

Cite this: *Chem. Sci.*, 2015, 6, 6496

Catalytic two-electron reduction of dioxygen catalysed by metal-free [14]triphyrin(2.1.1)[†]

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The catalytic two-electron reduction of dioxygen (O₂) by octamethylferrocene (Me₈Fc) occurs with a metal-free triphyrin (HTrip) in the presence of perchloric acid (HClO₄) in benzonitrile (PhCN) at 298 K to yield Me₈Fc⁺ and H₂O₂. Detailed kinetic analysis has revealed that the catalytic two-electron reduction of O₂ by Me₈Fc with HTrip proceeds via proton-coupled electron transfer from Me₈Fc to HTrip to produce H₃Tripp^{•+}, followed by a second electron transfer from Me₈Fc to H₃Tripp^{•+} to produce H₃Tripp, which is oxidized by O₂ via formation of the H₃Tripp/O₂ complex to yield H₂O₂. The rate-determining step in the catalytic cycle is hydrogen atom transfer from H₃Tripp to O₂ in the H₃Tripp/O₂ complex to produce the radical pair (H₃Tripp^{•+} HO₂[•]) as an intermediate, which was detected as a triplet EPR signal with fine-structure by the EPR measurements at low temperature. The distance between the two unpaired electrons in the radical pair was determined to be 4.9 Å from the zero-field splitting constant (*D*).

Received 8th July 2015
Accepted 2nd August 2015

DOI: 10.1039/c5sc02465j

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Introduction

Utilization of natural energy to produce chemical energy consisting of earth-abundant elements is an essential technology for building a society based on the sustainable use of materials. Hydrogen peroxide (H₂O₂) produced by two-electron reduction of O₂ is a versatile and environmentally benign oxidant, which is widely used on a large industrial scale.^{1,2} Furthermore, H₂O₂ has been proposed as a sustainable energy carrier that can be used in fuel cells, where direct and efficient conversion of chemical to electrical energy is required.^{3–5} However, the anthraquinone process, currently used to produce H₂O₂ in industry, requires potentially explosive hydrogen and a noble metal catalyst.⁶ Extensive efforts have so far been devoted to provide an alternative way to produce H₂O₂ photochemically or thermally without the use of noble metal catalysts.^{7–13} In many cases, redox-active transition metal-based complexes such as cobalt,^{14–23} iron,^{24–27} and copper complexes,^{28–31} have been employed as O₂ reduction catalysts, because triplet O₂ is

inactive towards organic compounds due to spin restriction in the absence of an appropriate catalyst.³²

Recently, nitrogen-doped carbon materials have attracted increasing attention as an efficient metal-free catalyst for the catalytic reduction of O₂.^{33–35} However, the catalytic mechanism has yet to be well understood, because few spectroscopic studies to detect reaction intermediates in a catalytic cycle have been performed on heterogeneous systems. In homogeneous systems, reduced flavin analogues involved in flavoenzymes have so far been known to play a pivotal role in the catalytic reduction of O₂, which is a key step of biological oxidation.^{36,37} In particular, the deprotonated states of reduced flavin analogues, which are thermodynamically more able to reduce O₂ via an electron-transfer process, are considered to be a reactive intermediate in the reduction of O₂.³⁸

On the other hand, Girault and coworkers recently reported that the free base porphyrin has the ability to catalyse the two-electron reduction of O₂ using one-electron reductants such as ferrocene at liquid–liquid interfaces.³⁹ In such systems, although the catalytic mechanism of metal-free organocatalysts has yet to be clarified, the oxidation state of the organocatalyst is thought to remain the same during the catalytic reduction of O₂. Thus, no electron-transfer reduction of organic catalysts has been reported in relation to the catalytic reduction of O₂.

In this context, Nocera and coworkers recently reported the stabilization of the peroxide dianion within the cavity of a hexacarboxamide cryptand,⁴⁰ where strong hydrogen bond donors are arranged to completely surround the peroxide dianion with a partial positive charge. This result provides support for the proposal that metal-free organocatalysts, which have multiple hydrogen bonding moieties, can efficiently catalyse O₂ reduction.

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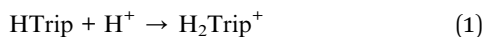
[†] Electronic supplementary information (ESI) available: Spectroscopic, kinetic and DFT data. See DOI: 10.1039/c5sc02465j

We report herein the catalytic two-electron reduction of O_2 by an one-electron reductant, octamethylferrocene (Me_8Fc), with metal-free [14]triphyrin(2.1.1) (denoted as HTrip in Chart 1)⁴¹ in the presence of $HClO_4$ in benzonitrile (PhCN) at 298 K. The catalytic mechanism for the O_2 reduction by Me_8Fc is clarified on the basis of a detailed kinetic study. Proton-coupled electron-transfer reduction of HTrip by Me_8Fc results in the formation of the reduced state of HTrip, and this resulting reduced HTrip is oxidized by O_2 to reproduce HTrip, indicating that HTrip acts as a metal-free catalyst for the reduction of O_2 by Me_8Fc in the presence of $HClO_4$ in PhCN. This discovery of a reactive intermediate in the catalytic O_2 reduction with a molecular organic catalyst provides valuable insight into the development of an efficient metal-free catalyst for the reduction of O_2 .

