

Supplementary Information

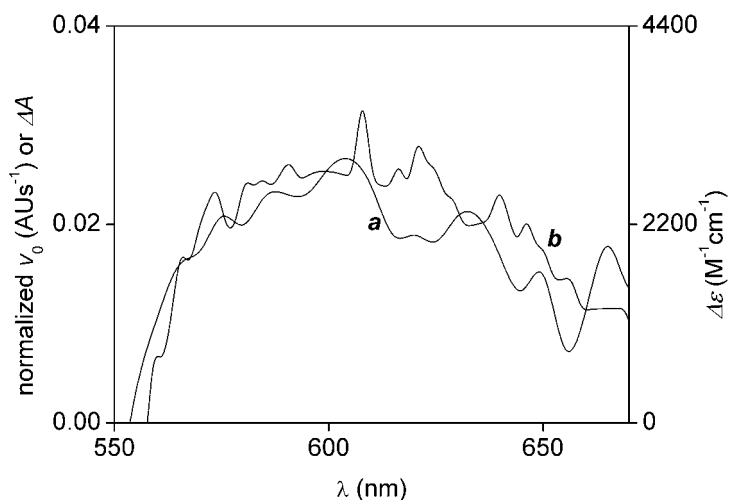
for

**Kinetics and Mechanism of the Oxidation of Water Soluble Porphyrin Fe<sup>III</sup>TPPS with  
Hydrogen Peroxide and Peroxomonosulfate Ion**

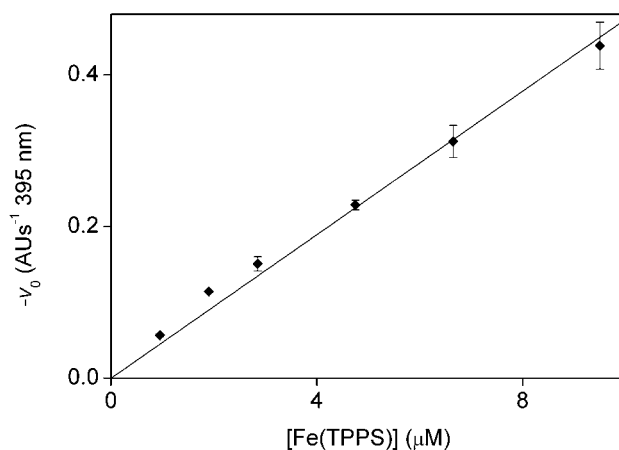
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21, Hungary, H-4010

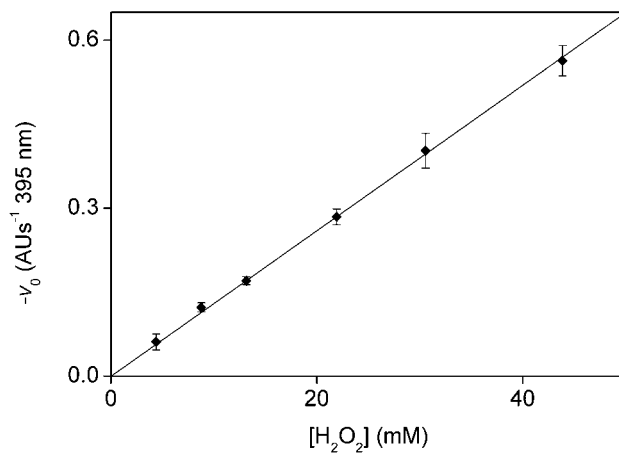
e-mail: [lenteg@delfin.unideb.hu](mailto:lenteg@delfin.unideb.hu) Tel: + 36 52 512-900/22373 Fax: + 36 52 489-667



