

Supplementary Information

In situ uncovering the catalytic cycle of electrochemical and chemical oxygen reduction mediated by iron porphyrin

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Experimental procedures

Chemicals. The chemicals were of analytical or higher grade and used as received without further purification unless otherwise stated. The catalyst 5,10,15,20-*meso*-tetraphenylporphyrin iron(III) perchlorate $[(\text{TPP})\text{Fe}^{\text{III}}]\text{ClO}_4$ was synthesized according to the reported method.^{S1} The supporting electrolyte tetrabutylammonium hexafluorophosphate $[\text{Bu}_4\text{N}][\text{PF}_6]$, 99% was purchased from Sigma-Aldrich. Perchloric acid (HClO_4 , 70% w/w) was purchased from Sinopharm Chemical Reagent. Decamethylferrocene (Me_{10}Fc , 99%) was purchased from Bide Pharmatech. Ferrocene (Fc , 99%) and chloranil (98%) were purchased from Aladdin. *N,N*-dimethylformamide (DMF, $\geq 99.9\%$, HPLC) was purchased from Energy Chemical. *n*-Butane (99.5%), nitrogen (N_2 , 99.5%), oxygen (O_2 , 99.999%), and oxygen- $^{18}\text{O}_2$ (97 atom% ^{18}O) were purchased from Beijing ZG Special Gases, Jinghui Gas, Xingchen Oxygen, and Mreda respectively.

Fabrication of dual micropipettes and carbon hybrid UMEs. Dual micropipettes were made from quartz theta capillaries (QT120-90-7.5, Sutter Instrument, USA) by a CO_2 -laser-based puller (P-2000, Sutter Instrument, USA) with a pulling program as follows:

HEAT 710, FIL 3, VEL 20, DEL 128, PULL 90,

HEAT 695, FIL 2, VEL 15, DEL 133, PULL 105.

Carbon hybrid UMEs were fabricated based on the pyrolysis of *n*-butane in the above dual-barrel micropipettes according to reported methods.^{S2,S3} The quartz dual micropipettes and carbon hybrid UMEs were characterized by the optical microscope (BX51, Olympus, Japan) and the scanning electron microscope (SEM) (S-4800, Hitachi, Japan) (Fig. S1).

Electrochemical measurements. The experiments of cyclic voltammetry (CV) were carried out on an electrochemical workstation (CHI 760E, Shanghai Chenhua Instrument, China) with a two-electrode setup (Cell 1) at the scan rate of $0.1 \text{ V}\cdot\text{s}^{-1}$. Rotating ring-disk voltammetry (RRDV) experiments were performed according to the reference^{S4} on an electrochemical workstation with a modulated speed rotator (AFMSRCE, Pine, USA) using the glassy carbon (GC) disk and the Pt ring as working electrodes (Cell 2) at the scan rate of $0.05 \text{ V}\cdot\text{s}^{-1}$ and the rotation rate of 400 rpm. All potentials in electrochemical measurements were calibrated with ferrocene. The Pt ring potential was held at $+0.55 \text{ V}$ vs. Fc^+/Fc . The number of electrons (n_{cat}) transferred in electrochemical oxygen reduction reaction (ORR) was calculated by the following equation:

$$n_{\text{cat}} = \frac{4I_{\text{D}}}{I_{\text{D}} + I_{\text{R}}/N} \quad (\text{S1})$$

where I_{D} is the GC disk current, I_{R} is the Pt ring current, and N is the collection efficiency equal to 0.37.

The electrochemical cells employed in this work are as follows:

Cell 1: Carbon | 0.5 mM $[(\text{TPP})\text{Fe}^{\text{III}}]\text{ClO}_4$ + 100 mM $[\text{Bu}_4\text{N}][\text{PF}_6]$ + 50 mM HClO_4 in DMF | Ag

Cell 2: GC and Pt | 0.5 mM $[(\text{TPP})\text{Fe}^{\text{III}}]\text{ClO}_4$ + 100 mM $[\text{Bu}_4\text{N}][\text{PF}_6]$ + 50 mM HClO_4 in DMF | Ag^+/Ag

Cell 3: Carbon | 0.5 mM $[(\text{TPP})\text{Fe}^{\text{III}}]\text{ClO}_4$ + 10 mM $[\text{Bu}_4\text{N}][\text{PF}_6]$ + 5 mM HClO_4 in DMF | Ag

