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

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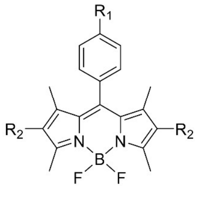
Abstract: Selective visible-light-driven O_2 reduction to H_2O_2 was realized by using BODIPY photosensitizers (PS) in the presence of ferrocene (Fc) as the reductant and acetic acid as the proton source. Mechanistic studies suggested that O_2 could be activated by $^3PS^*$ through an energy transfer pathway to give singlet oxygen ($^1O_2$) in the absence of Fc. However, with Fc, $^3PS^*$ was first reductively quenched to $PS^{\bullet-}$, which was able to reduce O_2 to the superoxide radical form in a subsequent electron transfer step.

The oxygen reduction reaction (ORR) is significant in both biology and energy conversion systems.[1-7] O_2 can be reduced either by two electrons to H_2O_2 or by four electrons to H_2O.[8] Although the $4e^-$ pathway is more energetically favored,[1] the $2e^-$ reduction of O_2 to H_2O_2 has been attracting increasing attention.[9-11] First, H_2O_2 is an alternative fuel.[12] H_2O_2 fuel cell has a 1.09 V output potential, a value that is comparable to the 1.23 V output potential of a H_2 fuel cell. Compared with H_2, H_2O_2 is much easier for storage and transportation. Second, H_2O_2 has been extensively used as an oxidant in industry.[13] The standard redox potential of H_2O_2 to H_2O is 1.78 V, a value even larger than that of O_2 to H_2O at 1.23 V. Moreover, the product from the oxidation with H_2O_2 is water.

Although transition-metal-based complexes have been examined as ORR catalysts,[14-28] few were shown to be selective for the $2e^-$ reduction of O_2 to H_2O_2. In addition, transition metal complexes can typically catalyze the disproportionation of H_2O_2 to O_2 and H_2O. As a result, the stability of produced H_2O_2 in the presence of metal catalysts is an issue. Recently, Fukuzumi and co-workers reported light-driven $2e^-$ ORR using various organic electron donor-acceptor molecules.[29,30] These works are important to show the generation of H_2O_2 from a metal-free and light-driven ORR system. Photocatalytic H_2O_2 production from H_2O and O_2 by metal-based[31-34] and metal-free carbon nitride catalysts[35-37] have also received attention.

Boron-dipyrromethene (BODIPY) is a class of metal-free dyes, which have been used for labelling and sensing.[38,39] Recently, BODIPY has been used as photosensitizers for light-driven oxidation of organic substrates with O_2.[40-43] BODIPY has the following properties: (1) the strong absorption in the visible light range; (2) the high stability under photoirradiation; (3) the high yield of long-lived triplet excited state; and (4) the easily tuned photophysical feature by structural modification. Importantly, in the reactions, organic substrates were oxidized by O_2, and H_2O_2 was identified as the reduction product. On the basis of these results, we are interested in examining the possibility of light-driven ORR using BODIPY. Herein we report selective visible-light-driven O_2 reduction to H_2O_2 using various BODIPY photosensitizers in the presence of Fc as the reductant and acetic acid as the proton source. Mechanistic studies were performed to better understand the reaction pathways leading to O_2 activation. This work is important to show an example of selective light-driven O_2 reduction to H_2O_2 and also to shed light on photocatalytic oxidation of organic substrates with O_2 using BODIPY photosensitizers.

A variety of BODIPY derivatives were examined (Scheme 1). Typically, O_2-saturated acetonitrile containing BODIPY (0.5 mM), Fc (50 mM), and acetic acid (500 mM) was irradiated with a xenon lamp (280 W, λ = 400-780 nm) in a water bath at 25 °C. The formed ferrocenium cation (Fc^+) was identified by its characteristic UV-vis absorption band at 620 nm (Fig. S1). The amount of produced H_2O_2 was obtained by the iodometric titration method (Fig. S2). Control experiments showed that BODIPY, light, Fc, and acetic acid were all essential for catalytic O_2 reduction (Table S1). The plots of formed Fc^+ and H_2O_2 versus time are depicted in Fig. 1a. From the slopes of these lines, the formation rates of Fc^+ and H_2O_2 was determined to be 0.35 and 0.17 μmol min^{-1}, respectively. The quantity of formed Fc^+ was nearly two times the quantity of formed H_2O_2, a ratio that is consistent with the reaction stoichiometry shown in Eqn (1). This result indicates the selective $2e^-$ reduction of O_2 in this light-driven system with BODIPY. This selectivity was further confirmed by calculating the amount of O_2 consumed and the amount of H_2O_2 generated (see Electronic Supplementary Information ESI for details).



