Supplementary Information

Solution Behavior of Iron(III) and Iron(II) Porphyrins in DMSO and Reaction with Superoxide. Effect of Neighboring Positive Charge on Thermodynamics, Kinetics and Nature of Iron-(Su)peroxo Product

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Bulk electrolysis of $[Fe^{III}(tBuTPP)(DMSO)_2]^+$ and characterization of $[Fe^{III}(tBuTPP)OH]$ and $([Fe^{III}(tBuTPP)])_2O$.

In order to obtain the Fe(II) form of the complex, bulk electrolysis of $[Fe^{III}(tBuTPP)(DMSO)_2]^+$ was performed according to our previous study.[5] Due to the moisture sensitivity of $[Fe^{III}(tBuTPP)(DMSO)_2]^+$ the composition of reactant and product solutions was dependent on a water/hydroxide content in DMSO, as defined by two equilibria in Scheme S1 (Figure S1). The composition of solutions affects the electrochemical processes.

Scheme S1

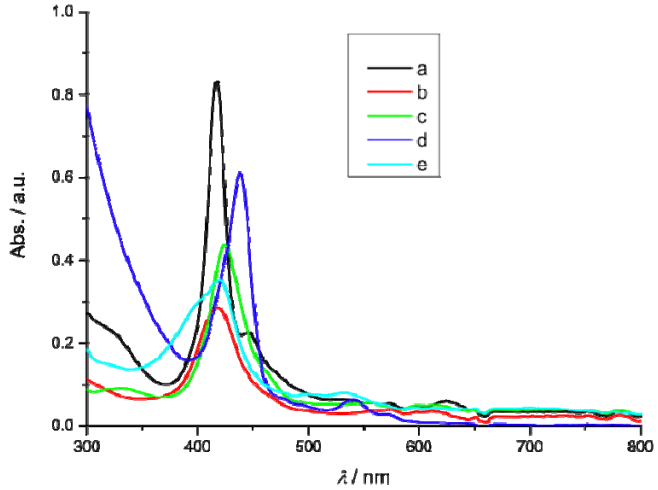

Figure S1. UV/Vis spectra of $[Fe^{III}(tBuTPP)(DMSO)_2]^+$ (c = 2 x 10^{-5} M in DMSO with 0.1 M Bu_4NPF_6) and species according to Scheme S1 upon addition of base or acid: a) mixture of $[Fe^{III}(tBuTPP)]_2O$ and $[Fe^{III}(tBuTPP)OH]$; b) $[Fe^{III}(tBuTPP)]_2O$ (saturated solution); c) mixture of $[Fe^{III}(tBuTPP)OH]$ and $[Fe^{III}(tBuTPP)(DMSO)_2]$; d) $[Fe^{III}(tBuTPP)OH]$; e) $[Fe^{III}(tBuTPP)(DMSO)_2]^+$.

In the commercially available "dry" DMSO the Fe(III) complex is present as a mixture of bis-DMSO and hydroxo species (Figure S1c). Upon addition of proton sources (water or diluted acid) the pure bis-DMSO complex is obtained (Figure S1e). Upon addition of base at first the hydroxo complex is observed (Figure S1d), whereas gradually, upon addition of a large excess of base (in the form of solid tetrabutylammonium hydroxide, TBAOH) the equilibrium (Scheme S1) shifts to dimer formation. In DMSO it is not possible to push the equilibrium completely to the dimer (Figure S1a). The dimer can be isolated as a precipitate from basic CH_2Cl_2 solution (see Experimental section) and by dissolving it in DMSO a pure solution of it can be obtained (Figure S1b). Due to its low solubility, even its saturated solution shows relatively weak absorption bands. Characteristic UV/Vis absorptions are summarized in Table S1. The characterization of these species helped us to identify the side reactions and products along the reaction path with superoxide (*vide infta*).

Table S1: UV/Vis parameters of the species in Figure S1.

Species	Soret band / nm (ε / L mol^{-1} cm^{-1})	Q bands / nm (ε / L mol^{-1} cm^{-1})
$[Fe^{III}(tBuTPP)(DMSO)_2]^+$	404 sh (15400), 419 (17600)	496 sh (3850), 535 (4000), 719 (2095)
$[Fe^{III}(tBuTPP)OH]$	416 sh (14900), 438 (30600)	540 (3100), 573 (1400)
$[Fe^{III}(tBuTPP)]_2O$	417	560 (sh), 574, 613

If in the starting solution a mixture of $[Fe^{III}(tBuTPP)(DMSO)_2]^+$ and $[Fe^{III}(tBuTPP)OH]$ is present, reduction to the Fe^{II} form (n = 1, 2) (Figure S2) is incomplete at a potential of -0.2 V, yielding a mixture of $[Fe^{II}(tBuTPP)(DMSO)_n]$ (n = 1, 2) and $[Fe^{III}(tBuTPP)OH]$. Because of the hydroxo compound's high stability and its more negative redox potential, complete reduction to the iron(II) complex was not possible. Use of a more negative potential leads first to quantitative production of the hydroxo compound and then to decomposition of solvent and the porphyrin complex (Figure S2). Quantitative production of $[Fe^{II}(tBuTPP)(DMSO)_n]$ (n = 1, 2) could only be achieved by applying at first a very positive potential of 1.6 V, which transforms the mixture of hydroxo and bis-DMSO complexes to pure $[Fe^{III}(tBuTPP)(DMSO)_2]^+$. This process can be monitored by UV/Vis spectroscopy (Figure S3). After that, quantitative reduction to $[Fe^{II}(tBuTPP)(DMSO)_n]$ (n = 1, 2) was successful at E = -0.6 V (Figure S4).

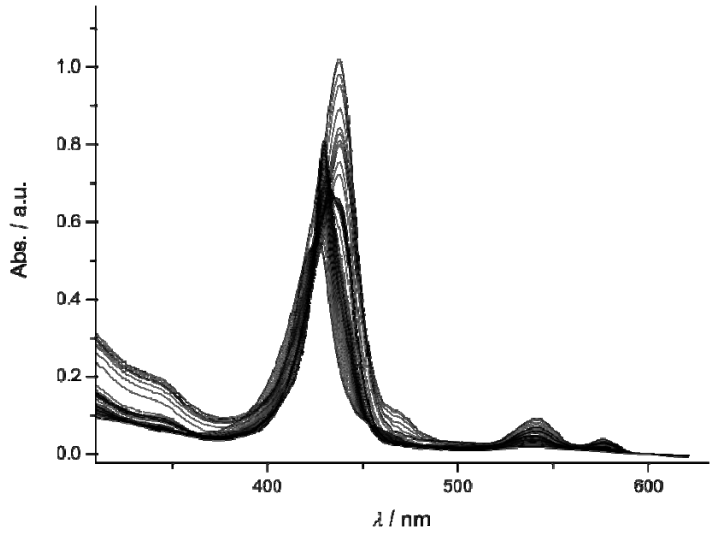

Figure S2: UV/vis spectra for electrochemical reduction (60 min) of $[Fe^{III}(tBuTPP)(DMSO)_2]^+$ (c = 2 x 10^{-5} M; I = 0.1 M) in DMSO with 0.1 M Bu_4NPF_6 in presence of moisture. A mixture of $[Fe^{II}(tBuTPP)(DMSO)_n]$ (n = 1, 2) and $[Fe^{III}(tBuTPP)OH]$ was firstly obtained at E = -0.2 V and pure $[Fe^{III}(tBuTPP)OH]$ was obtained at more negative potential.