In situ MS setup and measurements. The experimental setup of the in situ EC-MS included a carbon hybrid UME, an oxygenated setup, a potentiostat, a piezoelectric pistol, and an MS detector (Scheme 1a and Fig. S3).^{S3,S5} The experimental setup of the in situ CR-MS included a quartz dual micropipette, an oxygenated setup, a piezoelectric pistol, and an MS detector (Scheme

1b and Fig. S3). When the potential is applied at the constant potential in EC-MS experiments or the reductant Me₁₀Fc was added in CR-MS experiments, the piezoelectric pistol pumps and samples analytes into the mass spectrometer after every 30 seconds of electrolysis or reaction to repeat at least three times. Pulse spray was achieved with a piezoelectric pistol (Milty Zerostat 3, Goldring, UK).^{S6} The primary ions or charged droplets, generated in the ambient atmosphere by the piezoelectric pistol, pass charges to the sample loading capillary, causing a secondary electrospray to occur from the tip of the capillary. The ionic compounds from the analyte solution can be directly analyzed by MS. The neutral compound could be ionized by charges passed from the primary ions or charged droplets and then detected by MS. MS analysis of intermediates was conducted on a linear ion trap mass spectrometer (LTQ XL, Thermo Scientific, USA) in the positive ion mode.

UV-vis spectroscopy measurements. The chemical ORR catalyzed by [(TPP)Fe^{III}]ClO₄ (0.05 mM) under conditions of limiting O₂ (0.7 mM) and excess Me₁₀Fc (5 mM) and HClO₄ (5 mM) in DMF was characterized by using the SX20 stopped-flow spectrophotometer equipped with a UV region Photodiode Array operating over the wavelength region 180-725 nm.^{S7} The concentration of Me₁₀Fc⁺ was determined from the absorbance at 715 nm. The standard curve of Me₁₀Fc⁺ was determined by reacting excess chloranil (10 mM) with different concentrations of Me₁₀Fc (1-5 mM) in DMF containing 5 mM HClO₄ (Fig. S7). The n_{cat} consumed in chemical ORR was calculated by the following equation:

$$n_{\text{cat}} = \frac{c_{\text{Me}_{10}\text{Fc}^+}}{c_{\text{O}_2}} \quad (\text{S2})$$

where $c_{\text{Me}_{10}\text{Fc}^+}$ is the Me₁₀Fc⁺ concentration and c_{O_2} is the O₂ concentration.

Catalysts	Driven methods	Characterization methods	Intermediates	Reference
[(TPP)Fe ^{III}]ClO ₄	Electrochemically Chemically (Me ₁₀ Fc)	EC-MS CR-MS Stopped-flow UV-vis spectroscopy	[(TPP)Fe ^{III} -O ₂ ⁻] [(TPP)Fe ^{III} -O ₂ H] ⁺ [(TPP)Fe ^{III} -O ₂ H ₂] ⁺ [(TPP)Fe ^V =O] ⁺ [(TPP)Fe ^{IV} -OH] ⁺ [(TPP)Fe ^{III}] ⁺ [(TPP)Fe ^{II}]	This work
[(TPP)Fe ^{III}](Cl)	Electrochemically	ESI-MS	[(TPP)Fe ^{IV} -OH] ⁺	<i>J. Am. Chem. Soc.</i> 2024 , <i>146</i> , 15619-15626
FeEs ₄ TPP-Fe	Electrochemically	SERRS-RDE	HS Fe ^{II} LS Fe ^{III} -OOH Fe ^{IV} =O HS Fe ^{III}	<i>ACS Catal.</i> 2016 , <i>6</i> , 6838-6852
[(TPP)Fe ^{III}]OTf	Chemically (Me ₁₀ Fc)	Stopped-flow UV-vis spectroscopy	Fe ^{III} -O ₂ ⁻ (253 K) Fe ^{II} (above 273 K) Fe ^{III} (all cases)	<i>J. Am. Chem. Soc.</i> 2019 , <i>141</i> , 8315-8326
⁶ LFeCu ⁶ LFe	Chemically (Me ₁₀ Fc)	Stopped-flow UV-vis spectroscopy	Fe ^{III} -OOH (213 K) Fe ^{II} (RT)	<i>Proc. Natl. Acad. Sci. U. S. A.</i> 2011 , <i>108</i> , 13990-139944

Table S1. A summary and comparison for detecting intermediates in ORR catalyzed by iron porphyrins.