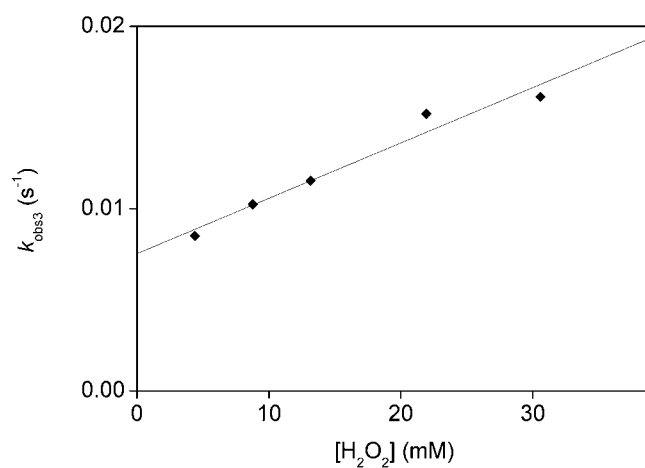
**Fig. S1** Comparison of normalized absorbance changes for the first phase (*a*, with  $\text{HSO}_5^-$ ) and normalized initial rates (*b*, with  $\text{H}_2\text{O}_2$ ) as a function of wavelength during the reaction of  $\text{Fe}^{\text{III}}$ TPPS with  $\text{HSO}_5^-$  and  $\text{H}_2\text{O}_2$ .  $[\text{Fe}^{\text{III}}\text{TPPS}] = 6.9 \mu\text{M}$  (*a*),  $9.5 \mu\text{M}$  (*b*);  $[\text{HSO}_5^-] = 2.95 \text{ mM}$  (*a*);  $[\text{H}_2\text{O}_2] = 8.77 \text{ mM}$  (*b*);  $\text{pH} = 1.30$  (*a*),  $3.05$  (*b*); optical path length =  $1.00 \text{ cm}$ ;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ). The relatively strong noise in the data is due to the fact that values are obtained from the differences of very small absorbance readings.



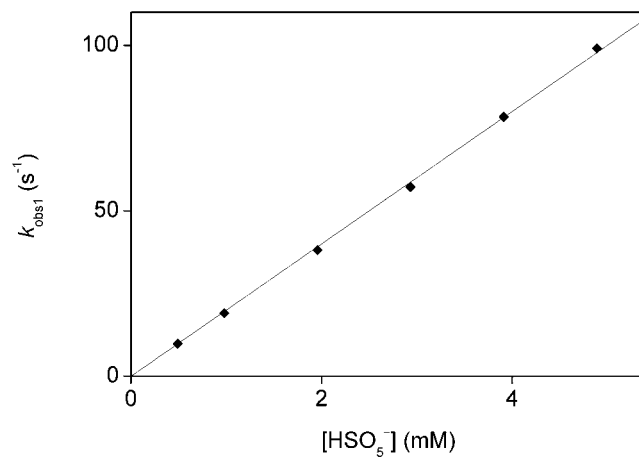
**Fig. S2** Dependence of initial rates on the concentration of  $\text{Fe}^{\text{III}}$ TPPS during the reaction of  $\text{Fe}^{\text{III}}$ TPPS with  $\text{H}_2\text{O}_2$ .  $[\text{H}_2\text{O}_2] = 30.6 \text{ mM}$ ;  $\text{pH} = 3.05$ ; optical path length =  $1.00 \text{ cm}$ ;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ).



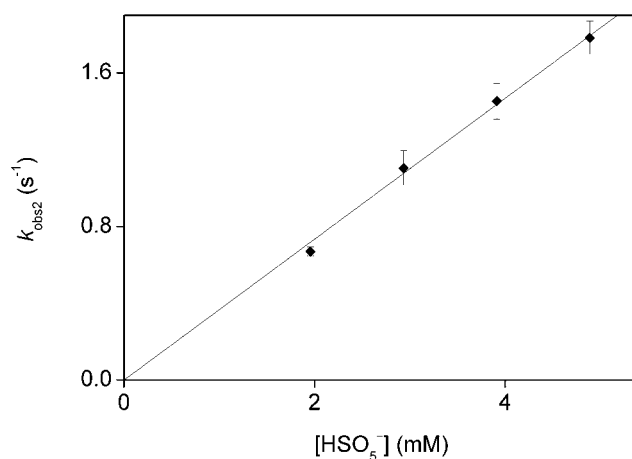
**Fig. S3** Dependence of initial rates on the concentration of H<sub>2</sub>O<sub>2</sub> during the reaction of Fe<sup>III</sup>TPPS with H<sub>2</sub>O<sub>2</sub>. [Fe<sup>III</sup>TPPS] = 9.5 μM; pH = 3.05; optical path length = 1.00 cm; *T* = 25.0 °C; *I* = 0.1 M (NaClO<sub>4</sub>).



