

## *Electronic Supplementary Information*

### **Selective visible-light-driven oxygen reduction to hydrogen peroxide using BODIPY photosensitizers**

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### **General methods and materials.**

Manipulations of air- and moisture-sensitive materials were performed under nitrogen using standard Schlenk line techniques. All reagents were purchased from commercial suppliers and used as received unless otherwise noted. Dry solvents, acetonitrile and dichloromethane, were purified by passage through activated alumina. BODIPY derivatives were synthesized using methods reported previously.<sup>1,2</sup> <sup>1</sup>H NMR measurements were made on a Bruker spectrometer operating at 400 MHz. Electronic absorption spectra were acquired using a U-3900H spectrophotometer. Fluorescence measurements were made using a F-7000 HITACHI fluorescence spectrophotometer.

### **Emission quenching experiments.**

Emission quenching experiments were made using a F-7000 HITACHI fluorescence spectrophotometer. With the addition of Fc, the emission quenching of PS-1 in acetonitrile under a N<sub>2</sub> atmosphere was monitored. There was no change in the shape, but the intensity of the emission significantly decreased with the addition of Fc.

### **Apparent quantum yield (AQY).**

The AQY was measured under the standard reaction conditions with a 520-nm irradiation light (280 W xenon lamp using the cut-off filter). The AQY is defined as follow:  $AQY (\%) = \text{Number of reacted photons} / \text{Number of incident photons} \times 100\%$ . The light intensity was determined to be 40.0 mW cm<sup>-2</sup> at the sample position for the

whole irradiation area of 2 cm<sup>2</sup> using a xenon lamp at room temperature. The amount of produced H<sub>2</sub>O<sub>2</sub> was determined by the iodometric titration method.

### **Spectroscopic measurements.**

The amount of formed H<sub>2</sub>O<sub>2</sub> was determined by the iodometric titration method. The dilute acetonitrile solution after the ORR was treated with an excess amount of sodium iodide (NaI). The amount of I<sub>3</sub><sup>-</sup> formed was determined by its characteristic absorption at  $\lambda_{\text{max}} = 361 \text{ nm}$  ( $\epsilon = 25,000 \text{ M}^{-1} \text{ cm}^{-1}$ , Fig. S2).<sup>3</sup> The corresponding ferrocenium cation (Fc<sup>+</sup>,  $\lambda_{\text{max}} = 620 \text{ nm}$ ,  $\epsilon = 330 \text{ M}^{-1} \text{ cm}^{-1}$ ) was monitored by electronic absorption spectroscopy (Fig. S1).<sup>3</sup>

### **Electron paramagnetic resonance (EPR) spectroscopy.**

X-band continuous wave EPR measurements were carried out on a Bruker E500 EPR spectrometer at a microwave frequency of 9.45 GHz using a liquid nitrogen cooling system. The EPR spectra were measured at 90 K with a modulation amplitude of 0.3 mT, a modulation frequency of 100 kHz, and a microwave power of 10.02 mW. The mixture of (a) PS-1 (0.1 mM) and DMPO (20 mM), (b) PS-1 (0.1 mM), Fc (1.5 mM) and DMPO (20 mM), (c) PS-1 (0.1 mM) and TEMP (0.12 M), and (d) PS-1 (0.1 mM), Fc (1.5 mM) and TEMP (0.12 M) in O<sub>2</sub>-saturated acetonitrile was stirred in the dark. The solution was then frozen at 90 K after visible light irradiation by xenon lamp (280 W,  $\lambda = 400\text{-}780 \text{ nm}$ ) for 600 s.

### **Nanosecond time-resolved transient difference absorption spectroscopy.**

Nanosecond time-resolved transient difference absorption spectroscopy was measured on laser flash photolysis. The laser flash photolysis apparatus including a 100 mL flow cuvette with a 5 mm optical path length. Excitation pulses (532 nm, 3 mJ per pulse, 7 ns, 10 Hz) were selected from a Nd<sup>3+</sup>: YAG laser (Quanta-Ray PRO-230; Spectra physics, Santa Clara, CA) with probe light from a xenon lamp (CW, 300 W; LDLS-EQ-1500; Energetip Technology Inc., Woburn, MA), using 520 nm, 400-750 nm for the PS-1 triplet excited state as detected with a photodiode (model S3071, Hamamatsu Photonics, Hamamatsu, Japan) attached to a Trivista spectrograph monochromator (Princeton Instruments, Trenton, NJ). All kinetics traces were stored and averaged with a digital storage oscilloscope (bandwidth 600 MHz; Teledyne LeCroy WaveSurfer 64Xs, Chestnut Ridge, NY). For kinetics analyses, profiles of optical density change ( $\Delta O.D.$ ) with time following pulsed excitation were fitted to a one exponential model function. The concentration of PS-1 was 15  $\mu$ M. All measurements were carried out in a thermostated room (23 °C) using fresh solution prepared under reduced light conditions.