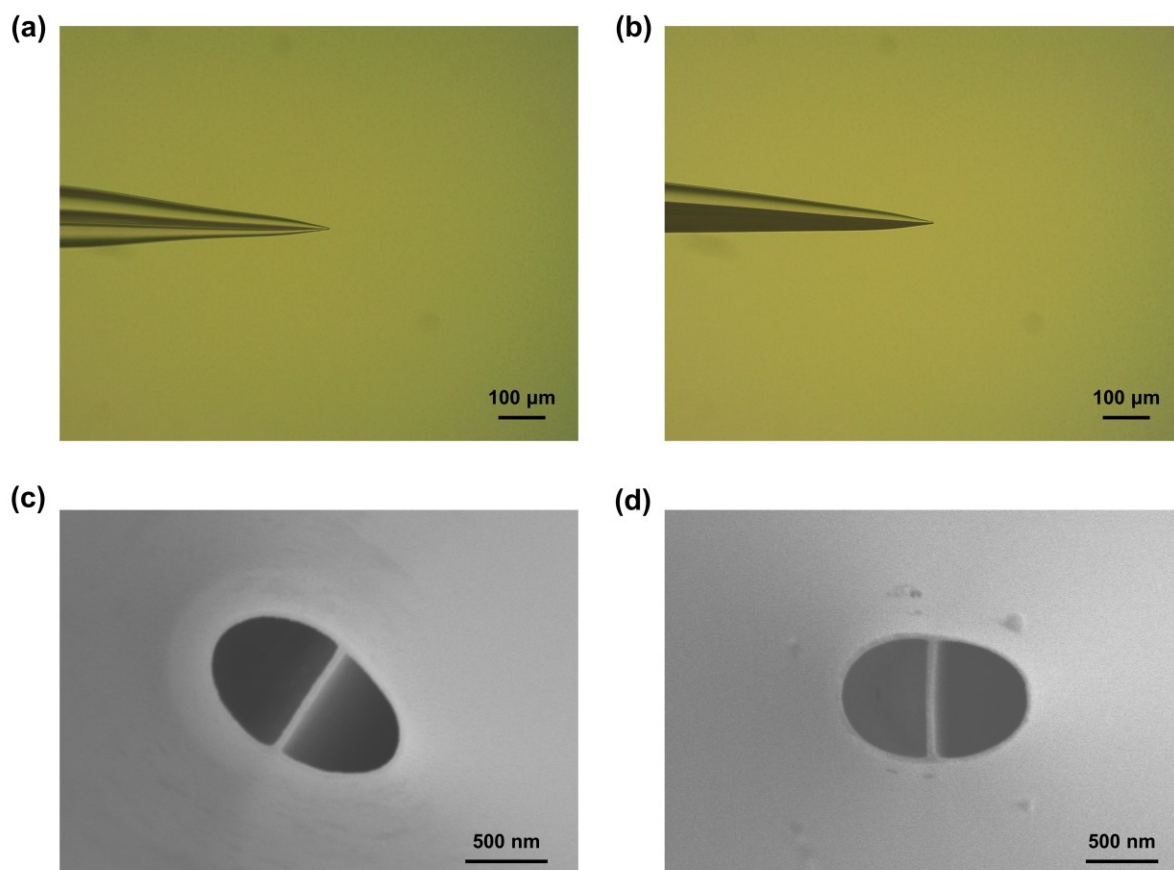


Fig. S1 Optical microscope images of the side of (a) a quartz dual micropipette and (b) a carbon hybrid UME. SEM images of the tip of (c) a quartz dual micropipette and (d) a carbon hybrid UME.