PS-**1**, R_1=H, R_2=I
PS-**2**, R_1=H, R_2=Br
PS-**3**, R_1=CO_2Me, R_2=I
PS-**4**, R_1=CO_2Me, R_2=Br
PS-**5**, R_1=CN, R_2=I
PS-**6**, R_1=CF_3, R_2=Br
PS-**7**, R_1=OCH_3, R_2=Br
PS-**8**, R_1=Br, R_2=Br
PS-**9**, R_1=H, R_2=Cl
PS-**10**, R_1=CF_3, R_2=Cl

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Scheme 1 Molecular structures of used BODIPY derivatives.

$$O_2 + 2Fc + 2H^+ \xrightarrow[hv]{PS} H_2O_2 + 2Fc^+ \qquad \text{Eqn (1)}$$

The ORR turnover numbers (TONs) with different BODIPY derivatives were determined (Table S2). All BODIPY derivatives examined are active by functioning as photosensitizers for the visible-light-driven ORR. It is worth noting that the maximum TON expected under experimental conditions is 50.0 due to the solubility of Fc in acetonitrile. Several conclusions can be made. (1) PS-**1** is the most efficient one among BODIPY derivatives examined. (2) The increase of irradiation time, acid concentration or light intensity, leads to the increase of TON. (3) BODIPY is less stable in entries using strong acids, such as hydrochloric and perchloric acids. In addition, for PS-**1**, the apparent quantum yield for H_2O_2 production was 0.86% under the irradiation of λ = 520 nm (see ESI for details).

The stability of BODIPY photosensitizer was evaluated. As shown in Fig. 1b, the UV-vis spectra of the reaction mixture before and after ORR under 4-h illumination display negligible difference. In addition, BODIPY can be recovered and reused for many cycles, further showing its stability by functioning as photosensitizer in the visible-light-driven ORR.

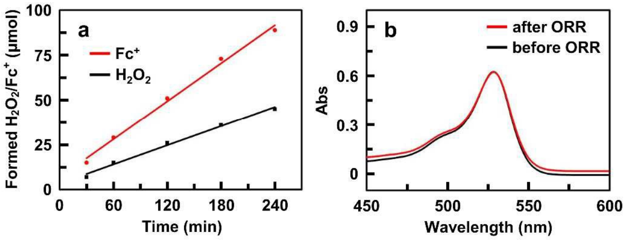

Fig. 1 (a) Plots of formed H_2O_2 and Fc^+ versus time in an O_2-saturated acetonitrile with PS-**1** (0.5 mM), Fc (50 mM), and acetic acid (500 mM) under irradiation (λ = 400-780 nm). (b) UV-vis spectra of PS-**1** in acetonitrile before and after ORR.

In order to better understand the mechanism, we studied the reductive quenching of PS-**1** with Fc in acetonitrile under N_2. We found that PS-**1** showed strong luminescence with an emission peak at 569 nm in the absence of Fc at room temperature (Fig. 2a). However, the emission of PS-**1** gradually decreases with the addition of Fc. Importantly, the quenching constant of K = 168 M^{-1} could be determined (Fig. 2b), indicating the presence of interaction between the excited state of PS-**1** and Fc. The reductive quenching of excited PS-**1** by Fc is therefore possible in the light-driven ORR.

Electron paramagnetic resonance (EPR) spectroscopy was used to probe intermediates formed during ORR. Complexes 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were used as probes for $O_2^{\bullet-}$ and $^1O_2$, respectively. The mixture of PS-**1** and DMPO in an O_2-saturated acetonitrile displayed no signal (Fig. 3a), indicating that the oxidative quenching of excited PS-**1** by O_2 to produce PS-$\mathbf{1}^{\bullet+}$ and $O_2^{\bullet-}$ was not likely under experimental conditions. However, in the presence of Fc, the above solution displayed a signal assigned to the DMPO-$O_2^{\bullet-}$ adduct upon irradiation (Fig. 3b). This result suggests that $O_2^{\bullet-}$ was produced in the solution of PS-**1** and Fc upon irradiation. We proposed that excited PS-**1** was first reductively quenched by Fc and the resulted PS-$\mathbf{1}^{\bullet-}$ transferred one electron to O_2 to give PS-**1** and $O_2^{\bullet-}$.