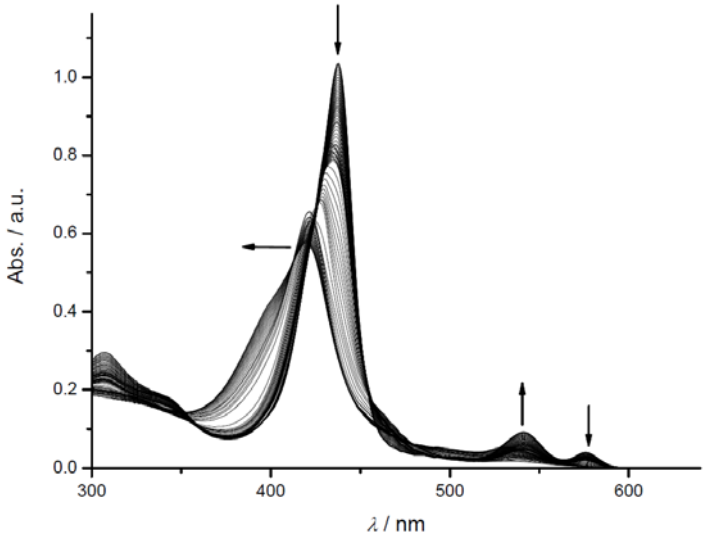

Figure S3: UV/vis spectra obtained by applying potential of 1.6 V (6 min) on the mixture of $[Fe^{III}(tBuTPP)OH]$ and $[Fe^{III}(tBuTPP)(DMSO)_2]^+$ (total concentration = 2 x 10^{-5} M; I = 0.1 M) in DMSO with 0.1 M Bu_4NPF_6, resulting in pure $[Fe^{III}(tBuTPP)(DMSO)_2]^+$.

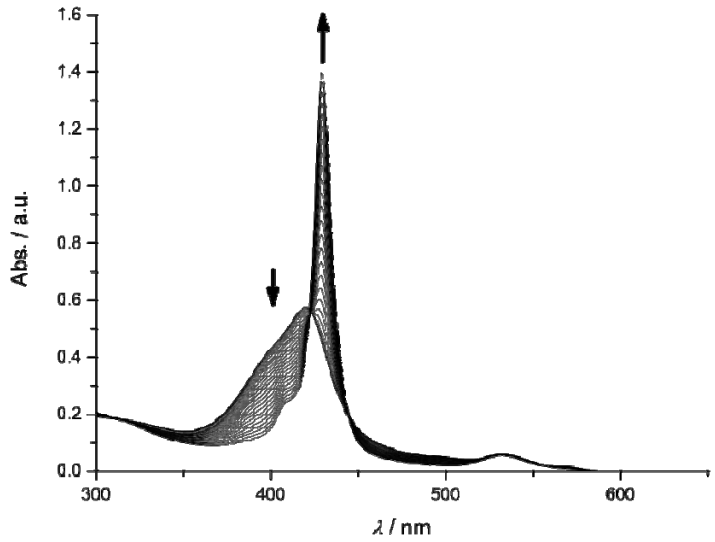

Figure S4. UV/Vis spectra accompanying electrochemical reduction (10 min) of $[Fe^{III}(tBuTPP)(DMSO)_2]^+$ (c = 2 x 10^{-5} M; I = 0.1 M) in DMSO with 0.1 M Bu_4NPF_6 to $[Fe^{II}(tBuTPP)(DMSO)_n]$ (n = 1, 2) at E = -0.6 V.

Effect of Temperature and Pressure on the Equilibrium Constant K_{DMSO}.

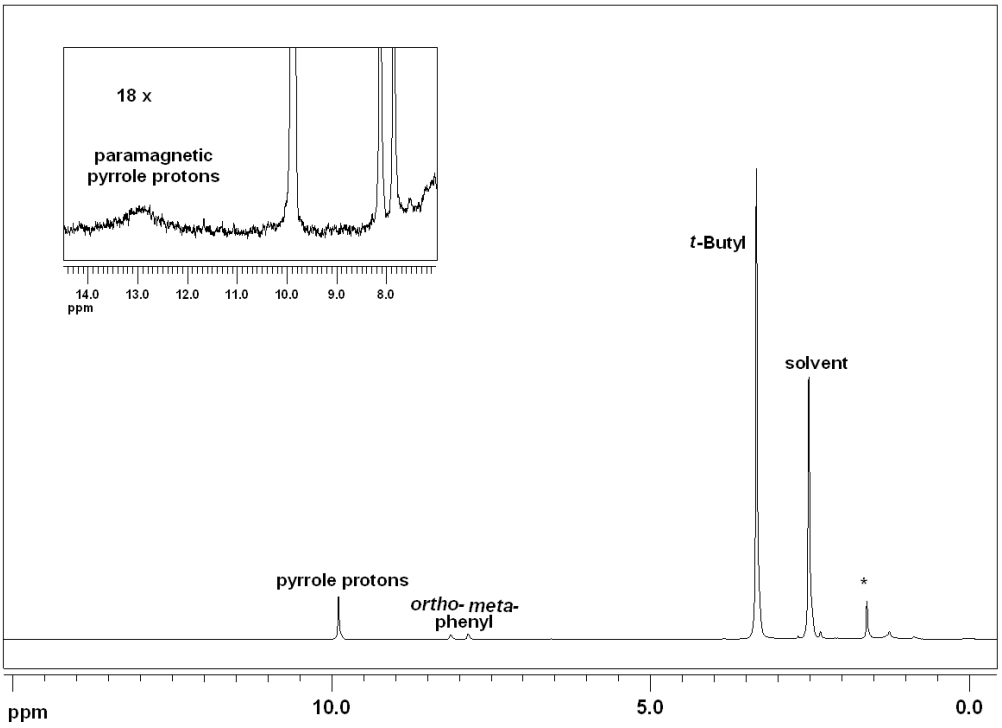

Figure S5: ^{1}H NMR spectrum of $[Fe^{II}(tBuTPP)(DMSO)_n]$ (n = 1, 2) (room temperature and atmospheric pressure); assignment of proton shifts for $[Fe^{II}(tBuTPP)(DMSO)_2]$, * corresponds to *t*-Butyl group of $[Fe^{II}(tBuTPP)(DMSO)]$; conditions: spectrum taken after chemical reduction of $[Fe^{III}(tBuTPP)Cl]$ (2mM) in DMSO-d_6 by excess of $Na_2S_2O_4$.