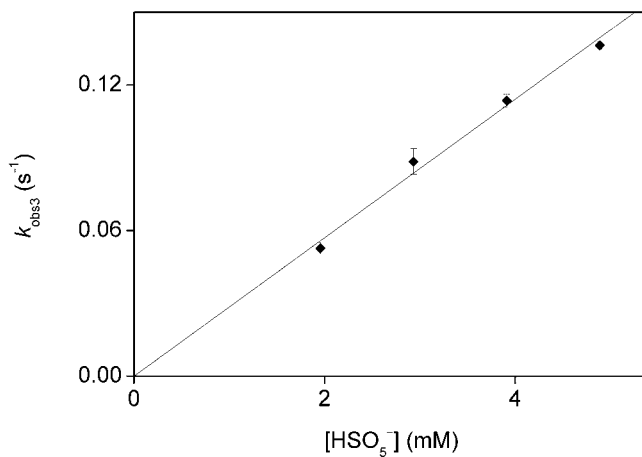
**Fig. S4** Dependence of pseudo first order rate constant  $k_{\text{obs3}}$  on the oxidant concentration during the reaction of Fe<sup>III</sup>TPPS with H<sub>2</sub>O<sub>2</sub>. [Fe<sup>III</sup>TPPS] = 9.5 μM; pH = 3.05; *T* = 25.0 °C; *I* = 0.1 M (NaClO<sub>4</sub>).



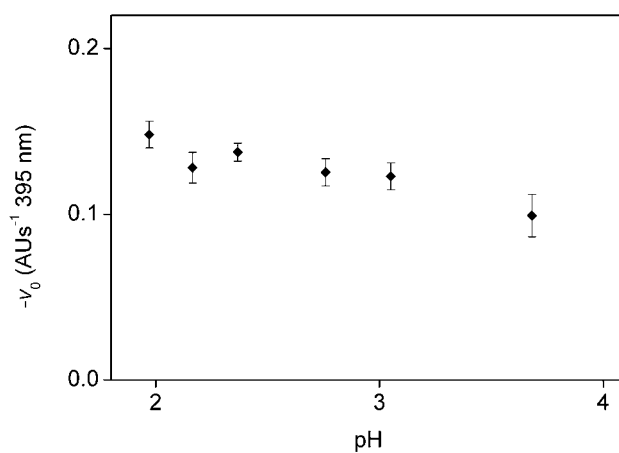
**Fig. S5** Dependence of pseudo first order rate constant  $k_{\text{obs1}}$  on the oxidant concentration during the reaction of  $\text{Fe}^{\text{III}}\text{TPPS}$  with  $\text{HSO}_5^-$ .  $[\text{Fe}^{\text{III}}\text{TPPS}] = 6.9 \mu\text{M}$ ;  $\text{pH} = 1.30$ ;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ).