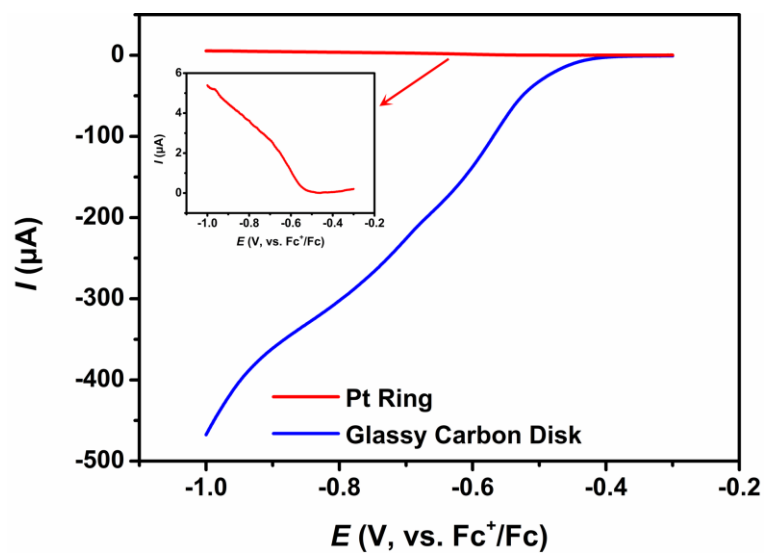


Fig. S2 RRDV curves of 0.5 mM $[(\text{TPP})\text{Fe}^{\text{III}}]\text{ClO}_4$ in DMF under 1 atm O_2 (Cell 2). The current on the GC disk (blue) indicates the catalytic ORR. The current on the Pt ring (red, enlarged to show in the inner image) indicates the oxidation of H_2O_2 generated in ORR.

E (V, vs. Fc^+/Fc)	-0.6	-0.7	-0.8	-0.9
n_{cat}	3.92	3.88	3.87	3.87

Table S2. The number of electrons transferred in electrochemical ORR which RRDV determined.

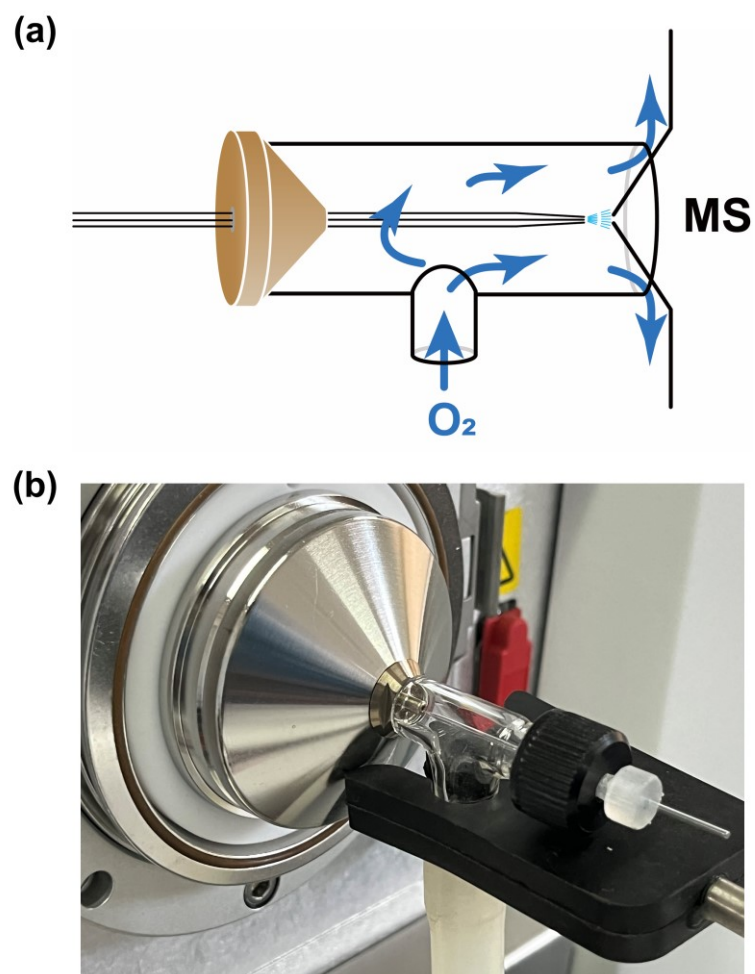


Fig. S3 Schematic illustration (a) and photograph (b) of the in situ oxygenated MS setup.