Results and discussion

Protonation of HTrip with $HClO_4$

HTrip was protonated by addition of perchloric acid ($HClO_4$) to an air-saturated benzonitrile (PhCN) solution of HTrip. The characteristic absorption bands for HTrip at 524 and 581 nm decreased in intensity, with an increase in the absorption band at 565 nm, exhibiting clean isosbestic points, as shown in Fig. 1a. As can be seen in Fig. 1b, the absorbance change at 565 nm is saturated in the presence of 1 equiv. of $HClO_4$. Thus, HTrip is protonated to afford H_2Trip^+ , as given by eqn (1).



The pK_a value of H_2Trip^+ in PhCN was estimated to be 15.6 from the titration of HTrip with trifluoroacetic acid (TFA), as shown in Fig. S1 in the ESI.† The pK_a value of H_2Trip^+ is slightly larger than that of free base porphyrin analogues.⁴² There is no further protonation due to strong repulsion between NH protons in the small macrocyclic ligand, as reported previously.⁴¹

Electrochemical measurements of HTrip in the presence of $HClO_4$

Electrochemical measurements of HTrip were performed in deaerated PhCN containing 0.10 M TBAPF₆, as shown in Fig. 2. A cyclic voltammogram of HTrip exhibits reversible reduction waves at $E_{1/2} = -1.13$ and -1.37 V (vs. SCE), which correspond to the first and second one-electron reduction of HTrip. The first

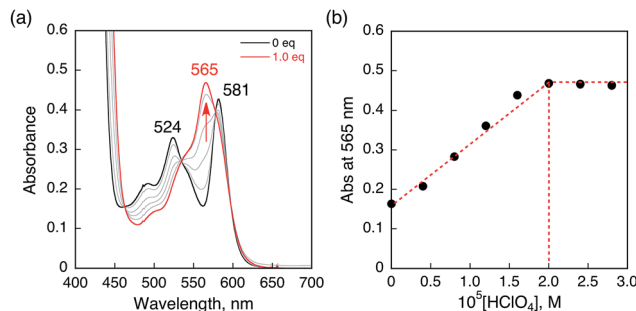


Fig. 1 (a) Absorption spectral changes of HTrip (2.0×10^{-5} M) upon the addition of $HClO_4$ in air-saturated PhCN at 298 K. (b) Absorbance change profile at 565 nm.

one-electron oxidation occurs at $E_{1/2} = 1.04$ V, which is followed by an irreversible oxidation (Fig. 2a). The formation of $HTrip^{\cdot+}$ was detected by UV-vis absorption spectra in the electrochemical reduction of HTrip at a controlled potential of -1.25 V vs. SCE in the thin-layer cell, as shown in Fig. S2 in the ESI.† By addition of $HClO_4$, the first reduction potential of HTrip was positively shifted from $E_{1/2} = -1.13$ V to -0.31 V (vs. SCE) because of the protonation of HTrip, but the reduction became irreversible (Fig. 2b). In such a case, proton-coupled electron transfer from an electron donor with the one-electron oxidation potential, which is less negative than -0.31 V, to HTrip may be thermodynamically feasible (*vide infra*).

Electron-transfer reduction of HTrip in the presence of $HClO_4$

No electron transfer from Me_8Fc to HTrip occurred in the absence of $HClO_4$ in PhCN at 298 K, as indicated by the more negative $E_{1/2}$ value of HTrip (-1.13 V vs. SCE) as compared with that of Me_8Fc (-0.04 V vs. SCE).⁸ However, the addition of more than two equiv. of $HClO_4$ to a deaerated PhCN solution of Me_8Fc and HTrip resulted in the appearance of an absorption band at 738 nm due to H_3Trip with clean isosbestic points, as shown in Fig. 3. It should be noted that no electron transfer from Me_8Fc to H_2Trip^+ occurred in the presence of one equiv. of $HClO_4$, as shown in Fig. 3b. These results indicate that uphill electron transfer from Me_8Fc to H_2Trip^+ is coupled with protonation of H_2Trip^+ to produce $H_3Trip^{\cdot+}$, followed by fast electron transfer from Me_8Fc to $H_3Trip^{\cdot+}$ to yield H_3Trip . Thus, the second protonation in fact occurs by coupling with reduction of H_2Trip^+ (i.e. $H_3Trip^{\cdot+}$ is accessible but not H_3Trip^{2+}). The stoichiometry of the overall reaction is given in Scheme 1.

The rate of proton-coupled electron-transfer reduction of H_2Trip^+ (k_{et}) to form $H_3Trip^{\cdot+}$ was determined from the dependence of the observed rate constant (k_{obs}) on concentrations of Me_8Fc and $HClO_4$, as shown in Fig. 4. The k_{obs} value was determined from the increase in absorbance at 738 nm due to H_3Trip , which obeyed first-order kinetics (Fig. S3 in the ESI†). The k_{obs} value increased linearly with increasing concentrations of Me_8Fc and $HClO_4$, as shown in Fig. 5. Thus, the rate of formation of H_3Trip is given by eqn (2).

$$d[H_3Trip]/dt = k_{et}[H_2Trip^+][HClO_4][Me_8Fc] \quad (2)$$

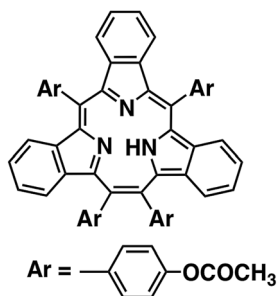


Chart 1 Structure of HTrip.