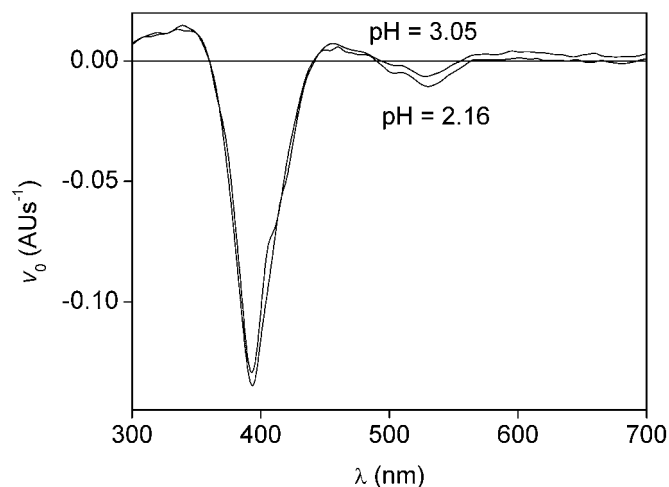
**Fig. S6** Dependence of pseudo first order rate constant  $k_{\text{obs2}}$  on the oxidant concentration during the reaction of  $\text{Fe}^{\text{III}}\text{TPPS}$  with  $\text{HSO}_5^-$ .  $[\text{Fe}^{\text{III}}\text{TPPS}] = 6.9 \mu\text{M}$ ;  $\text{pH} = 1.30$ ;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ).



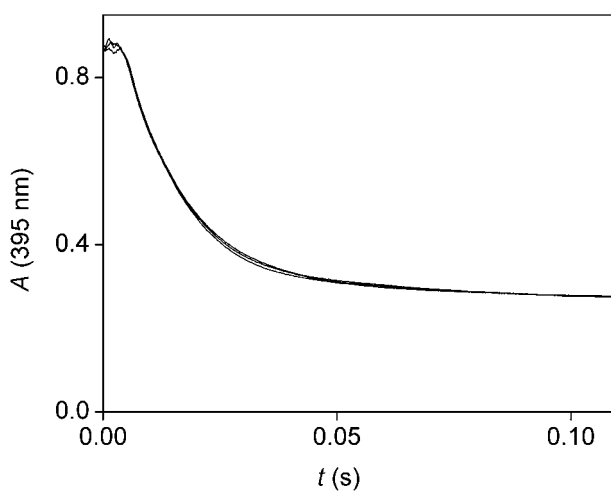
**Fig. S7** Dependence of pseudo first order rate constant  $k_{\text{obs}3}$  on the oxidant concentration during the reaction of  $\text{Fe}^{\text{III}}\text{TPPS}$  with  $\text{HSO}_5^-$ .  $[\text{Fe}^{\text{III}}\text{TPPS}] = 6.9 \mu\text{M}$ ;  $\text{pH} = 1.30$ ;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ).



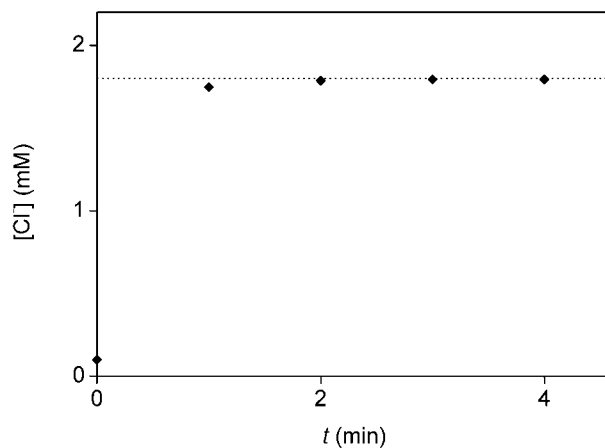
**Fig. S8** Dependence of initial rates on pH during the reaction of  $\text{Fe}^{\text{III}}\text{TPPS}$  with  $\text{H}_2\text{O}_2$ .  $[\text{Fe}^{\text{III}}\text{TPPS}] = 9.5 \mu\text{M}$ ;  $[\text{H}_2\text{O}_2] = 8.77 \text{ mM}$ ; optical path length = 1.00 cm;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ).