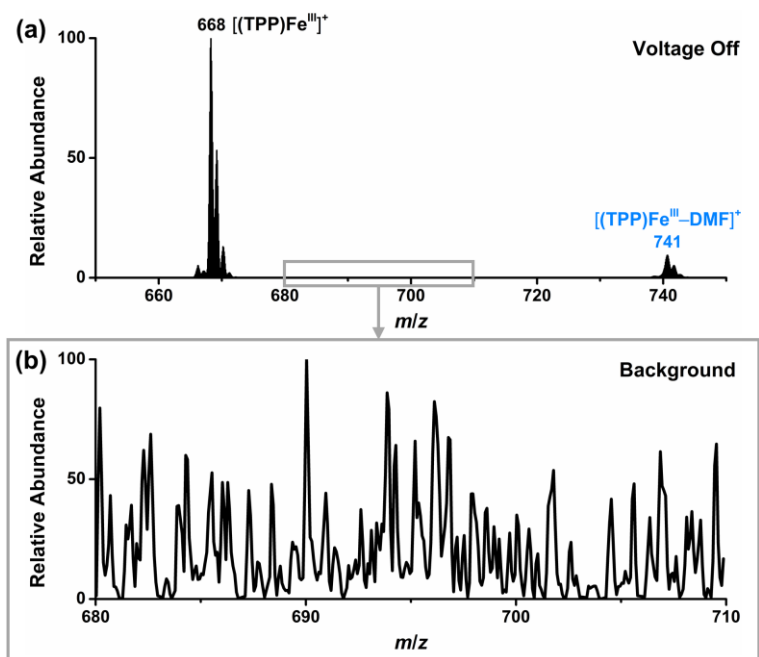


Fig. S4 Mass spectra of $[(\text{TPP})\text{Fe}^{\text{III}}]^+$ in DMF when the voltage was off (Cell 3).

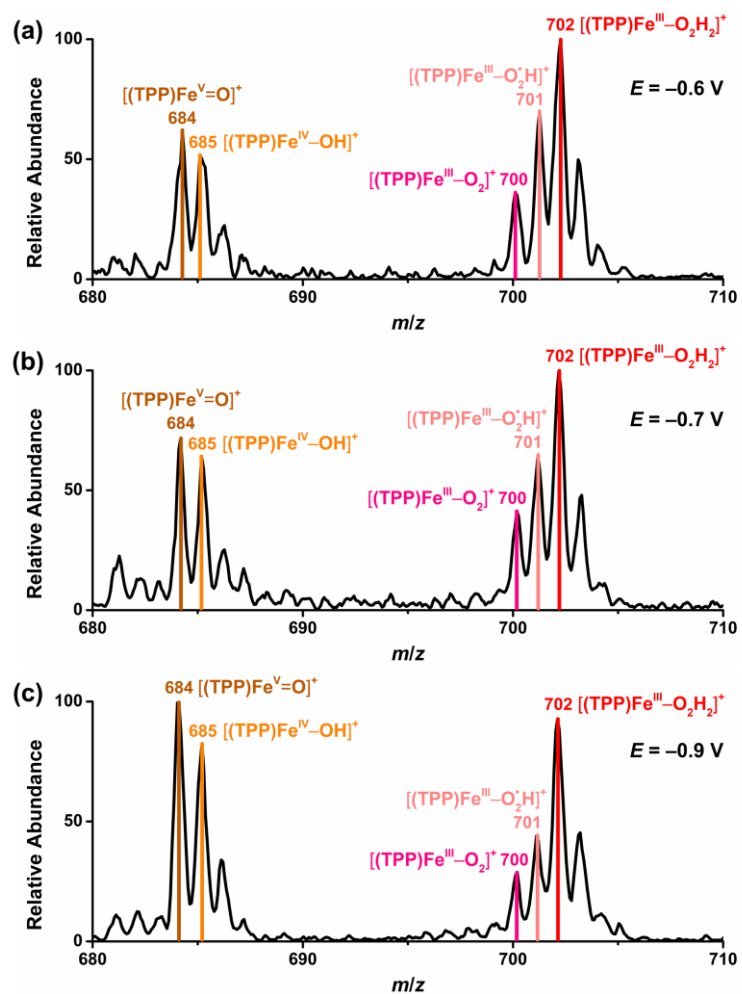


Fig. S5 Mass spectra of electrochemical ORR catalyzed by $[(\text{TPP})\text{Fe}^{\text{III}}]^+$ in DMF when the voltage was applied at (a) -0.6 V , (b) -0.7 V , and (c) -0.9 V vs. Fc^+/Fc , respectively.

