])$  for DPBF in the mixture with Gd-DVDMS or Lu-DVDMS upon irradiation with a laser at 532 nm.

## VI. Quantum yield of Lu-DVDMS phosphorescence

To characterize the ability of Lu-DVDMS phosphorescent emission, quantum yield ( $\Phi_p$ ) of the phosphorescence at 706 nm in air-saturated methanol solution was measured. In the measurement, comparison method was applied. Gd-DVDMS was used as the reference with quantum yield of 1.5% in methanol.<sup>1</sup> The relationship between  $\Phi_p$  of Lu-DVDMS and that of Gd-DVDMS was described by the following equation,<sup>12</sup>

$$\Phi_p = \Phi_r \left( \frac{I}{A} \right) \left( \frac{A_r}{I_r} \right), \quad (\text{S4})$$

where  $\Phi_r$  and  $\Phi_p$  are the phosphorescence quantum yields of Gd-DVDMS and Lu-DVDMS in methanol.  $A_r$  and  $A$  are the absorbance of Gd-DVDMS and Lu-DVDMS at 532 nm, respectively.  $I_r$  and  $I$  are the integrated emission intensities of Gd-DVDMS and Lu-DVDMS under the illumination of 532 nm laser, respectively. Figure S4 shows the luminescence spectra of Gd-DVDMS and Lu-DVDMS (500  $\mu\text{M}$ ) under the same conditions (excited by 532 nm laser). The experimental conditions and calculated quantum yields of Lu-DVDMS in methanol are shown in Table S1.  $\Phi_p$  of Lu-DVDMS was determined to be 0.33%.

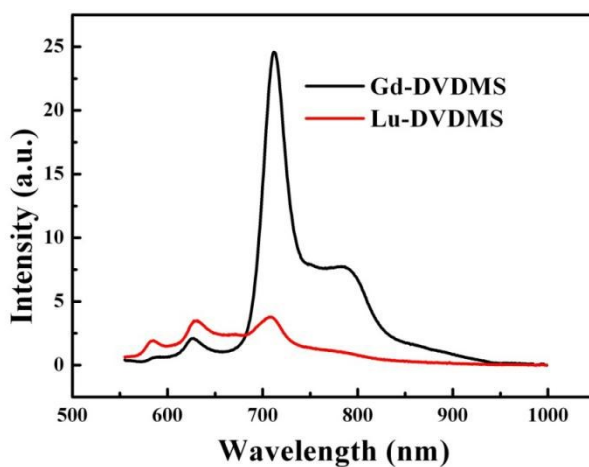


Figure S4. The luminescence spectra of Gd-DVDMS and Lu-DVDMS (500  $\mu\text{M}$ ) under the same conditions (excited by 532 nm laser).

Table S1. Experimental conditions and calculated phosphorescence quantum yield of Lu-DVDMS in methanol.

Samples	Concentration ( $\mu\text{M}$ )	$\lambda_{\text{ex}}$ (nm)	$A$	$I$ (a.u.)	$\Phi_p$ (%)
Gd-DVDMS	150	532	0.96	1458090	1.50
Lu-DVDMS	150	532	0.95	320286	0.33