### **O<sub>2</sub> selectivity measurements.**

The concentration of O<sub>2</sub> in acetonitrile was determined by the spectroscopic titration method using the photooxidation of 10-methyl-9,10-dihydroacridine with O<sub>2</sub>.<sup>4</sup> An air-saturated acetonitrile solution (2.0 mL, [O<sub>2</sub>] = 2.6 mM) containing PS-1 (0.5 mM), Fc (25 mM), and acetic acid (25 mM) was photoirradiated with a xenon

lamp (280 W,  $\lambda = 400\text{-}780$  nm) in a water bath at 25 °C for 70 min. After this reaction, the O<sub>2</sub> concentration was determined to be 0.97 mM. The amount of O<sub>2</sub> consumed is 3.26  $\mu\text{mol}$ . The amount of H<sub>2</sub>O<sub>2</sub> formed is 3.18  $\mu\text{mol}$ . The selectivity for H<sub>2</sub>O<sub>2</sub> formation based on the amount of O<sub>2</sub> reduced is 97.5%.

### **Electron transfer pathways from Fc to the excited state of PS-1.**

The excited-state reduction ( $E_{\text{red}}^*$ ) and oxidation ( $E_{\text{ox}}^*$ ) potentials can be calculated using the equation  $E_{\text{red}}^* = E_{\text{red}} + \Delta E_{\text{S/T}}$  and  $E_{\text{ox}}^* = E_{\text{ox}} - \Delta E_{\text{S/T}}$ , where  $\Delta E_{\text{S}}$  and  $\Delta E_{\text{T}}$  are calculated from the peak wavelengths of fluorescence and phosphorescence spectra, respectively. The ground-state reduction ( $E_{\text{red}}$ ) and oxidation ( $E_{\text{ox}}$ ) potentials can be determined by cyclic voltammetry in deaerated acetonitrile. For PS-1, the ground-state reduction potential  $E_{\text{red}} = -0.90$  V (vs SCE), the ground-state oxidation potential  $E_{\text{ox}} = 1.32$  V (vs SCE). The peak wavelength of the fluorescence for PS-1 is 569 nm, and the  $\Delta E_{\text{S}}$  for the singlet excited state is 2.18 V. The peak wavelength of the phosphorescence for PS-1 is 827 nm, the  $\Delta E_{\text{T}}$  for the triplet excited state is 1.5 V. Thus, the redox potentials of PS-1 in the singlet excited state:  ${}^1E_{\text{red}}^* = -0.90$  V + 2.18 V = 1.28 V (vs SCE) and  ${}^1E_{\text{ox}}^* = 1.32$  V - 2.18 V = -0.86 V (vs SCE). The redox potentials of PS-1 in the triplet excited state:  ${}^3E_{\text{red}}^* = -0.90$  V + 1.5 V = 0.6 V (vs SCE) and  ${}^3E_{\text{ox}}^* = 1.32$  V - 1.5 V = -0.18 V (vs SCE).

For Fc, the redox potential  $E_{1/2} = 0.38$  V (vs SCE), which is smaller than both the singlet excited state reduction potential (1.28 V) and the triplet excited state reduction potential (0.6 V) of PS-1. From a thermodynamic point of view, Fc could

transfer electron to both the singlet and triplet excited states of PS-1. However, PS-1 is a triplet photosensitizer, which has much longer lifetime in its triplet excited state ( $\mu\text{s}$  level) than in the singlet excited state (ns level). When PS-1 is irradiated by visible light, it first turns into its singlet excited state and then quickly converts to its triplet excited state via the intersystem crossing process. As a result, we believe that the electron transfer pathway is from Fc to the triplet excited state of PS-1.

**Table S1** Control experiments showing that BODIPY, light, Fc, and acetic acid are all essential for the ORR.

Entry	O <sub>2</sub>	AcOH	BODIPY	light	Fc	H <sub>2</sub> O <sub>2</sub>	Fc <sup>+</sup>
1	none	√	√	√	√	none	none
2	√	none	√	√	√	none	none
3	√	√	none	√	√	none	none
4	√	√	√	none	√	none	none
5	√	√	√	√	none	none	none

Reaction conditions: BODIPY (0.5 mM), acetic acid (500 mM) and Fc (50 mM) in an O<sub>2</sub>-saturated acetonitrile solution irradiated by a xenon lamp (140 W,  $\lambda = 400\text{-}780$  nm) for 4 h. H<sub>2</sub>O<sub>2</sub> and Fc<sup>+</sup> were determined by the iodide titration method and electronic absorption spectroscopy, respectively.