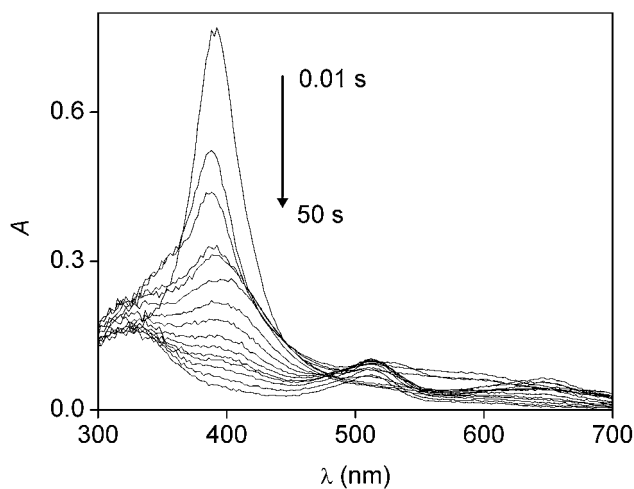
**Fig. S9** Comparison of initial rates measured at two different pH values as a function of wavelength during the reaction of  $\text{Fe}^{\text{III}}\text{TPPS}$  with  $\text{H}_2\text{O}_2$ .  $[\text{Fe}^{\text{III}}\text{TPPS}] = 9.5 \mu\text{M}$ ;  $[\text{H}_2\text{O}_2] = 30.6 \text{ mM}$ ; optical path length = 1.00 cm;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ). The curves are identical within experimental error limits proving that a change in pH does not influence the first reaction.



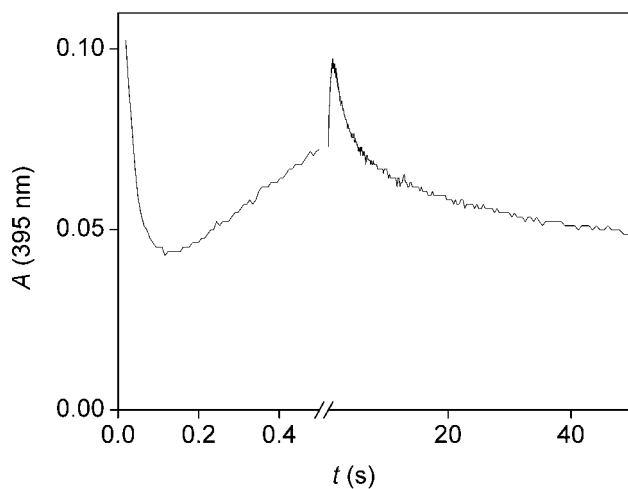
**Fig. S10** Three kinetic traces measured at different pH values during the reaction of  $\text{Fe}^{\text{III}}\text{TPPS}$  with  $\text{H}_2\text{O}_2$ .  $[\text{Fe}^{\text{III}}\text{TPPS}] = 9.5 \mu\text{M}$ ;  $[\text{H}_2\text{O}_2] = 3.91 \text{ mM}$ ; pH = 1.30, 1.58, 1.97; optical path length = 1.00 cm;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ). The curves are identical within experimental error limits proving that a change in pH does not influence the reaction.



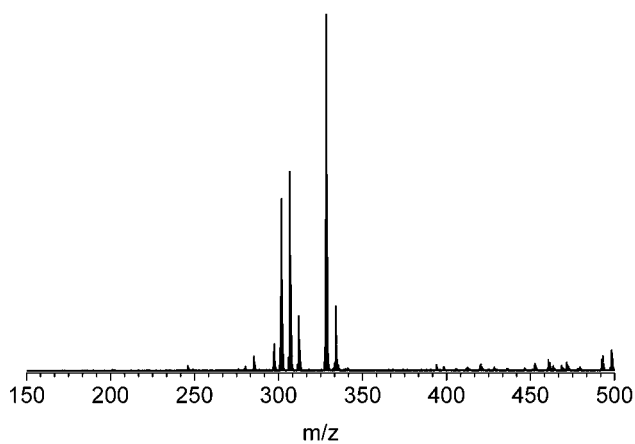
**Fig. S11** Chloride ion concentration as a function of time during the reaction of 2,4,6-trichlorophenol with  $\text{HSO}_5^-$  catalyzed by  $\text{Fe}^{\text{III}}\text{TPPS}$ .  $[\text{Fe}^{\text{III}}\text{TPPS}] = 3.1 \mu\text{M}$ ;  $[\text{HSO}_5^-] = 101 \text{ mM}$ ;  $[\text{2,4,6-trichlorophenol}] = 1.80 \text{ mM}$ ;  $\text{pH} = 1$ ;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $I = 0.3 \text{ M}$  ( $\text{KNO}_3$ ). The dotted line is the initial concentration of 2,4,6-trichlorophenol and confirms that one equivalent of chloride ion is formed within a minute.