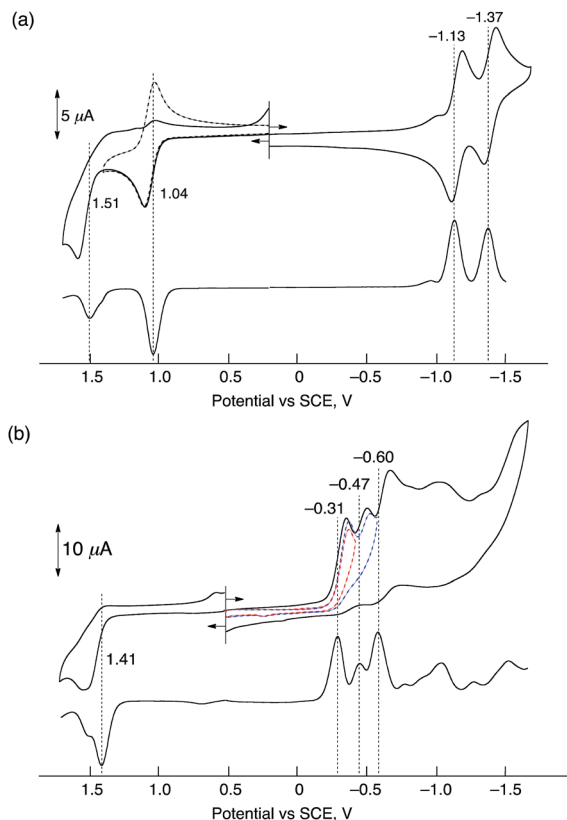
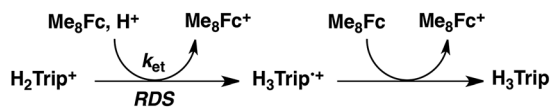


Fig. 2 Cyclic voltammograms (upper) and differential pulse voltammograms (lower) of deaerated PhCN solutions of H₂Trip (1.0×10^{-3} M) recorded in the presence of TBAPF₆ (0.10 M) (a) without HClO₄ and (b) with HClO₄ (1.0×10^{-2} M); sweep rate: 100 mV s⁻¹ for CV and 4 mV s⁻¹ for DPV.



Scheme 1

The k_{et} value is determined from the slope of the linear plot of k_{obs} vs. $[\text{Me}_8\text{Fc}]$ and $[\text{HClO}_4]$ to be $(9.8 \pm 0.2) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$. The k_{et} value of the proton-coupled electron-transfer reduction of H₂Trip⁺ by Me₁₀Fc was also determined from the slope of the linear plot of k_{obs} vs. $[\text{Me}_{10}\text{Fc}]$ and $[\text{HClO}_4]$ to be $(3.1 \pm 0.3) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$ (Fig. S4–S6 in the ESI†). The k_{et} value for Me₁₀Fc is larger than that for Me₈Fc because Me₁₀Fc ($E_{\text{ox}} = -0.08 \text{ V}$ vs. SCE) is a stronger electron donor than Me₈Fc (-0.04 V vs. SCE).²⁸

The formation of H₃Trip was also confirmed by the electrochemical reduction of H₂Trip⁺ monitored by the UV-vis spectral change at an applied potential of -0.30 V vs. SCE in the thin-layer cell, as shown in Fig. S7 (in the ESI†). The product obtained after the electrochemical reduction of H₂Trip⁺ at -0.30 V displayed the characteristic absorption band at 738 nm. The same absorption band was seen in the chemical reduction of H₂Trip⁺ by Me₈Fc in the presence of HClO₄ (Fig. 2).

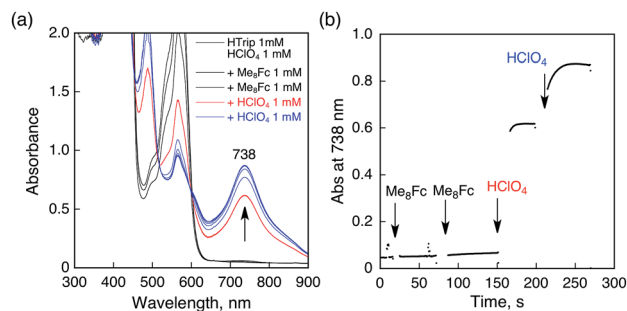


Fig. 3 (a) Absorption spectral changes upon addition of Me₈Fc (1.0×10^{-3} and 2.0×10^{-3} M) to a deaerated PhCN solution of H₂Trip⁺ (1.0×10^{-3} M) in the presence of HClO₄ (1.0×10^{-3} M) at 298 K in a quartz cuvette (light path length = 1 mm) (black); absorption spectral change upon addition of HClO₄ (1.0×10^{-3} M) to the solution indicated by the black line (red); absorption spectral change upon addition of HClO₄ (1.0×10^{-3} M) to the solution indicated by the red line (blue). (b) Absorption change at 738 nm upon addition of various concentrations of Me₈Fc and HClO₄.

When O₂ was introduced to a deaerated PhCN solution of H₃Trip produced by the proton-coupled electron transfer from Me₈Fc to H₂Trip in the presence of HClO₄, the absorption band at 738 nm due to H₃Trip was immediately changed to a new absorption band at 720 nm, which can be attributed to the formation of the O₂ complex, as shown in Scheme 2 (*vide infra*). Subsequently, this spectrum decreased gradually, accompanied by the regeneration of H₂Trip as shown in Fig. 6. This indicates that H₃Trip was readily oxidized by O₂ to produce H₂Trip and H₂O₂ (Scheme 2).