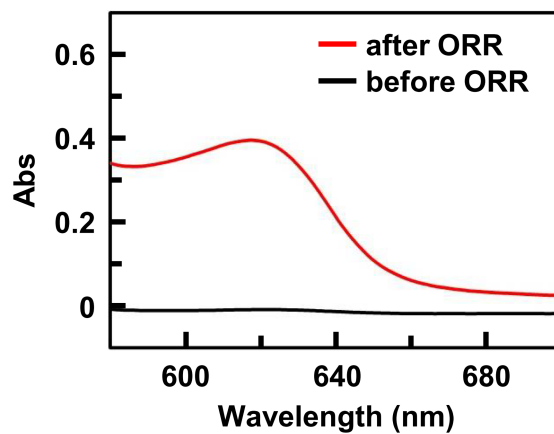
**Table S2** Optimization of reaction conditions<sup>a</sup>

Entry	Photosensitizer	Acid	Time	TON <sup>b</sup>
1 <sup>a/c</sup>	PS-1	acetic acid	4 h	9.1/11.2
2	PS-2	acetic acid	4 h	6.5
3	PS-3	acetic acid	4 h	5.2
4	PS-4	acetic acid	4 h	7.3
5	PS-5	acetic acid	4 h	4.2
6	PS-6	acetic acid	4 h	7.5
7	PS-7	acetic acid	4 h	5.5
8	PS-8	acetic acid	4 h	7.8
9	PS-9	acetic acid	4 h	2.3
10	PS-10	acetic acid	4 h	4.5
11	PS-1	oxalic acid	4 h	7.5
12	PS-1	propionic acid	4 h	5.2
13 <sup>d</sup>	PS-1	hydrochloric acid	4 h	29.3
14	PS-1	formic acid	4 h	8.3
15 <sup>d</sup>	PS-1	perchloric acid	4 h	39.6
16 <sup>e</sup>	PS-1	acetic acid	0.5 h	7.1
17 <sup>e</sup>	PS-1	acetic acid	1 h	15.2
18 <sup>e</sup>	PS-1	acetic acid	2 h	26.3
19 <sup>e</sup>	PS-1	acetic acid	3 h	36.1
20 <sup>e</sup>	PS-1	acetic acid	4 h	45.1

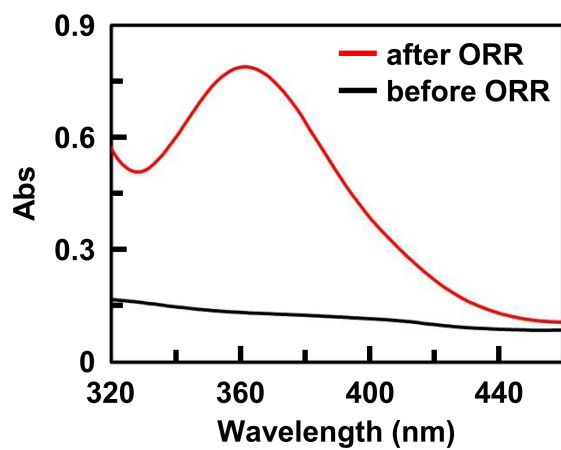
<sup>a</sup>BODIPY (0.5 mM), acid (500 mM), Fc (50 mM), O<sub>2</sub>-saturated acetonitrile (2 mL), xenon lamp (140 W,  $\lambda$  = 400-780 nm), 25 °C, 4 h. <sup>b</sup>H<sub>2</sub>O<sub>2</sub> was identified by iodometric titration for TON calculation. <sup>c</sup>Acid (1000 mM). <sup>d</sup>Photosensitizer decomposition.

<sup>e</sup>Xenon lamp (280 W,  $\lambda$  = 400-780 nm).





**Fig. S1** UV-vis absorption spectra of the reaction mixture before (black line) and after (red line) the ORR, showing the characteristic absorption band of  $\text{Fc}^+$  at 620 nm.



**Fig. S2** UV-vis absorption spectra of the reaction mixture before (black line) and after (red line) the ORR. The reaction mixture was treated with an excess amount of sodium iodide for H<sub>2</sub>O<sub>2</sub> detection.

**Reference:**

- S1. X. F. Wang, S. S. Yu, C. Wang, D. Xue and J. L. Xiao, *Org. Biomol. Chem.*, 2016, **14**, 7028-7037.
- S2. M. Z. Wang, Y. Y. Zhang, T. Wang, C. Wang, D. Xue and J. L. Xiao, *Org. Lett.*, 2016, **18**, 1976-1979.
- S3. T. Honda, T. Kojima and S. Fukuzumi, *J. Am. Chem. Soc.*, 2012, **134**, 4196-4206.
- S4. S. Fukuzumi, S. Mochizuki and T. Tanaka, *Inorg. Chem.*, 1989, **28**, 2459-2465.