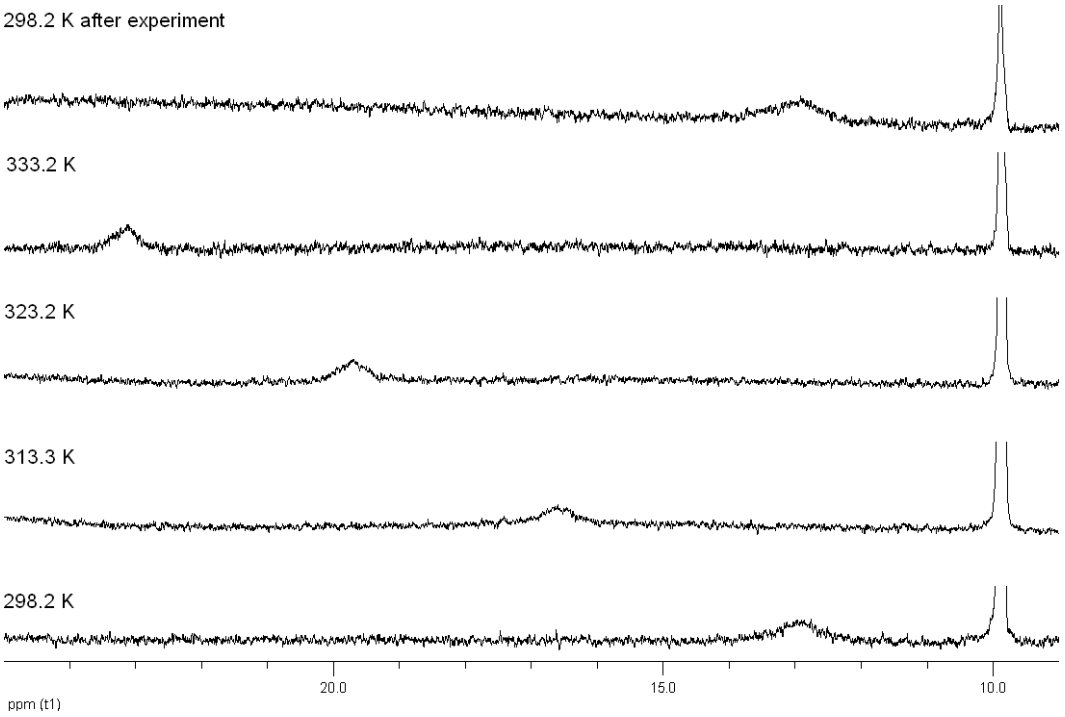

Figure S6: ^{1}H NMR spectrum of [Fe^{II}(tBuTPP)$(DMSO)_n$] (n = 1, 2) taken at different temperatures; conditions: spectrum taken after chemical reduction of [Fe^{III}(tBuTPP)Cl] (2mM) in DMSO-d_6 by excess of $Na_2S_2O_4$.

In analogy to Fe(III) porphyrins with spin admixed states[4] and analogous complex with covalently attached crown ether,[5] the percentage of the low-spin species is calculated according to eq. (1) (δ is the chemical shift of the pyrrole protons of the equilibrium mixture; the limiting value for the low-spin species is ca. 9 ppm[2] and for the high-spin species ca. 60 ppm).[3]

$$Int(\%) = \left[\frac{(60-\delta)}{51}\right] \times 100\% \qquad (1)$$

The species distribution at different temperatures and pressures is summarized in

Table S2. The values show that mostly the low-spin bis-DMSO complex exists in solution. From the results in Table S2 the equilibrium constant KDMSO can be calculated according to eq. (2) (in which the activity of solvent is considered to be 1) and the data are summarized in Table S2. On the basis of the temperature and pressure dependent data for KDMSO the

corresponding thermodynamic parameters can be estimated according to equations (3) and (4), respecdtively.4

$$K_1 = [HS]/[LS] \quad (2)$$

[HS]: high-spin *mono*-DMSO complex concentration

[LS]: low-spin *bis*-DMSO complex concentration

[DMSO] = 14.08 M.

$$\ln(K) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

$$\left(\frac{\partial \ln(K)}{\partial P}\right)_T = \frac{-\Delta V^\circ}{RT} \quad (4)$$

Table S2: Low-spin/high-spin species distribution for [Fe^{II}(tBuTPP)$(DMSO)_n$] (n = 1, 2) and the values of the equilibrium constant K_{DMSO} at different temperatures and pressures calculated according to eq. (1).

***T* / K**	**δ / ppm**	**% low-spin**	**% high-spin**	**K_{DMSO}**
298.2	12.88	92.4	7.6	0.082 ± 0.002
313.2	16.51	85.3	14.7	0.172 ± 0.002
323.2	19.63	79.2	20.8	0.262 ± 0.003
333.2	23.11	72.3	27.7	0.383 ± 0.003
***p* / MPa (at 325.2 K)**	**δ / ppm**	**% low-spin**	**% high-spin**	**K_{DMSO}**
2	20.05	78.3	21.7	0.277 ± 0.003
30	18.80	80.8	19.2	0.238 ± 0.003
90	16.50	85.3	14.7	0.172 ± 0.002
150	14.40	89.4	10.6	0.118 ± 0.002

The reaction enthalpy $\Delta H°$ was obtained from the slope and the reaction entropy $\Delta S°$ from the intercept of the plot of $\ln(K_{DMSO})$ versus $1/T$ (see Figure S7). The reaction volume $\Delta V°$ results from the slope of the plot of $\ln(K_{DMSO})$ versus pressure (see Figure 1 in manuscript).

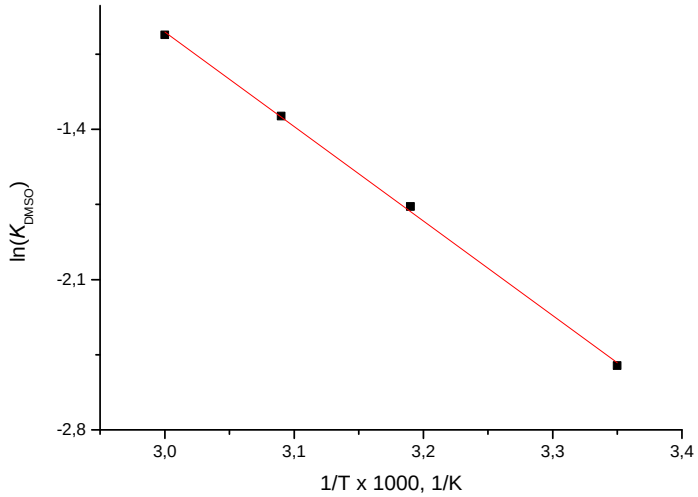

Figure S7: Plot of temperature dependent $\ln(K_{DMSO})$ against $1/T$ for $[Fe^{II}(tBuTPP)(DMSO)_n]$ (n = 1, 2) system.

ESI and cryospray mass spectrometry.

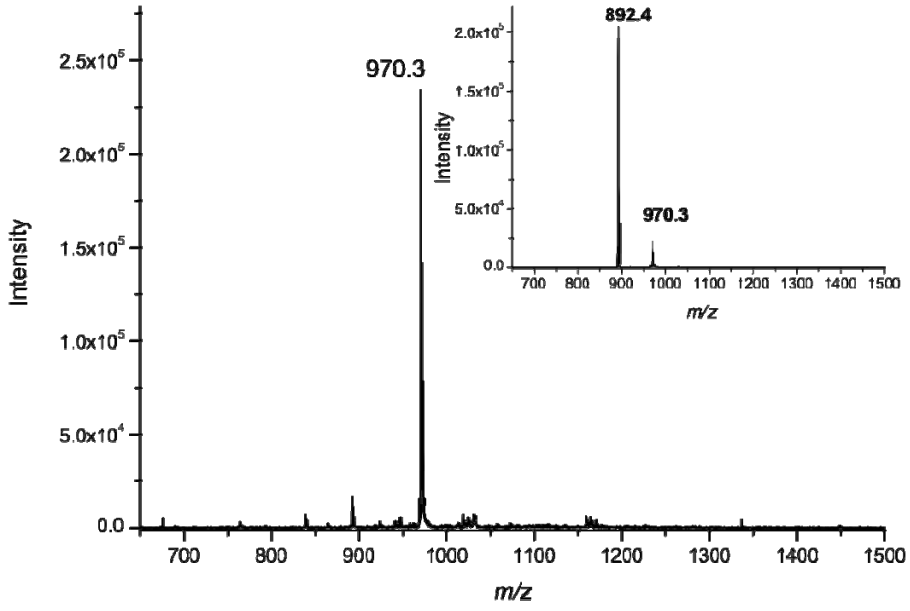

Figure S8: ESI mass spectrometry of $[Fe^{III}(tBuTPP)(DMSO)_2]^+$; peak at m/z = 970.3 is $[Fe^{III}(tBuTPP)(DMSO)]^+$; Inset shows MS/MS experiment, m/z = 892.4 is $[Fe^{III}(tBuTPP)]^+$.