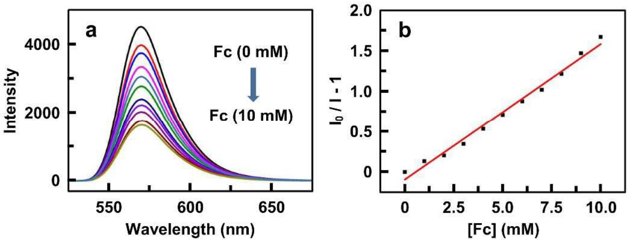

Fig. 2 (a) The emission spectra of PS-**1** (0.5 mM) in acetonitrile at 25 °C with increasing amounts of Fc (0-10 mM) under a 446 nm excitation. (b) The Stern-Volmer plot of PS-**1** vs [Fc].

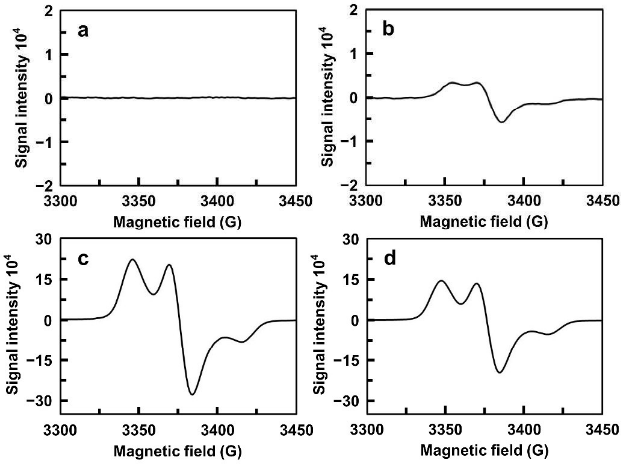

Fig. 3 EPR studies. (a) PS-**1** (0.1 mM) and DMPO (20 mM); (b) PS-**1** (0.1 mM), Fc (1.5 mM) and DMPO (20 mM); (c) PS-**1** (0.1 mM) and TEMP (0.12 M); (d) PS-**1** (0.1 mM), Fc (1.5 mM) and TEMP (0.12 M). All measurements were done in O_2-saturated acetonitrile at 90 K under irradiation by a xenon lamp (280 W, 400-780 nm) for 600 s.

In a separate experiment, the mixture of PS-**1** and TEMP in an O_2-saturated acetonitrile displayed a strong signal assigned to the TEMP-$^1O_2$ adduct (Fig. 3c). However, in the presence of Fc, the TEMP-$^1O_2$ signal significantly decreased (Fig. 3d). This result suggests that in the absence of Fc, energy transfer from excited PS-**1** to O_2 is the dominant process, leading to the formation of $^1O_2$. However, in the presence of Fc, excited PS-**1** could be reductively quenched. Subsequent electron transfer to O_2 could happen to give $O_2^{\bullet-}$. The latter process has been identified in the above DMPO-based experiments. Importantly, Fukuzumi and co-workers reported that electron transfer from Fc to $^1O_2$ is endergonic (ΔG^0_{et} = 0.26 eV).[44] Therefore, it is not likely that $^1O_2$ is first formed by the energy transfer from excited PS-**1** to O_2 and is then consumed by Fc. It is worth noting that even in the presence of Fc, the energy transfer from excited PS-**1** to O_2 still exists because of the detection of the TEMP-$^1O_2$ EPR signal. This competition between electron and energy transfer has also been reported previously.[45-47]

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Nanosecond time-resolved transient difference absorption spectra are used to detect ^{3}PS-**1*** (Fig. 4a). With pulsed excitation at 532 nm, bleaching at 520 nm is observed. Transient absorption at 420 nm and 550-700 nm are characteristics for BODIPY.[48] The lifetime of ^{3}PS-**1*** is 13.1 µs (Fig. 4b). Electron transfer from Fc to ^{3}PS-**1*** was monitored by the decay at 520 nm at various [Fc] (Fig. 5a). The rate obeyed pseudo-first-order kinetics, and the rate constant increased linearly with [Fc]. The second-order rate constant of electron transfer from Fc to ^{3}PS-**1*** is 1.05×10^{10} M^{-1} s^{-1} (Fig. 5b). The energy transfer from ^{3}PS-**1*** to O_2 was also monitored by the decay at 520 nm at various [O_2] (Fig. 5c). The rate obeyed pseudo-first-order kinetics, and the rate constant increased in proportional to [O_2]. The second-order rate constant of energy transfer from ^{3}PS-**1*** to O_2 is 9.1×10^{8} M^{-1} s^{-1} (Fig. 5d).