Catalytic two-electron reduction of O₂ by Me₈Fc with H₂Trip in the presence of HClO₄

The proton-coupled electron-transfer reduction of H₂Trip by Me₈Fc (Scheme 1) and the oxidation of the resulting reduced H₂Trip (H₃Trip) by O₂ (Scheme 2) indicate that H₂Trip acts as a metal-free catalyst for the reduction of O₂ by Me₈Fc in the presence of HClO₄ in PhCN. Indeed, the addition of Me₈Fc to air-saturated PhCN at 298 K containing a catalytic amount of

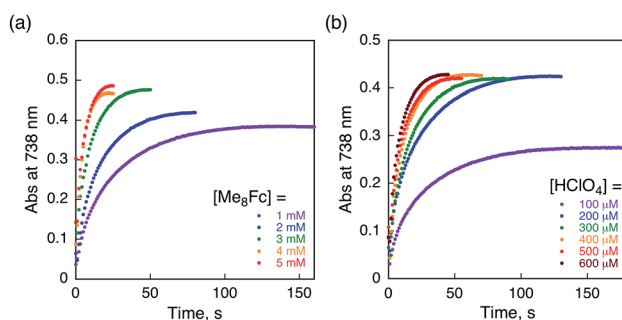


Fig. 4 Time profiles of absorbance at 738 nm due to H₃Trip in the reduction of H₂Trip⁺ (2.5×10^{-5} M) (a) by various concentrations of Me₈Fc in the presence of HClO₄ (3.0×10^{-4} M) and (b) by Me₈Fc (2.0×10^{-3} M) in the presence of various concentrations of HClO₄ in deaerated PhCN at 298 K.



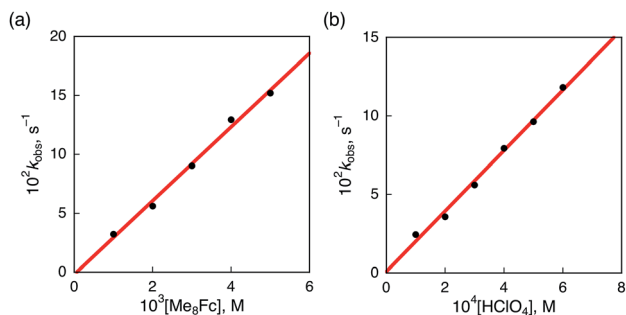


Fig. 5 (a) Plot of k_{obs} vs. $[\text{Me}_8\text{Fc}]$ for the reduction of H_2Trip^+ ($2.5 \times 10^{-5} \text{ M}$) by various concentrations of Me_8Fc in the presence of HClO_4 ($3.0 \times 10^{-4} \text{ M}$) in PhCN at 298 K. (b) Plot of k_{obs} vs. $[\text{HClO}_4]$ for the reduction of H_2Trip^+ ($2.5 \times 10^{-5} \text{ M}$) by Me_8Fc ($2.0 \times 10^{-3} \text{ M}$) in the presence of various concentrations of HClO_4 in deaerated PhCN at 298 K.

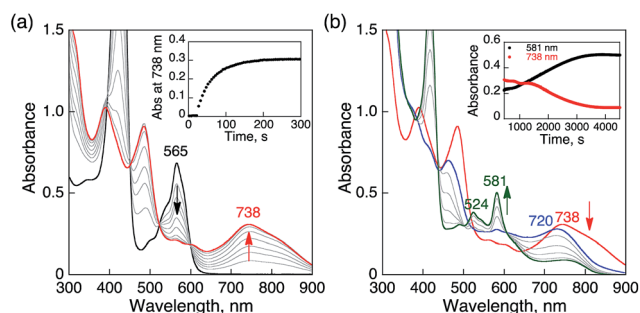
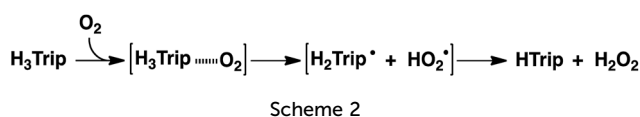


Fig. 6 (a) Absorption spectral changes produced by electron transfer from Me_8Fc ($1.0 \times 10^{-4} \text{ M}$) to H_3Trip ($2.5 \times 10^{-5} \text{ M}$) in the presence of HClO_4 ($1.0 \times 10^{-4} \text{ M}$) in deaerated PhCN at 298 K. (b) Absorption spectral changes upon introducing O_2 to a deaerated PhCN solution of (a). The red and green lines show the spectrum of H_3Trip before and after introducing O_2 by O_2 gas bubbling, respectively. The blue line shows the spectrum due to precursor complex. Insets show absorption time profiles.

HTrip and a large excess of HClO_4 resulted in the efficient oxidation of Me_8Fc by O_2 to yield Me_8Fc^+ , as shown in Fig. 7a.

The formation of Me_8Fc^+ was monitored by a rise in absorbance at 750 nm due to Me_8Fc^+ (Fig. 7b). When an excess amount of Me_8Fc relative to O_2 (*i.e.*, $[\text{O}_2]$ limiting conditions) was employed, the concentration of produced Me_8Fc^+ ($1.9 \times 10^{-3} \text{ M}$) was twice that of O_2 ($9.4 \times 10^{-4} \text{ M}$). In addition, the stoichiometric production of H_2O_2 was confirmed by iodometric titration, as shown in Fig. S8 (in the ESI†). In contrast, when an excess amount of O_2 relative to Me_8Fc (*i.e.*, $[\text{Me}_8\text{Fc}]$ limiting conditions) was employed, the concentration of produced H_2O_2 ($1.0 \times 10^{-3} \text{ M}$) was half that of Me_8Fc ($2.0 \times 10^{-3} \text{ M}$), where the amount of H_2O_2 was determined by the reaction with $[(\text{TMC})\text{Fe}^{\text{II}}](\text{OTf})_2$ ($\text{TMC} = 1,4,8,11\text{-tetramethyl-}$