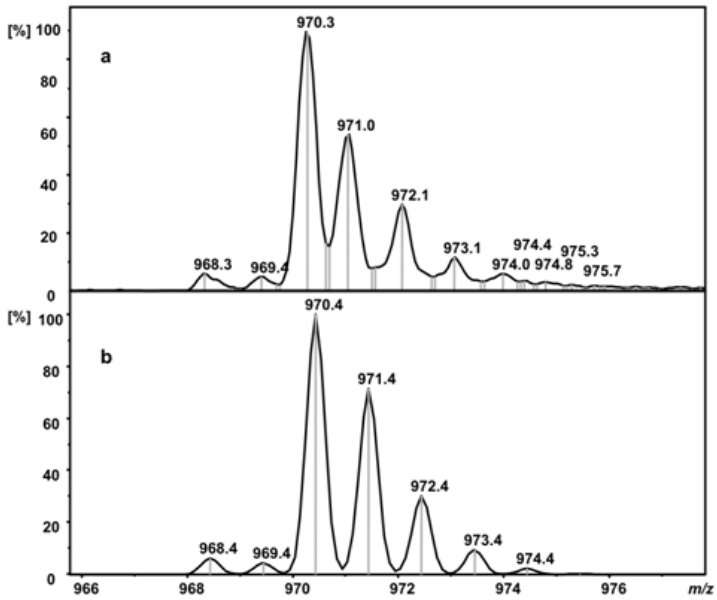

Figure S9: Comparison of measured and calculated isotopic distribution; a) spectrum of $[Fe^{III}(tBuTPP)(DMSO)]^+$, b) calculation of $[Fe^{III}(tBuTPP)(DMSO)]^+$ ($C_{62}H_{66}FeN_4OS$).

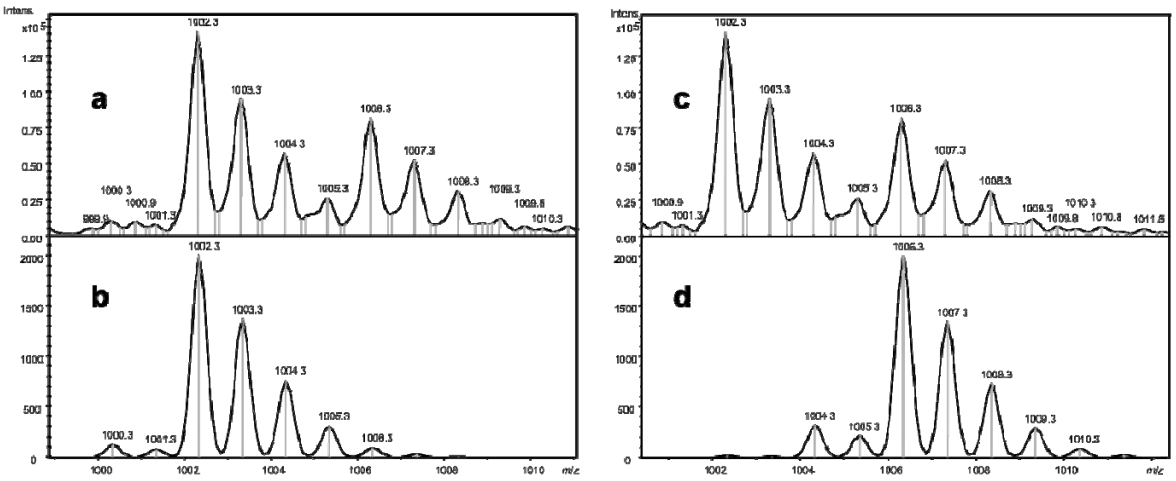

Figure S10: Comparison of measured and calculated isotopic distribution; a) spectrum of $\{K^+ + K[Fe^{III}(tBuTPP)(O_2^{2-})]\}$, b) calculation of $\{K^+ + K[Fe^{III}(tBuTPP)(O_2^{2-})]\}$ ($C_{60}H_{60}FeN_4K_2O_2$), c) spectrum of $\{K^+ + K[Fe^{III}(tBuTPP)(^{18}O_2^{2-})]\}$ (some residual a) in spectrum), d) calculation of $\{K^+ + K[Fe^{III}(tBuTPP)(^{18}O_2^{2-})]\}$ ($C_{60}H_{60}FeN_4K_2{}^{18}O_2$).

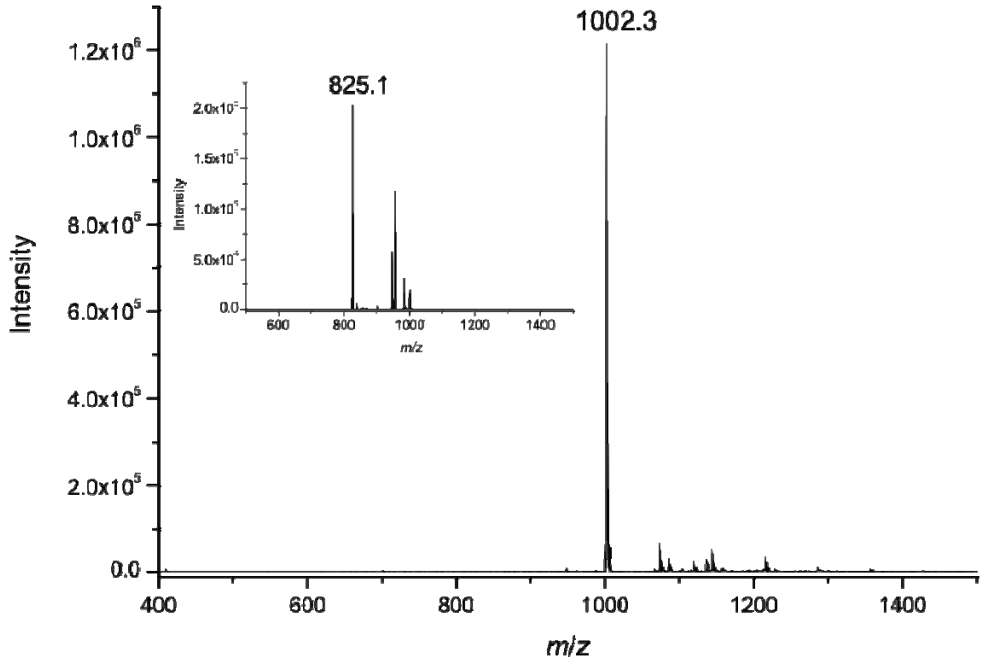

Figure S11: Mass spectrum of {K^+ + K[Fe^{III}(tBuTPP)(O_2^{2-})]}. Inset: MS/MS of *m/z* = 1002.3 (porphyrin fragments at *m/z* = 825.1, 958.1, 946.2 and 984.1 which could not further be clarified).

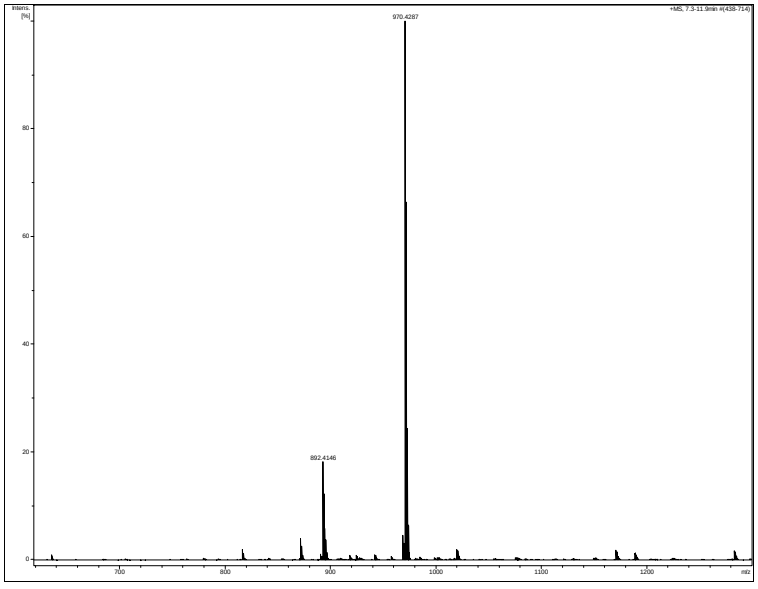

Figure S12: Ultra-high-resolution cryospray mass spectrum of [Fe^{III}(tBuTPP)$(DMSO)_2$]$^+$ obtained at -30 °C from the MeCN/DMSO (70:30) solvent mixture.