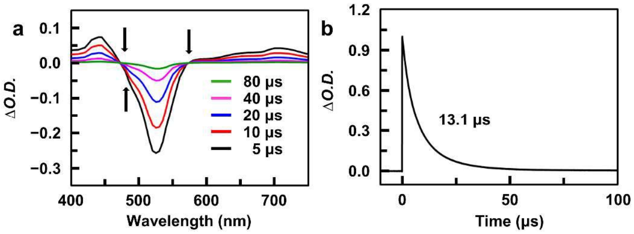


Fig. 4 (a) Nanosecond time-resolved transient difference absorption spectra of PS-**1** (15 µM) after pulsed laser excitation (λ_{ex} = 532 nm). (b) Decay of PS-**1** at 520 nm at 23 °C.

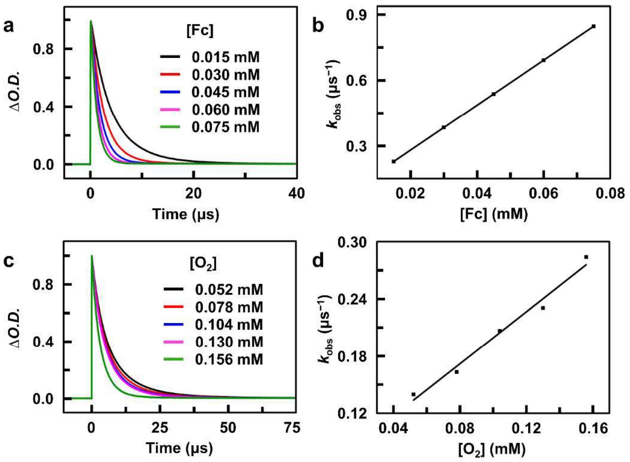
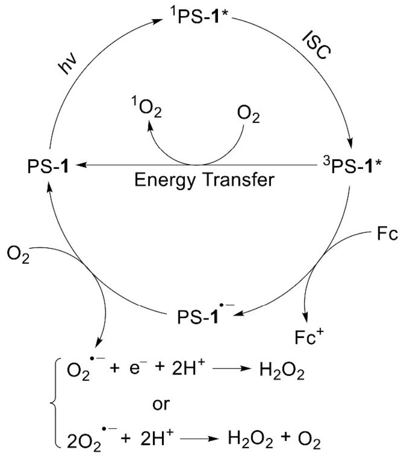


Fig. 5 (a, c) Normalized decay time profile of ^{3}PS-**1*** (produced by laser excitation of 15 µM PS-**1** at λ_{ex} = 532 nm) at 520 nm at various concentrations of Fc and O_2, respectively. (b, d) Plot of pseudo-first-order rate constant (k_{obs}) for electron transfer from Fc to ^{3}PS-**1*** against [Fc] and for energy transfer from ^{3}PS-**1*** to O_2 against [O_2].

On the basis of these results, we proposed a mechanism for the light-driven ORR with PS-**1** (Scheme 2). PS-**1** is first photoexcited to its singlet excited state and is then quickly converted to the triplet excited state via the intersystem crossing (ISC) process. The reductive quenching of excited PS-**1** by Fc takes place to produce Fc^{+} and PS-**1**$^{\bullet-}$.[49] Calculations indicate that the electron transfer from Fc to both the singlet and triplet excited states of PS-**1** is thermodynamically possible (see ESI for details). Considering that the lifetime of a triplet excited state is much longer than that of a singlet excited state, we believe that the electron transfer pathway is from Fc to ^{3}PS-**1***. Subsequent electron transfer from PS-**1**$^{\bullet-}$ to O_2 happens to give PS-**1** and $O_2^{\bullet-}$. The resulted $O_2^{\bullet-}$ can be further reduced by one electron to give H_2O_2 or can disproportionate in the presence of acids to give H_2O_2 and O_2. It is extremely difficult, if it is possible, to study the reaction details of the conversion from $O_2^{\bullet-}$ to H_2O_2 because of the difficulty to keep $O_2^{\bullet-}$ in a stable state.[50,51]



Scheme 2 Proposed mechanism for the selective O_2 reduction to H_2O_2 with PS-**1**.

In conclusion, we report the selective visible-light-driven O_2 reduction to H_2O_2 in a metal-free system. A variety of BODIPY derivatives were used as the photosensitizer. EPR measurements manifested that O_2 could be activated to $^{1}O_2$ by excited PS-**1** through an energy transfer pathway. However, in the presence of Fc, exited PS-**1** was first reductively quenched. The resulted PS$^{\bullet-}$ was able to reduce O_2 to give $O_2^{\bullet-}$, which was able to convert to H_2O_2 through further one-electron reduction or disproportionation. This work is an example showing the selective generation of H_2O_2 from ORR in a metal-free and light-driven system. Our results are also valuable to shed light on photocatalytic oxidation of organic substrates with O_2 using BODIPY photosensitizers.

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