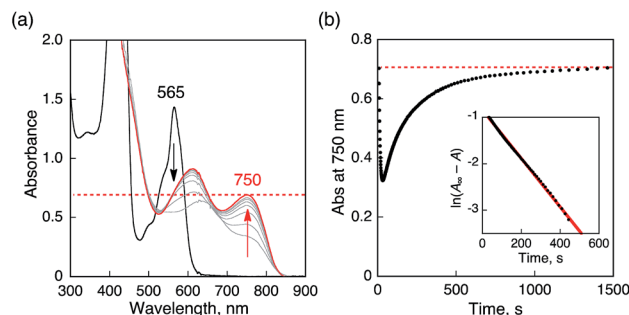
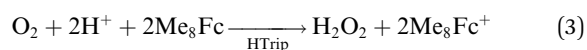


Fig. 7 (a) Absorption spectral changes in the two-electron reduction of O_2 ($9.4 \times 10^{-4} \text{ M}$) by Me_8Fc ($1.0 \times 10^{-2} \text{ M}$) with HTrip ($5.0 \times 10^{-5} \text{ M}$) in the presence of HClO_4 ($1.0 \times 10^{-2} \text{ M}$) in PhCN at 298 K. The black and red lines show the spectra before and after addition of Me_8Fc , respectively. The dotted line is the absorbance at 750 nm due to $1.9 \times 10^{-3} \text{ M}$ of Me_8Fc^+ . (b) Time profile of absorbance at 750 nm due to Me_8Fc^+ . Inset shows first-order plot.

1,4,8,11-tetraazacyclotetradecane) to produce the corresponding Fe(IV)-oxo complex $[(\text{TMC})\text{Fe}^{\text{IV}}(\text{O})]^{2+}$, as shown in Fig. S9 (in the ESI†).⁴³ Thus, the stoichiometry of the catalytic reduction of O_2 by Me_8Fc has been firmly established, as given in eqn (3).



The rate of formation of Me_8Fc^+ in the catalytic reduction of O_2 with excess Me_8Fc and HClO_4 in Fig. 7b obeys first-order kinetics. It should be noted that the oxidation of Me_8Fc by O_2 hardly occurred in the absence of HTrip under the present experimental conditions, as shown in Fig. S10 (in the ESI†). When Me_8Fc was replaced by weaker one-electron reductants such as ferrocene (Fc : $E_{\text{ox}} = 0.37 \text{ V vs. SCE}$) and dimethylferrocene (Me_2Fc : $E_{\text{ox}} = 0.26 \text{ V vs. SCE}$), no changes in the absorption band of H_2Trip^+ at 565 nm were observed, as shown in Fig. S11 (in the ESI†). When Me_8Fc was replaced by a stronger one-electron reductant, *i.e.*, decamethylferrocene (Me_{10}Fc : $E_{\text{ox}} = -0.10 \text{ V vs. SCE}$), greatly enhanced oxidation of Me_{10}Fc occurred with the decrease in absorbance at 565 nm due to H_2Trip^+ (Fig. S12a in the ESI†). In the case of Me_{10}Fc , however, the oxidation of Me_{10}Fc by O_2 occurred without HTrip in the presence of HClO_4 in PhCN (Fig. S12c in the ESI†). These results indicate that the reduction of H_2Trip^+ to produce H_3Trip is essential in the catalytic reduction of O_2 to produce H_2O_2 .

When a metal complex of HTrip , $\eta^5\text{-cyclopentadienyliron(II) [14]triphyrin(2.1.1)}$ ($\text{CpFe}^{\text{II}}\text{Trip}$),^{41c} was employed as an O_2 reduction catalyst instead of HTrip for comparison, however, the addition of HClO_4 to an air-saturated PhCN solution of $\text{CpFe}^{\text{II}}\text{Trip}$ resulted in a spectral change, as shown in Fig. S13 (in the ESI†). The characteristic absorption bands of $\text{CpFe}^{\text{II}}\text{Trip}$ at 545 nm and 608 nm disappeared upon the addition of HClO_4 with the appearance of new absorption bands at 565 nm, which can be attributed to those of H_2Trip^+ . This indicates that $\text{CpFe}^{\text{II}}\text{Trip}$ was easily demetallated and protonated to afford H_2Trip^+ in the presence of HClO_4 , as shown in Fig. S13 (in the ESI†).



Kinetics and mechanism of the catalytic two-electron reduction of O₂ by Me₈Fc with HTrip