**Fig. S12** Spectral observations during the reaction of  $\text{Fe}^{\text{III}}\text{TPPS}$  with  $\text{HSO}_5^-$ .  $[\text{Fe}^{\text{III}}\text{TPPS}] = 6.9 \mu\text{M}$ ;  $[\text{HSO}_5^-] = 2.95 \text{ mM}$ ;  $\text{pH} = 3.05$ ; optical path length = 1.00 cm;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ); reaction times: increasing time intervals from 0.01 s to 50 s.

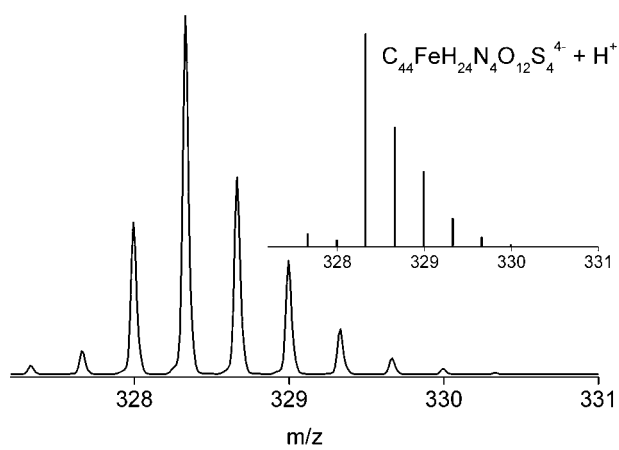
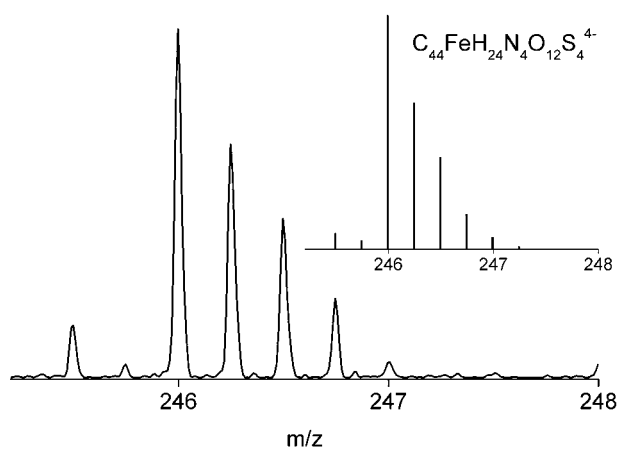


**Fig. S13** Sample kinetic trace measured during the reaction of  $\text{Fe}^{\text{III}}\text{TPPS}$  with  $\text{HSO}_5^-$  on two time scales.  $[\text{Fe}^{\text{III}}\text{TPPS}] = 6.9 \mu\text{M}$ ;  $[\text{HSO}_5^-] = 2.95 \text{ mM}$ ;  $\text{pH} = 1.30$ ; optical path length = 1.00 cm;  $T = 25.0 \text{ }^\circ\text{C}$ ;  $I = 0.1 \text{ M (NaClO}_4)$ ;