## VII. Stability and photostability of the oxygen indicator

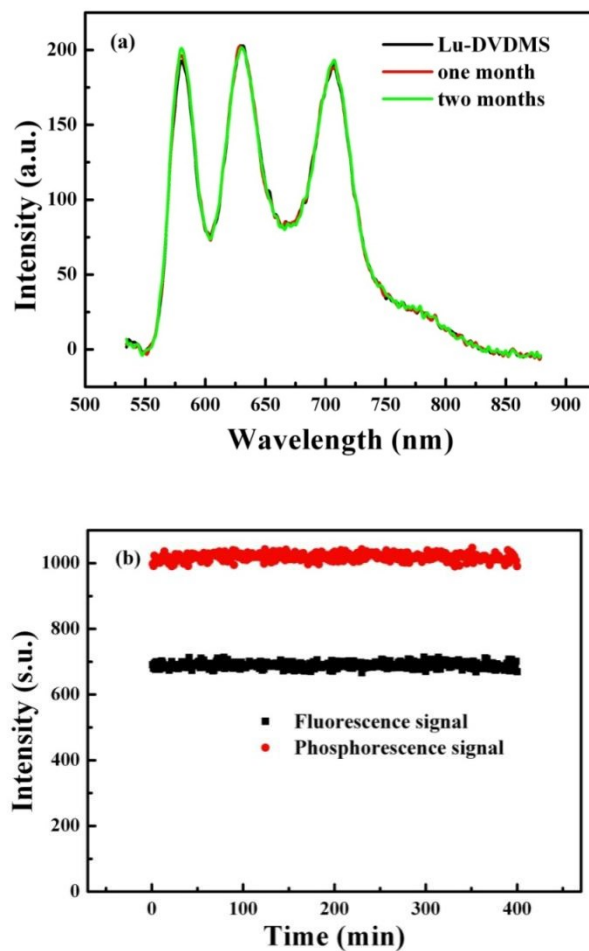


Figure S5. (a) The stability of Lu-DVDMS in two months, (b) Continuous values of fluorescence (black) and phosphorescence (red) signals of Lu-DVDMS (500  $\mu\text{M}$ ) under the irradiation of 405 nm laser at 2  $\text{mW}/\text{cm}^2$  for 120 min.

## VIII. Response time for the oxygen indicator



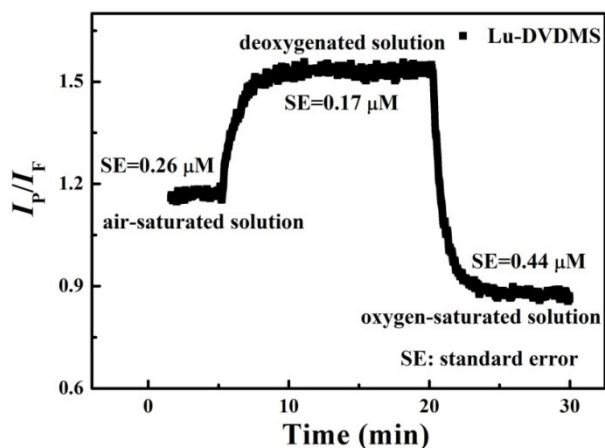


Figure S6. The change of the fluorescence ratio upon switching between different concentrations of oxygen.

### IX. The mass spectrum of Lu-DVDMS

The mass spectrum of the porphyrin (DVDMS) coordinated to Lu(III) (Lu-DVDMS) was recorded. In the measurement, an LCQ fleet ion trap mass spectrometer (Thermo Scientific, San Jose, CA) in positive ion mode was used to record the signals from the solution of Lu-DVDMS. The  $m/z$  peak of Lu-DVDMS appears at about 1537.92, which corresponds to the theoretical value of  $[2\text{Lu}+\text{DVDMS}-2\text{Na}+3\text{H}]^+$  (1537.19).

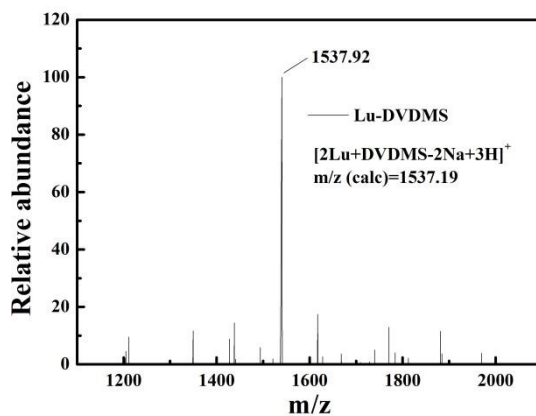


Figure S7. Mass spectroscopic data of Lu-DVDMS.

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