The dependence of the first-order rate constant for the formation of Me₈Fc⁺ on the concentrations of HTrip, HClO₄, Me₈Fc, and O₂ was examined, as shown in Fig. S14 (in the ESI[†]), where the first-order rate constants were determined from the initial slopes of the first-order plots in order to avoid further complication due to the deactivation of the catalyst during the reactions, as shown in Fig. S15 (in the ESI[†]). The observed first-order rate constant (k_{obs}) was proportional to the concentration of HTrip, whereas the k_{obs} value remained constant irrespective of the concentration of HClO₄ or Me₈Fc (Fig. 8). Although no degradation of HTrip occurred under the present acidic conditions (Fig. S16 in the ESI[†]), the turnover number (TON) based on HTrip was determined to be more than 40 when the lower concentration of HTrip (1.3×10^{-5} M) was employed, as shown in Fig. S14a (in the ESI[†]). Because the catalytic rate depends only on the concentrations of HTrip and O₂, the rate-determining step in the catalytic cycle must be the reaction of H₃Trip with O₂ in Scheme 3. The dependence of the initial rate of formation of Me₈Fc⁺ on the concentration of O₂ shows saturation behaviour at large concentrations of O₂ (Fig. 8d). Such saturation behaviour is consistent with the formation of the O₂ complex (H₃Trip/O₂) in the oxidation of H₃Trip with O₂ (Fig. 6b and Scheme 3). The overall catalytic cycle is shown in Scheme 3, where proton-coupled electron transfer from Me₈Fc to HTrip is followed by a second electron transfer from Me₈Fc to H₃Trip^{•+} to produce H₃Trip, which is slowly oxidized by O₂ via the H₃Trip/O₂ complex as the rate-determining step. Because the direct reaction between H₃Trip and O₂ in the H₃Trip/O₂ complex is spin-forbidden, the reaction may proceed via hydrogen atom transfer from H₃Trip to O₂ in the H₃Trip/O₂ complex to produce the (H₂Trip[•]/HO₂[•]) intermediate, followed by a rapid second hydrogen transfer from H₂Trip[•] to HO₂[•] to yield H₂O₂, accompanied by regeneration of HTrip (Scheme 3). According to Scheme 3, the rate of formation of Me₈Fc⁺ is given by eqn (4),

$$d[\text{Me}_8\text{Fc}^+]/dt = k_{\text{cat}}[\text{H}_3\text{Trip}/\text{O}_2], \quad (4)$$

where k_{cat} is the rate constant of the hydrogen atom transfer from H₃Trip to O₂ in the H₃Trip/O₂ complex. Because the concentration of the H₃Trip/O₂ complex is given by eqn (5)

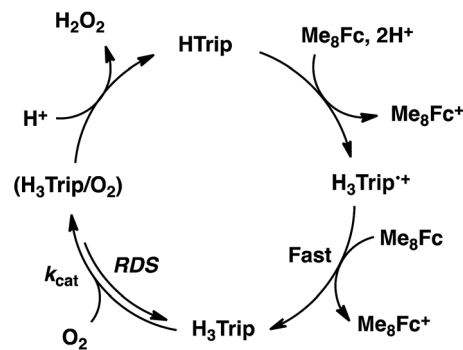
$$[\text{H}_3\text{Trip}/\text{O}_2] = K[\text{HTrip}][\text{O}_2]/(1 + K[\text{O}_2]), \quad (5)$$

using the formation constant (K), the initial concentration of HTrip, which is converted to H₃Trip in the catalytic reaction, and the concentration of O₂, eqn (4) is rewritten as eqn (6).

$$d[\text{Me}_8\text{Fc}^+]/dt = k_{\text{cat}}K[\text{HTrip}][\text{O}_2]/(1 + K[\text{O}_2]) \quad (6)$$

This kinetic equation agrees with the experimental observations in Fig. 8. The k_{cat} and K values were determined from the dependence of the catalytic rate on the concentration of O₂ (Fig. 8d) to be 0.5 s^{-1} and $8.4 \times 10^2 \text{ M}^{-1}$, respectively.

Although the radical pair (H₂Trip[•]/HO₂[•]) in Scheme 3 cannot be detected during the catalytic reaction, the formation of the



Scheme 3

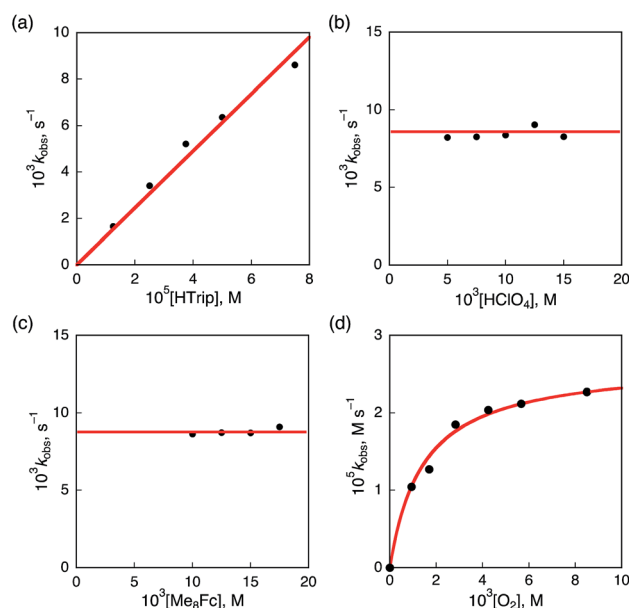


Fig. 8 Plots of (a) k_{obs} vs. $[\text{HTrip}]$ for the two-electron reduction of O₂ (9.4×10^{-4} M) by Me₂Fc (1.0×10^{-2} M) with various concentrations of HTrip in the presence of HClO₄ (1.0×10^{-2} M) in PhCN; (b) k_{obs} vs. $[\text{HClO}_4]$ for the two-electron reduction of O₂ (9.4×10^{-4} M) by Me₈Fc (1.0×10^{-2} M) with HTrip (5.0×10^{-5} M) in PhCN at 298 K; (c) k_{obs} vs. $[\text{Me}_8\text{Fc}]$ for the two-electron reduction of O₂ (9.4×10^{-4} M) by various concentrations of Me₈Fc with HTrip (5.0×10^{-5} M) in the presence of HClO₄ (1.0×10^{-2} M) in PhCN at 298 K; and (d) k_{obs} vs. $[\text{O}_2]$ for the two-electron reduction of O₂ by Me₈Fc (1.0×10^{-2} M) with HTrip (5.0×10^{-5} M) in the presence of HClO₄ (1.0×10^{-2} M) in PhCN at 298 K.