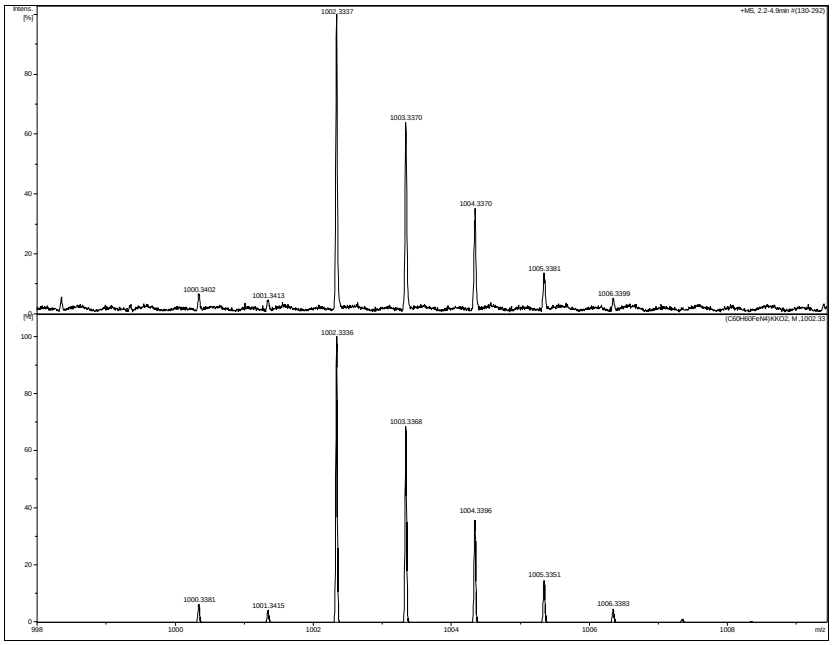

Figure S13: Comparison of measured and calculated isotopic distribution; above: ultra-high-resolution cryospray mass spectrum of {K^+ + K[Fe^{III}(tBuTPP)(O_2^{2-})]} obtained at -30 °C from the reaction mixture in MeCN/DMSO (70:30); below: calculation of {K^+ + K[Fe^{III}(tBuTPP)(O_2^{2-})]} ($C_{60}H_{60}FeN_4K_2O_2$).

Kinetics and thermodynamics.

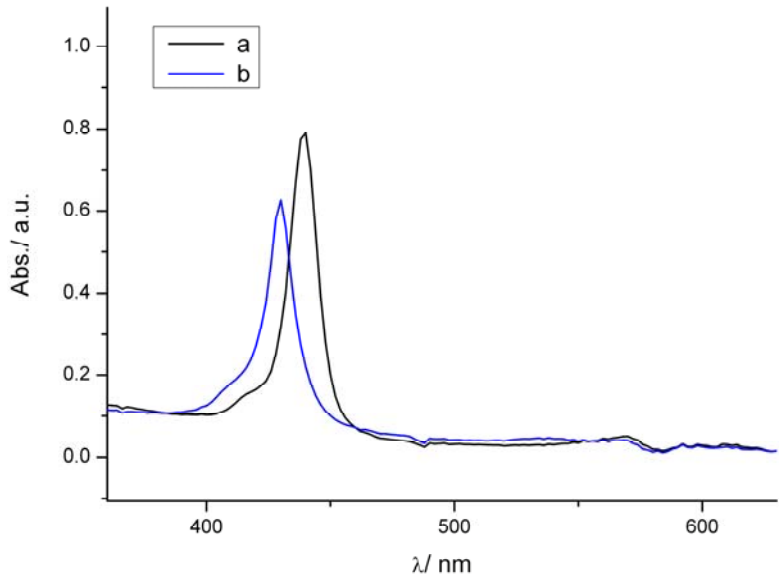

Figure S14: UV/vis spectra of: [Fe^{III}(tBuTPP)(O_2^{-})]$^-$ (10^{-5} M) in DMSO (a) and after bubbling of moist air resulting in spectrum of [Fe^{II}(tBuTPP)$(DMSO)_n$] (b).

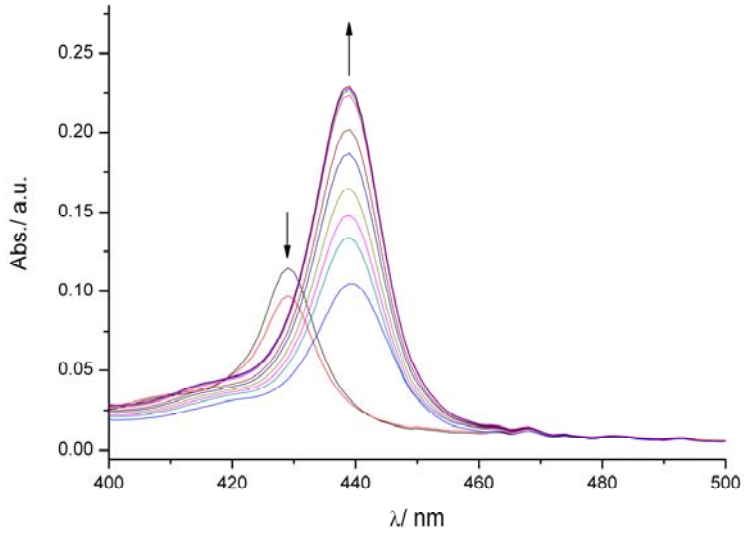

Figure S15: Titration of a solution of [Fe^{II}(tBuTPP)$(DMSO)_n$] (n = 1, 2) (2 x 10^{-6} M) with O_2^- in DMSO at 25° C (*I* = 0.1 M Bu_4NPF_6).

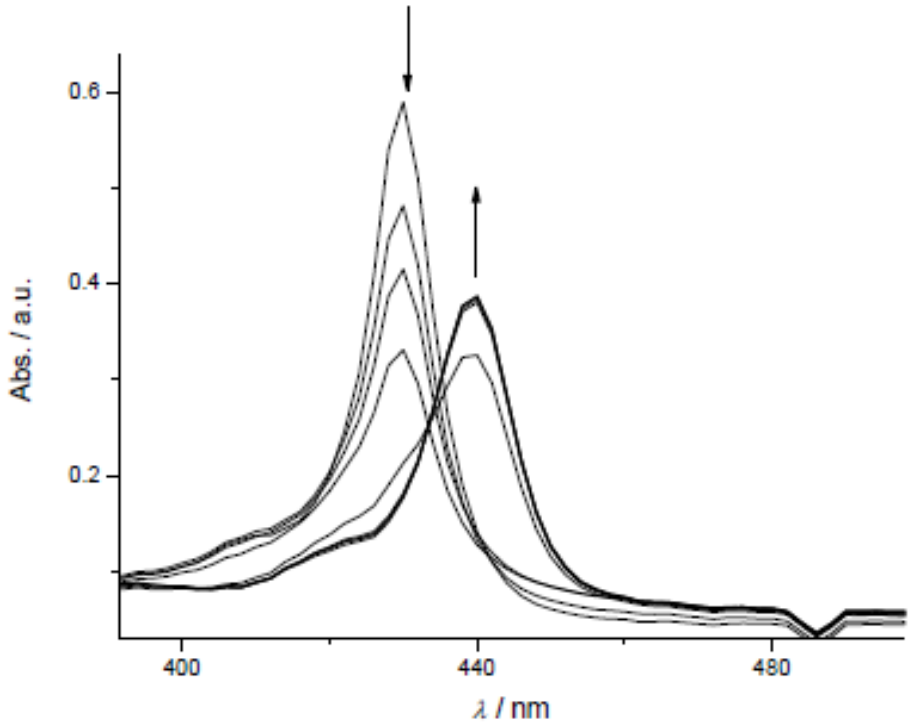

Figure S16: Titration of a solution of [Fe^{II}(tBuTPP)$(DMSO)_n$] (n = 1, 2) (10^{-5} M) and 18-crown-6 (10^{-4} M) with O_2^- in DMSO at 25° C (*I* = 0.1 M TBAP).

