Supporting Information

Water-soluble nitroxyl porphyrin complexes Fe$^{II}$TPPSHNO and Fe$^{II}$TPPSNO$^-$ obtained from isolated Fe$^{II}$TPPSNO$^\cdot$

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Supplementary Information

Figure S1. 4-fluoro-N-hydroxybenzenesulfonamide (fluoro-PA)

Figure S2. FT-IR spectra of Na₄Fe³⁺TPPSNO⁺ in Fluorolube.
Figure S3. MeOH-\(d^4\) NMR \(^1\)H spectra obtained for the elemental analysis sample of Fe\(^{II}\)TPPSNO\(^-\)Na\(_4\).

| δ(ppm) | Integration | Asignment |
|--------|-------------|------------|
| 2.17   | 17.41       | CH\(_3\)COCH\(_3\) |
| 3.33   | -           | CH\(_3\)OH  |
| 4.88   | 31.76       | H\(_2\)O   |
| 5.50   | 2.16        | CH\(_2\)Cl\(_2\)* |
| 8.75   | 8.38        | TPPS sulphonate meta H |
| 10.75  | 8           | TPPS sulphonate ortho H |

Table S1. Signal assignation for the \(^1\)H RMN spectra shown in Figure S4.

*Traces of CH\(_2\)Cl\(_2\) were present inside the glovebox where the NMR tube was prepared.

Figure S4. UV-Vis spectral changes observed for Fe\(^{II}\)TPPSHNO formation at pH =6 and its subsequent deprotonation.
Figure S5. UV-Vis spectral changes observed for Fe\textsuperscript{II}TPPSNO\textsuperscript{−} formation at pH = 12 and its subsequent protonation to pH = 6, showing Fe\textsuperscript{II}TPPSHNO formation.

Figure S6. Fe\textsuperscript{II}TPPSNO\textsuperscript{−} reduction at pH = 5.

Figure S7. Fe\textsuperscript{II}TPPSNO\textsuperscript{−} reduction at pH = 6.

Figure S8. Fe\textsuperscript{II}TPPSNO\textsuperscript{−} reduction at pH = 7.

Figure S9. Fe\textsuperscript{II}TPPSNO\textsuperscript{−} reduction at pH = 8.
Figure S10. Fe$^{II}$TPPSNO$^\cdot$ reduction at pH = 9

Figure S11. Fe$^{II}$TPPSNO$^\cdot$ reduction at pH = 10

Figure S12. Fe$^{II}$TPPSNO$^\cdot$ reduction at pH = 11
Figure S13. Experimental measurements along with expected behavior for pKa = 9.70. The slope for $E_{\text{RED}}$ vs. pH including the data points preceding the pKa is 52mV, fairly close to the expected value of 59 mV per pH unit.

Measurements at different scan rates proved that the porphyrin became adsorbed on the electrode surface during the measurements, since $\ln(v_{\text{SCAN}})$ vs. peak potential plots gave a linear relationship. We do not know the reason why the compounds adsorb, nor if the adsorption is related to the irreversibility of the wave. Preliminary experiments of the same porphyrin in organic media resulted in a reversible wave, which suggests the aqueous media could be responsible for this particular behaviour.

Figure S14. Kinetic integral method plots for the spontaneous reoxidation of Fe$^{II}$TPPSHNO to Fe$^{II}$TPPSNO$^*$ at pH = 6, using the deconvoluted Fe$^{II}$TPPSHNO absorbance traces.

Kinetic differential method plots (pH =6, 2 mM, dithionite reductant)

A ln(rate) vs. ln([FeHNO]) plot made with different selected experiments of varying initial Fe$^{II}$TPPSHNO concentration is shown in Figure S15. The instant rate was also calculated from the derivative of the observed analytical formula for [FeHNO](t) for every point in a given experiment and ln(rate) vs ln([FeHNO]) plots are shown for two experiments in Figures S16 and S17. As expected for a first order reaction, the slope of these plots is $\approx 1$. 
Figure S15. Kinetic differential method plots for the spontaneous reoxidation of Fe\textsuperscript{III}TPPS\textsubscript{HNO} to Fe\textsuperscript{III}TPPS\textsubscript{NO}\textsuperscript{•} for different experiments with different initial concentrations. The observed slope approaches 1 rather than 2, as expected for a first order reaction.

Figure S16. Kinetic differential method plots for the spontaneous reoxidation of Fe\textsuperscript{III}TPPS\textsubscript{HNO} to Fe\textsuperscript{III}TPPS\textsubscript{NO}\textsuperscript{•} for all data points of a given experiment. The observed slope approaches 1 rather than 2, as expected for a first order reaction.
Figure S17. Kinetic differential method plots for the spontaneous reoxidation of Fe\textsuperscript{II}TPPSHNO to Fe\textsuperscript{II}TPPSNO\textsuperscript{•} for all data points for another given experiment. The observed slope approaches 1 rather than 2, as expected for a first order reaction.

Selected fittings of the kinetic data in the different experimental conditions specified in Table 2.

Figure S18. Deconvoluted Fe\textsuperscript{II}TPPSHNO absorbance time traces at 418 nm registered after its formation in 2 mM phosphate buffer pH = 6, reducing agent: Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4}.
**Figure S19.** Deconvoluted FeII\textsuperscript{TPPSHNO absorbance time traces at 418 nm registered after its formation in 2mM phosphate buffer pH = 6, reducing agent: Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4}, sulphite excess.

**Figure S20.** Deconvoluted Fe\textsuperscript{III}TPPSHNO absorbance time traces at 418 nm registered after its formation in 2 mM phosphate buffer pH = 6, in D\textsubscript{2}O, reducing agent: Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4}.
Figure S21. Deconvoluted Fe$^{II}$TPPSHNO absorbance time traces at 418 nm registered after its formation in 2 mM phosphate buffer pH = 6, reducing agent: Cr$^{II}$EDTA.

Figure S22. Deconvoluted Fe$^{II}$TPPSHNO absorbance time traces at 418 nm registered after its formation in 2 mM citrate buffer pH = 5, reducing agent: Na$_2$S$_2$O$_4$. 
Figure S23. Deconvoluted Fe\textsuperscript{II}TPPSHNO absorbance time traces at 418 nm registered after its formation in 2 mM phosphate buffer at pH = 7, reducing agent: Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4}.

Figure S24. Deconvoluted Fe\textsuperscript{II}TPPSHNO absorbance time traces at 418 nm registered after its formation in 2 mM phosphate buffer pH = 7, reducing agent: Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4}, with excess N-Me-Imidazole.
Figure S25. Deconvoluted Fe\textsuperscript{III}TPPSHNO absorbance time traces at 418 nm registered after its formation in water, reducing agent: Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4}.

Arrhenius plot

An Arrhenius plot for the reoxidation reaction in the temperature range 9-48°C is shown in Figure S26. The resulting slope corresponds to an activation energy of 13 ± 8 kcal/mol.

Figure S26. ln(k) vs 1/T plot for the FeHNO reoxidation reaction in the temperature range 9 – 48°C.