radical pair (H₂Trip[•]/HO₂[•]) was successfully detected by EPR measurements using 1-benzyl-1,4-dihydronicotinamide dimer [(BNA)₂]⁴⁴ as an electron donor to produce H₃Trip under photoirradiation at low temperature. The observed EPR spectrum in aerated PhCN in the presence of HClO₄ at low temperature is shown in Fig. 9. A triplet fine structure EPR signal was observed as well as the typical anisotropic signals for HO₂[•] with the g_{\parallel} value of 2.0341, and isotropic signals for H₂Trip[•] at 2.0030.^{45,46} From the zero-field splitting value ($D = 230$ G), the distance (r) between two unpaired electrons was determined using the relation $D = 27\,800/r^3$ ⁴⁷ to be 4.9 Å. This distance is consistent with the estimated distance between O₂ and H₃Trip in the H₃Trip/O₂ complex by DFT calculations (Fig. 9b).

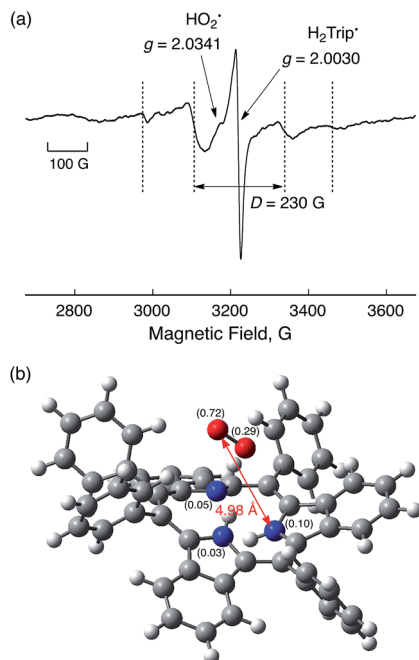


Fig. 9 EPR spectrum observed after the reduction of HTrip (1.0×10^{-3} M) by (BNA) $_2$ (2.0×10^{-3} M) in the presence of HClO $_4$ (1.0×10^{-3} M) in aerated PhCN under photoirradiation using a high-pressure Hg lamp (1000 W) measured at 80 K. Experimental conditions: Microwave frequency 9.0 GHz, microwave power 1.0 mW, modulation frequency 100 kHz, and modulation width 10 G. (b) Optimized structure of H $_3$ Trip/O $_2$ calculated by DFT with calculated spin-density values given in parentheses at the UB3LYP/6-31G(d) level of theory.

Conclusion

Metal-free triphyrin acts as an efficient catalyst for the two-electron reduction of O $_2$ by Me $_8$ Fc to produce H $_2$ O $_2$ in the presence of HClO $_4$ in PhCN at 298 K. The rate-determining step (RDS) in the catalytic cycle has been found to be hydrogen atom transfer from H $_3$ Trip to O $_2$ in the H $_3$ Trip/O $_2$ complex to produce the radical pair (H $_3$ Trip $^{\bullet+}$ /HO $_2^{\bullet}$), which was detected as a triplet species by EPR at 80 K. The distance between the two unpaired electrons (4.9 Å) determined from the zero-field splitting constant (D) agrees with the distance in the H $_3$ Trip/O $_2$ complex calculated by DFT. The present study provides valuable insight into the catalytic mechanism of the two-electron reduction of O $_2$ with an organic catalyst, and may lead to the development of more efficient metal-free organic catalysts for the selective two-electron reduction of O $_2$ to produce H $_2$ O $_2$.

Experimental section

General procedure

Chemicals were purchased from commercial sources and used without further purification, unless otherwise noted. Perchloric acid (HClO $_4$, 70%), trifluoroacetic acid (TFA), ferrocene (Fc), and 1,1-dimethylferrocene (Me $_2$ Fc) were purchased from Wako Pure Chemical Industries Ltd. Octamethylferrocene (Me $_8$ Fc) and decamethylferrocene (Me $_{10}$ Fc) were received from Sigma

Aldrich. Fc, Me $_2$ Fc, Me $_8$ Fc, and Me $_{10}$ Fc were purified by sublimation or recrystallization from ethanol. Benzonitrile (PhCN) used for spectroscopic and electrochemical measurements was distilled over phosphorus pentoxide prior to use.⁴⁸ [14]Triphyrin(2.1.1) [HTrip] was synthesized according to the reported procedure.⁴¹ Fe(II)(TMC)(OTf) $_2$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; OTf = CF $_3$ SO $_3$) was prepared according to a literature method.⁴³ Tetra-*n*-butylammonium hexafluorophosphate (TBAPF $_6$) was twice recrystallized from ethanol and dried *in vacuo* prior to use. 1 H NMR spectra (300 MHz) were recorded on a JEOL AL-300 spectrometer at room temperature and chemical shifts (ppm) were determined relative to tetramethylsilane (TMS). UV-vis absorption spectroscopy was carried out on a Hewlett Packard 8453 diode array spectrophotometer at room temperature using a quartz cell (light path length = 1 cm).