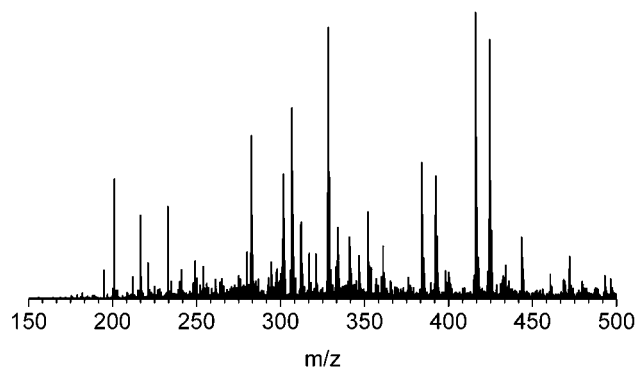


**Fig. S14** ESI-MS spectrum of an aqueous solution of  $\text{Fe}^{\text{III}}\text{TPPS}$ .

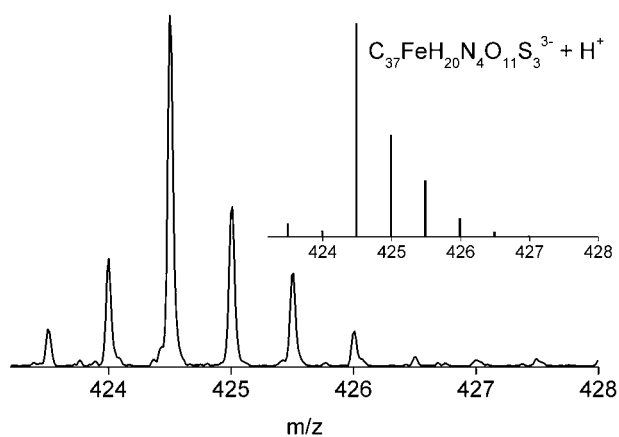




**Fig. S15** Detailed ESI mass spectra of the two dominant ions detected in the mass spectrum of an aqueous solution of  $Fe^{III}$ TPPS. Large graphs are the measured spectra, insets are simulated spectra for the ion with the composition shown.



**Fig. S16** ESI mass spectra of the products formed in the reaction of  $\text{Fe}^{\text{III}}$ TPPS with  $\text{HSO}_5^-$ .



**Fig. S17** Detailed ESI mass spectrum of one of the products formed in the reaction of  $\text{Fe}^{\text{III}}$ TPPS with  $\text{HSO}_5^-$ . The large graph is the measured spectrum, the inset is a simulated spectrum for the ion with the composition shown.

**Mathematical background of equation 4:**

Scheme 1 gives the following differential equations for the special case  $k_{obs1} (= k_1^H[H_2O_2]) = k_{obs2}$  ( $= k_{2a}^H[H_2O_2] + k_{2b}^H$ ):

$$\frac{d[Fe^{III}TPPS]}{dt} = -k_{obs12}[Fe^{III}TPPS]$$

$$\frac{d[Int_1]}{dt} = k_{obs12}[Fe^{III}TPPS] - k_{obs12}[Int_1]$$

$$\frac{d[Int_2]}{dt} = k_{obs12}[Int_1] - k_{obs3}[Int_2]$$

$$\frac{d[P_1]}{dt} = k_{obs3}[Int_2]$$

The solution of these simultaneous differential equations is the following (assuming that only  $Fe^{III}TPPS$  is present initially and  $[Fe^{III}TPPS] = c$ ):

$$[Fe^{III}TPPS] = ce^{-k_{obs12}t}$$

$$[Int_1] = k_{obs12}cte^{-k_{obs12}t}$$

$$[Int_2] = -\frac{k_{obs12}^2c}{(k_{obs3} - k_{obs12})^2}e^{-k_{obs12}t} + \frac{k_{obs12}^2c}{k_{obs3} - k_{obs12}}te^{-k_{obs12}t} + \frac{k_{obs12}^2c}{(k_{obs3} - k_{obs12})^2}e^{-k_{obs3}t}$$

$$[P_1] = c + \frac{k_{obs3}(2k_{obs12} - k_{obs3})c}{(k_{obs3} - k_{obs12})^2}e^{-k_{obs12}t} - \frac{k_{obs12}k_{obs3}c}{k_{obs3} - k_{obs12}}te^{-k_{obs12}t} - \frac{k_{obs12}^2c}{(k_{obs3} - k_{obs12})^2}e^{-k_{obs3}t}$$