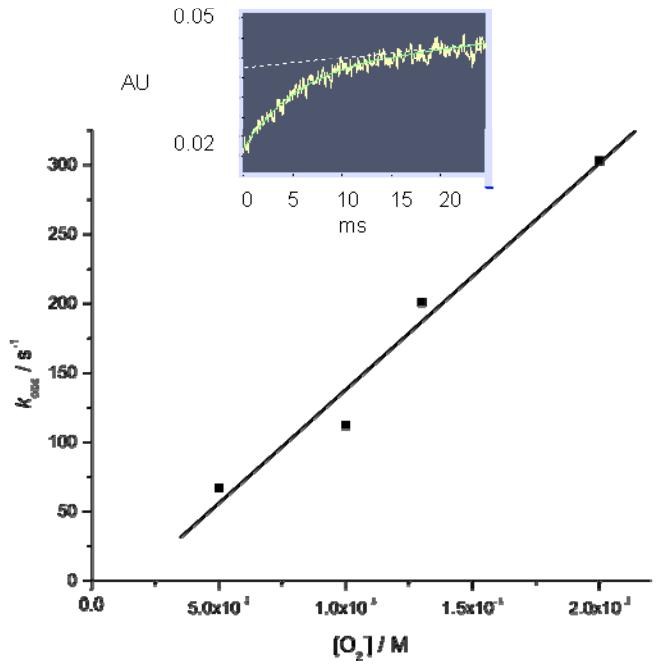

Figure S17. Plot of k_{obs} versus superoxide concentration for the reaction of $[Fe^{II}(tBuTPP)(DMSO)_n]$ (n = 1, 2) and KO_2 at 25° C in the presence of ten-fold excess of 18-crown-6 using a micro cuvette stopped-flow setup and different mixing volume ratios (I = 0.1 M Bu_4NPF_6). Inset: Trace at 440 nm of the reaction of 0.667 10^{-5} M $[Fe^{II}(tBuTPP)(DMSO)_n]$ (n = 1, 2) with 0.667 10^{-4} M 18-crown-6 and 1.33 10^{-3} M solution of KO_2 in DMSO (I = 0.1 M Bu_4NPF_6) and fit to a one exponential reaction.

Table S3: Superoxide concentrations and estimated k_{obs} values for the reaction of $[Fe^{II}(tBuTPP)(DMSO)_n]$ (n = 1, 2) and KO_2 at 25° C in the presence of ten-fold excess of 18-crown-6 using a micro cuvette stopped-flow setup and different mixing volume ratios (I = 0.1 M Bu_4NPF_6).

$[O_2^-]$ / M	**k_{obs} / s^{-1}**	**Mixing volume ratio, complex : O_2^-**
0.002	303 ±	micro cuvette, $[O_2^-]$ = 4 mM 1: 1
0.0013	201 ±	micro cuvette, $[O_2^-]$ = 4 mM 2 : 1
1E-3	112 ±	$[O_2^-]$ = 2 mM 1 : 1
5E-4	67 ±	$[O_2^-]$ = 1 mM 1 : 1

EPR spectroscopy.

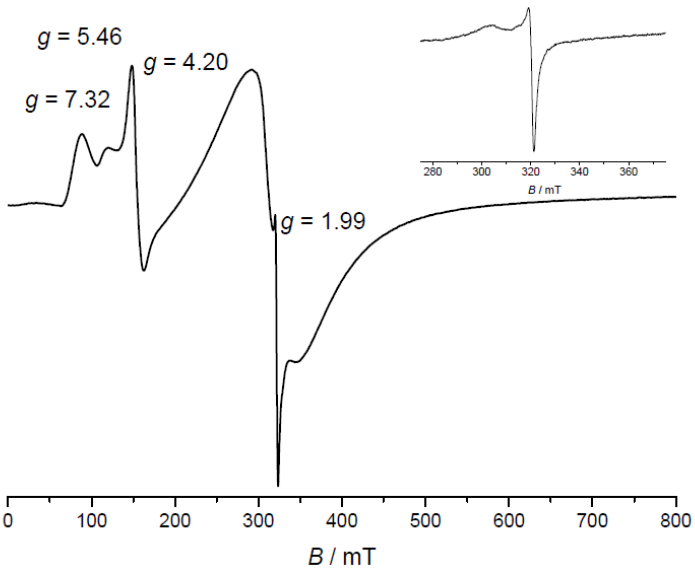

Figure S18: X-band EPR spectra of [Fe^{III}(tBuTPP)Cl] with KO_2 in DMSO, microwave frequency was 8.981173 GHz, *P* = 1 mW; Mod. width = 1.0 mT, sweep width 800 mT at 12 K; inset shows spectra at 77 K, microwave frequency was 8.980376 GHz, *P* = 1 mW; Mod. width = 1.0 mT, sweep width 100 mT.

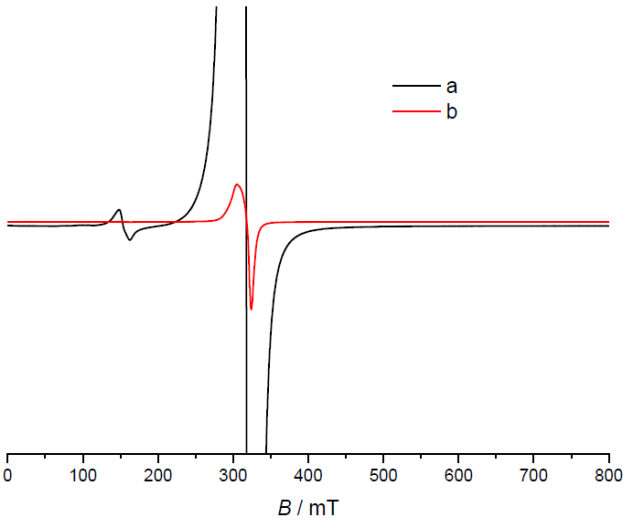

Figure S19: X-band EPR spectra of [Fe^{III}(tBuTPP)Cl] with KO_2 and ten-fold excess of 18-crown-6 in DMSO; a) at 12 K, microwave frequency was 8.985756 GHz, *P* = 1 mW; Mod. width = 1.0 mT, sweep width 800 mT; b) at 77 K, microwave frequency was 8.984888 GHz, *P* = 1 mW; Mod. width = 1.0 mT, sweep width 800 mT.

High pressure UV/vis measurements

Sample preparation was done in an Ar MBraun glovebox. A sample of K[Fe^{III}(tBuTPP)(O_2^{2-})] was prepared by addition of an excess of KO_2 to a 10^{-5} M solution of [Fe^{III}(tBuTPP)Cl] in a dry DMSO solution of 0.1 M TBAP. The suspension was stirred for 30 min. High pressure UV/vis spectra were recorded after filtration.