Spectroscopic measurements

The amount of hydrogen peroxide (H $_2$ O $_2$) produced was determined by titration with iodide ion: a dilute CH $_3$ CN solution (2.0 mL) of the product mixture (50 μ L) was treated with an excess amount of NaI, and the amount of I $_3^-$ formed was determined from the absorption spectrum (λ_{max} = 361 nm, ϵ = 2.8×10^4 M $^{-1}$ cm $^{-1}$).⁴⁹ The formation of H $_2$ O $_2$ in the catalytic O $_2$ reduction with HTrip was again confirmed by the reaction between H $_2$ O $_2$ and Fe(II)(TMC)(OTf) $_2$ to afford the corresponding Fe(IV)-oxo species. The amount of the Fe(IV)-oxo species produced was determined from the absorption spectrum (λ_{max} = 820 nm, ϵ = 400 M $^{-1}$ cm $^{-1}$).⁴³

The turnover numbers (TON = the number of moles of H $_2$ O $_2$ formed per mole of HTrip in the catalytic two-electron reduction of O $_2$) were determined from the concentration of produced Me $_8$ Fc $^+$ under catalytic conditions, where stoichiometric production of H $_2$ O $_2$ was confirmed by iodometric titration.

Kinetic measurements

Rate constants of oxidation of ferrocene derivatives by O $_2$ in the presence of a catalytic amount of HTrip and an excess amount of HClO $_4$ in PhCN at 298 K were determined by monitoring the appearance of an absorption band due to the corresponding ferrocenium ions (Fc $^+$, λ_{max} = 620 nm, ϵ_{max} = 330 M $^{-1}$ cm $^{-1}$; Me $_2$ Fc $^+$, λ_{max} = 650 nm, ϵ_{max} = 290 M $^{-1}$ cm $^{-1}$; Me $_8$ Fc $^+$, λ_{max} = 750 nm, ϵ_{max} = 410 M $^{-1}$ cm $^{-1}$; Me $_{10}$ Fc $^+$, λ_{max} = 780 nm, ϵ_{max} = 450 M $^{-1}$ cm $^{-1}$).¹⁴ At the wavelengths monitored, spectral overlap was observed with H $_3$ Trip (λ = 738 nm (ϵ = 1.6×10^3 M $^{-1}$ cm $^{-1}$)), H $_3$ Trip/O $_2$ (λ = 720 nm (ϵ = 1.2×10^3 M $^{-1}$ cm $^{-1}$)). The concentration of O $_2$ in an air-saturated PhCN solution was determined to be 1.7×10^{-3} M as reported previously.⁵⁰ The concentrations of ferrocene derivatives employed for the catalytic reduction of O $_2$ were much larger than that of O $_2$, as O $_2$ is the rate-limiting reagent in the reaction solution. The PhCN solutions containing various concentrations of O $_2$ for the kinetic measurements were prepared by N $_2$ /O $_2$ mixed gas bubbling using a KOFLOC GASBLENDER GB-3C. Typically, a PhCN stock solution of a ferrocene derivative was added using a



microsyringe to a PhCN solution containing HTrip and HClO₄ in a quartz cuvette (light path length = 1 cm).

Electrochemical measurements

Cyclic voltammetry (CV) measurements were performed on an ALS 630B electrochemical analyser and voltammograms were measured in deaerated PhCN containing 0.10 M TBAPF₆ as a supporting electrolyte at room temperature. A conventional three-electrode cell was used with a glassy carbon working electrode (surface area of 0.3 mm²) and a platinum wire as the counter electrode. The glassy carbon working electrode (BAS) was routinely polished with BAS polishing alumina suspension and rinsed with acetone before use. The potentials were measured with respect to the Ag/AgNO₃ (1.0 × 10⁻² M) reference electrode. All potentials (vs. Ag/AgNO₃) were converted to values vs. SCE by adding 0.29 V.⁵¹ Redox potentials were determined using the relation $E_{1/2} = (E_{pa} + E_{pc})/2$.

Spectroelectrochemical measurements

UV-visible spectroelectrochemical experiments were performed with a home-built thin-layer cell (1 mm) that had a light transparent platinum net working electrode. Potentials were applied and monitored with an ALS 730D electrochemical analyser.

EPR measurements

EPR spectra were measured on a JEOL X-band EPR spectrometer (JES-ME-LX) using a quartz EPR tube containing a deaerated frozen sample solution at 80 K. The internal diameter of the EPR tube is 4.0 mm, which is small enough to fill the EPR cavity but large enough to obtain good signal-to-noise ratios during the EPR measurements at low temperatures (at 80 K). EPR spectrum of HTrip^{•-} produced by the electrochemical reduction of HTrip was measured using a home-built three-electrode quartz EPR tube. Potentials were applied and monitored with an ALS 730D electrochemical analyser. EPR spectra were measured under nonsaturating microwave power conditions. The amplitude of modulation was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra. The g values were calibrated with a Mn²⁺ marker.

Theoretical calculations

Density functional theory (DFT) calculations were performed on a 32CPU workstation (PQS, Quantum Cube QS8-2400C-064). Geometry optimisations were carried out using the B3LYP/6-31G(d) level of theory⁵² for HTrip^{•-}, H₂Tri⁺, H₃Tri²⁺, H₃Tri^{•+}, and [H₃Tri/O₂]. All calculations were performed using Gaussian 09, revision A.02.⁵³ Graphical outputs of the computational results were generated with the GaussView software program (ver. 3.09) developed by Semichem, Inc.⁵⁴

Acknowledgements

This work was supported by grants from the Advanced Low Carbon Technology Research and Development (ALCA) and

SENTAN programs from Japan Science Technology Agency (JST) to S. F., the Japan Society for the Promotion of Science (JSPS: Grants 26620154 and 26288037 to K. O., 25288092 and 26105004 to H. Y. and 25-727 to K. M.), and the Green Photonics Project in NAIST sponsored by the MEXT (Japan).

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