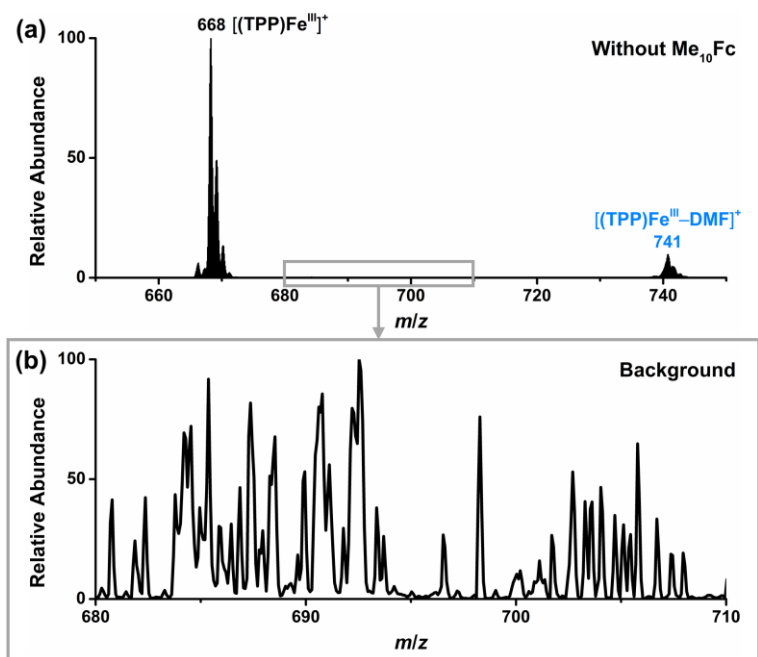


Fig. S6 Mass spectra of $[(\text{TPP})\text{Fe}^{\text{III}}]^+$ without Me_{10}Fc in DMF.

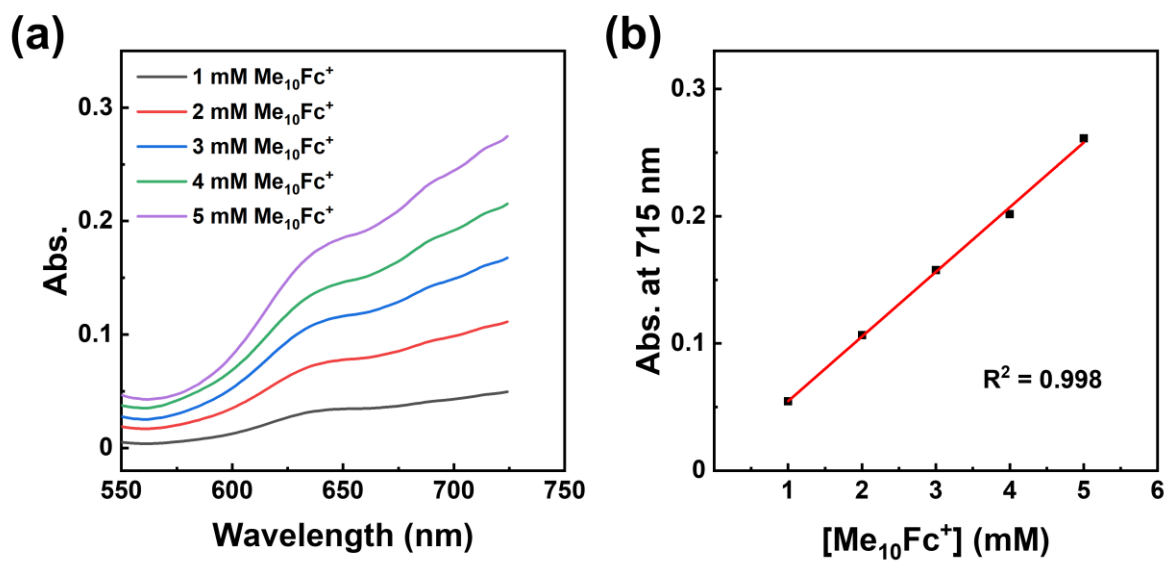


Fig. S7 (a) UV-vis spectra for the reaction of excess chloranil (10 mM) with different concentrations of Me₁₀Fc (1-5 mM) in DMF containing 5 mM HClO₄. (b) The standard curve of Me₁₀Fc⁺ which is determined by the absorbance at 715 nm.

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