The fact that these are the solutions are the differential equations is easily checked by substituting into the original equations. For example, the third differential equations is checked as an example:

$$\begin{aligned}
\frac{d[Int_2]}{dt} &= \frac{k_{obs12}^3 c}{(k_{obs3} - k_{obs12})^2} e^{-k_{obs12}t} - \frac{k_{obs12}^3 c}{k_{obs3} - k_{obs12}} t e^{-k_{obs12}t} + \frac{k_{obs12}^2 c}{k_{obs3} - k_{obs12}} e^{-k_{obs12}t} + \frac{-k_{obs3} k_{obs12}^2 c}{(k_{obs3} - k_{obs12})^2} e^{-k_{obs3}t} = \\
&= \frac{k_{obs3} k_{obs12}^2 c}{(k_{obs3} - k_{obs12})^2} e^{-k_{obs12}t} - \frac{k_{obs12}^3 c}{k_{obs3} - k_{obs12}} t e^{-k_{obs12}t} - \frac{k_{obs3} k_{obs12}^2 c}{(k_{obs3} - k_{obs12})^2} e^{-k_{obs3}t} \\
k_{obs12}[Int_1] - k_{obs3}[Int_2] &= k_{obs12}^2 c t e^{-k_{obs12}t} + \frac{k_{obs3} k_{obs12}^2 c}{(k_{obs3} - k_{obs12})^2} e^{-k_{obs12}t} - \frac{k_{obs3} k_{obs12}^2 c}{k_{obs3} - k_{obs12}} t e^{-k_{obs12}t} - \frac{k_{obs3} k_{obs12}^2 c}{(k_{obs3} - k_{obs12})^2} e^{-k_{obs3}t} = \\
&= \frac{k_{obs3} k_{obs12}^2 c}{(k_{obs3} - k_{obs12})^2} e^{-k_{obs12}t} - \frac{k_{obs12}^3 c}{k_{obs3} - k_{obs12}} t e^{-k_{obs12}t} - \frac{k_{obs3} k_{obs12}^2 c}{(k_{obs3} - k_{obs12})^2} e^{-k_{obs3}t}
\end{aligned}$$

All of  $Fe^{III}TPPS$ ,  $Int_1$ ,  $Int_2$ ,  $P_1$  can contribute to the absorbance signal, which is given as:

$$A = (A_1 + A_2)t e^{-k_{obs12}t} + A_3 e^{-k_{obs3}t} + E$$

Constants  $A_1$ ,  $A_2$ ,  $A_3$ , and  $E$  are related to the molar absorbances of the four species in the Scheme 1:

$$A_1 = \varepsilon_{Fe^{III}TPPS} c - \varepsilon_{Int2} \frac{k_{obs12}^2 c}{(k_{obs3} - k_{obs12})^2} + \varepsilon_{P_1} \frac{k_{obs3}(2k_{obs12} - k_{obs3})c}{(k_{obs3} - k_{obs12})^2}$$

$$A_2 = \varepsilon_{Int1} k_{obs12} c + \varepsilon_{Int2} \frac{k_{obs12}^2 c}{k_{obs3} - k_{obs12}} - \varepsilon_{P_1} \frac{k_{obs12} k_{obs3} c}{k_{obs3} - k_{obs12}}$$

$$A_3 = (\varepsilon_{Int2} - \varepsilon_{P_1}) \frac{k_{obs12}^2 c}{(k_{obs3} - k_{obs12})^2}$$

$$E = \varepsilon_{P_1} c$$