Spectral measurements at elevated pressure were performed in a pill-box cuvette on a Shimadzu UV-2101-PC spectrophotometer using a home-made high-pressure cell.[5] The high-pressure pump was purchased from NOVA SWISS (Nova Werke AG, CH-8307 Effretikon, Vogelsangstrasse); it allows measurements up to 150 MPa.

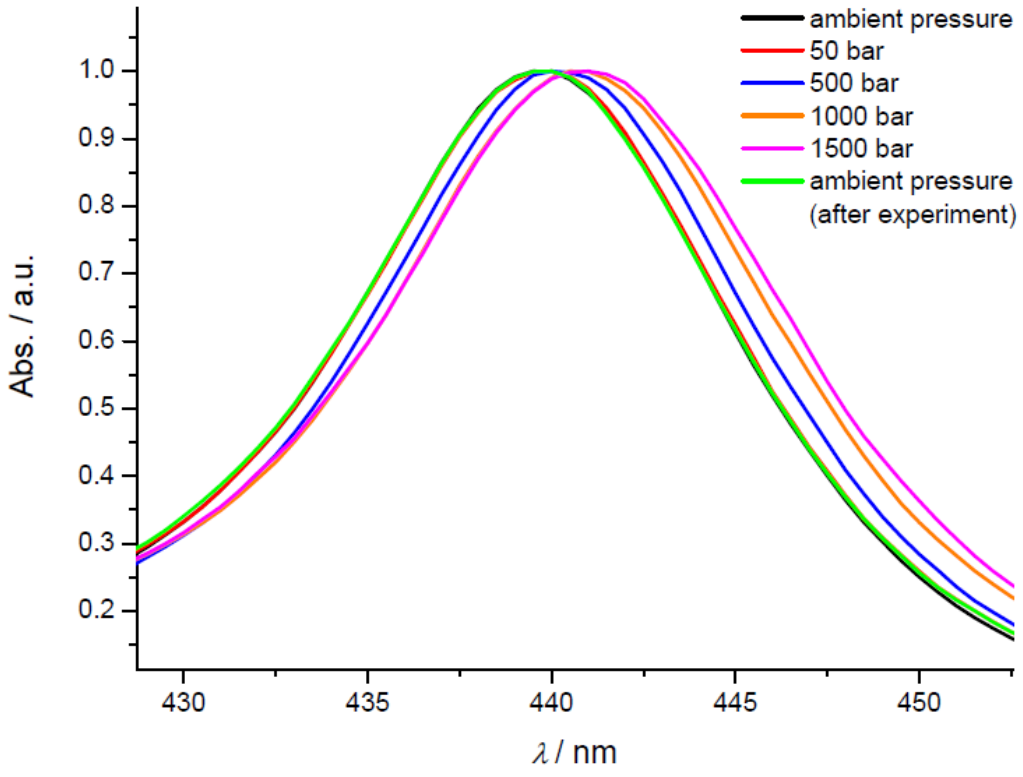

Figure S20: UV/vis spectra of K[Fe^{III}(TBuTPP)(O_2^{2-})] (10^{-5} M) at 35° C with added 18-crown-6 (10^{-4} M) at different pressures in presence of 0.1 M TBAP.

DFT calculations.

Geometry optimizations of the structures were performed with the Jaguar 6.0 program package[7] using the B3PW91 and B3LYP functionals, and a restricted open shell formalism. Standard DFT and pseudospectral grids were used throughout. The 6-31G(d) basis set was used on all atoms with the exception of the metal ions for which the standard Los Alamos effective core potentials[8] were used with the associated double-ζ, basis LACVP on potassium

and the triplet-ζ basis LACV3P[9] on iron. This combination is referred to as BSI. The calculated total energies of the optimized structures in vacuo, together with the total energy of the dissociated DMSO ligand, were used to compare the stability of the side-on and end-on complexes.

Optimized geometries and total energies if the investigated structures at the B3PW91/BSI level of theory

DMSO (using 5d functionals)
Total energy: -553.07635583763
Cartesian coordinates:

O1	2.1226422801	2.8437532970	-6.1976591981
S2	1.9205496300	2.2541176913	-4.8272057418
C3	2.6549002898	3.4065044061	-3.6174358257
H4	3.7345662822	3.4064096728	-3.7889061263
H5	2.4437939204	3.0669700463	-2.5983985123
H6	2.2615283637	4.4146084388	-3.7820143863
C7	0.1879299889	2.5640472880	-4.3445282648
H8	-0.0432346216	3.6272643470	-4.4638361893
H9	-0.4425895935	1.9783375632	-5.0186239587
H10	0.0214224316	2.2421193436	-3.3116343743

Doublet end-on {Fe^{II}(porphin) + O_2^-}
Total energy: -1261.86561343358
Cartesian coordinates:

C1	4.9680701560	2.5782823744	-0.2471418704
C2	5.4856200204	1.6315467797	-1.0731812081
C3	4.3637855406	0.9011911809	-1.6107602439
C4	4.4820753917	-0.1542521519	-2.5011909766
C5	3.4182617222	-0.8523494688	-3.0500532017
C6	3.5647217934	-1.9238965524	-4.0042535317
C7	2.3079754541	-2.3365392767	-4.3173793779
C8	1.4039080414	-1.5128209610	-3.5530910560
C9	-2.2994238399	-0.8786409440	-3.0641864259
C10	0.0230138036	-1.6105019068	-3.6176079675
C11	-2.8177317177	0.0856843652	-2.2581396340
C12	-1.6967390050	0.7497543813	-1.6400048941
C13	-1.8135973740	1.8056297205	-0.7494694616
C14	-0.7494070444	2.4844359748	-0.1764031382
C15	-0.8940485105	3.6061883325	0.7192355635
C16	0.3638539442	3.9985330912	1.0517321032
C17	1.2668544874	3.1159978066	0.3551768147
C18	-0.8660079232	-0.7953359558	-2.9342581418
C19	2.6472842146	3.2163023580	0.4155786332
C20	3.5352456110	2.4189957516	-0.2877454902
H21	5.4852018754	-0.4484863209	-2.8022545671
H22	5.4916724214	3.3242306161	0.3406291940
H23	6.5247189306	1.4322568985	-1.3102192339
H24	4.5132041507	-2.2943222217	-4.3776723863
H25	2.0032311150	-3.1192580887	-5.0034135724
H26	-2.8228855276	-1.5870919510	-3.6967575193
H27	-3.8582542541	0.3377473653	-2.0858255552
H28	-1.8419498211	4.0229108615	1.0410428644
H29	0.6718062583	4.8102512382	1.7015334077
H30	3.0662263948	3.9967103540	1.0470259346
H31	-0.3955895845	-2.3679586374	-4.2768360396

N32	-0.5126083327	0.2032639533	-2.0628598702
N33	0.5736248858	2.1987495539	-0.3897683716
N34	3.1811112262	1.3945485980	-1.1257201335
N35	2.0947317426	-0.6115290910	-2.7842061437
O36	1.3175588003	-0.5439751746	-0.1084824362
O37	1.8035852270	-0.1654963804	1.0298679540
Fe38	1.3330380717	0.7063522820	-1.4726797733
H39	-2.8174389147	2.1402737833	-0.4973451573

Quartet end-on {Fe^{II}(porphin) + O_2^-}

Total energy: -1261.85893474629

Cartesian coordinates:

C1	4.9607880271	2.5064602167	-0.2013793341
C2	5.4831244004	1.5997558130	-1.0727035390
C3	4.3648376908	0.9183731698	-1.6711421397
C4	4.4776359004	-0.1180984885	-2.5877859912
C5	3.4151324815	-0.8296605881	-3.1187586644
C6	3.5589599277	-1.9244907580	-4.0432265652
C7	2.3023230954	-2.3716906496	-4.3122591281
C8	1.3964946316	-1.5407919675	-3.5581696823
C9	-2.3125351212	-0.9290402484	-3.0415322769
C10	0.0133083895	-1.6568191745	-3.5994385981
C11	-2.8356680407	0.0681357235	-2.2767306339
C12	-1.7191406767	0.7658411117	-1.6932291637
C13	-1.8370072847	1.8402703190	-0.8265356934
C14	-0.7736019433	2.5100149490	-0.2358371468
C15	-0.9119879158	3.5805386791	0.7172488769
C16	0.3494932977	3.9330151044	1.0887568248
C17	1.2479080989	3.0793239584	0.3543397378
C18	-0.8789604209	-0.8288083814	-2.9298320468
C19	2.6307463640	3.1296215446	0.4605376433
C20	3.5282761589	2.3738895434	-0.2811782565
H21	5.4798917979	-0.4123971124	-2.8911966101
H22	5.4859016520	3.1964765052	0.4494544582
H23	6.5249809012	1.3959426227	-1.2921501062
H24	4.5040795822	-2.2970499025	-4.4221424325
H25	2.0020031878	-3.1859055133	-4.9623419605
H26	-2.8373030221	-1.6690372275	-3.6354366607
H27	-3.8781813471	0.3121434305	-2.1070342009
H28	-1.8557238650	3.9916294378	1.0572840273
H29	0.6562667802	4.6914785073	1.8000851227
H30	3.0482383795	3.8452716887	1.1651912894
H31	-0.4048090752	-2.4425161291	-4.2242304918
N32	-0.5354993171	0.2018528043	-2.0985498516
N33	0.5481346792	2.2272579515	-0.4528168780
N34	3.1831985661	1.4144609600	-1.1892898468
N35	2.0895020625	-0.6128137700	-2.8307110493
O36	1.4582063786	-0.4485570285	0.1983852819
O37	1.9213771351	-0.0457622799	1.3373163265
Fe38	1.3246062973	0.7357036865	-1.5399021359
H39	-2.8418804032	2.1712930939	-0.5730830239

Sextet end-on {Fe^{II}(porphin) + O_2^-}

Total energy: -1261.86370914682

Cartesian coordinates:

C1	4.8680651649	2.3867322331	0.2068114541
C2	5.4104473064	1.4103097929	-0.5746180354
C3	4.3038471315	0.7205005831	-1.2055593259
C4	4.4188230560	-0.3257429864	-2.1269157857
C5	3.3789882440	-0.9608118056	-2.8139171637
C6	3.5496174773	-1.9934522398	-3.8146260264

C7	2.3036204965	-2.3132767996	-4.2651328282
C8	1.3712177067	-1.4750860574	-3.5420194740
C9	-2.3611468481	-0.5726692110	-3.4376575341
C10	-0.0131603526	-1.4581237917	-3.7381845759
C11	-2.9010764887	0.4121929500	-2.6656147710
C12	-1.8171167661	0.9674859964	-1.8816138328
C13	-1.9303153921	2.0425864299	-0.9930666061
C14	-0.8950629476	2.6629937694	-0.2867752395
C15	-1.0434061483	3.8214372734	0.5692687150
C16	0.2012143478	4.1284749897	1.0324260536
C17	1.1117405401	3.1625540156	0.4549072741
C18	-0.9485262306	-0.6194690488	-3.1237245166
C19	2.4978580092	3.1536065188	0.6411277944
C20	3.4312568403	2.2950367358	0.0503291399
H21	5.4279834185	-0.6623982580	-2.3564778456
H22	5.3851495239	3.1136854539	0.8237341334
H23	6.4594907144	1.1774872423	-0.7220141917
H24	4.5012266077	-2.4081749140	-4.1289855652
H25	2.0324277990	-3.0397534281	-5.0234630635
H26	-2.8620533521	-1.2031401426	-4.1643260121
H27	-3.9327508645	0.7444385684	-2.6305853286
H28	-1.9791733901	4.3275732018	0.7802726251
H29	0.4867663538	4.9385710976	1.6947194668
H30	2.8993816952	3.9233581995	1.2977831647
H31	-0.4033267923	-2.1548443291	-4.4779555341
N32	-0.6601712288	0.3120314477	-2.1724126710
N33	0.4145701031	2.2902690351	-0.3270993065
N34	3.1289543586	1.2719971294	-0.7963636541
N35	2.0536592605	-0.6784388286	-2.6710710084
O36	0.9918401518	-0.7453858836	0.2862205804
O37	0.9116124651	-1.4936384762	1.3393862321
Fe38	1.1847970015	0.5030156134	-1.1473823984
H39	-2.9260326330	2.4619483739	-0.8627525991

Doublet side-on {Fe^{II}(porphin) + O_2^-}

Total energy: -1261.85078531366

Cartesian coordinates:

C1	1.0278417715	3.4928976073	0.1940754815
C2	0.0418175964	4.4288905106	0.6756925275
C3	-0.6943382060	-1.0205592004	-2.5169955119
C4	2.3861431712	3.5705090467	0.4842992327
C5	3.3432924215	2.6434870318	0.0978918249
C6	4.7634456988	2.8170928470	0.3091035103
C7	5.3773544198	1.7944816359	-0.3408325782
C8	4.3281302929	1.0045518142	-0.9461082600
C9	4.5605797175	-0.0387795899	-1.8307312254
C10	3.5807729719	-0.7246138772	-2.5407286775
C11	3.8469414756	-1.8444665185	-3.4099416167
C12	2.6346739040	-2.3289385266	-3.7963129277
C13	1.6418499574	-1.4998657498	-3.1577862945
C14	-2.1165628362	-1.2405488498	-2.6583939974
C15	0.2752117915	-1.7571734888	-3.1831136291
C16	-2.7317059684	-0.2340094043	-1.9844448409
C17	-1.6814823902	0.5958744219	-1.4370502360
C18	-1.1723264274	3.9295009852	0.3143488062
C19	-1.9027459237	1.8133648300	-0.8088472155
C20	-0.9134327890	2.6956609188	-0.3869509250
H21	5.5952019485	-0.3310019602	-1.9980279681
H22	-3.7931091240	-0.0389676532	-1.8780974007
H23	-2.1578584546	4.3324598292	0.5203881208
H24	0.2634866771	5.3266446699	1.2424531525
H25	2.7270420960	4.4312592529	1.0558344754

H26	-0.0619649204	-2.6009216129	-3.7813813242
H27	5.2118250070	3.6365588138	0.8602168022
H28	6.4382726797	1.5928305550	-0.4390316857
H29	4.8351050377	-2.2166960594	-3.6575449757
H30	2.4177633235	-3.1825652710	-4.4287507371
H31	-2.5639009245	-2.0504185923	-3.2240699414
N32	0.4291052934	2.4798846834	-0.4955407033
N33	3.1001150544	1.5090512999	-0.6239386568
N34	2.2383624222	-0.4996068317	-2.4473789952
N35	-0.4559583379	0.0716317609	-1.7333366023
O36	1.5517611362	-0.8105046385	0.0901893476
O37	0.9224710121	0.2088729114	0.7551084577
Fe38	1.3084572401	0.6914409473	-1.0396580350
H39	-2.9363423359	2.1087539016	-0.6434328563

Quartet side-on {Fe^{II}(porphin) + O_2^-}
Total energy: -1261.86678542276
Cartesian coordinates:

C1	0.8111800646	3.5535759854	0.4922969190
C2	-0.2091972650	4.4692226464	0.9554413810
C3	-0.7869781038	-0.8345256600	-2.5566924713
C4	2.1740505669	3.7104084274	0.7511432459
C5	3.1993469018	2.8777603147	0.3060847540
C6	4.6115951024	3.0960099304	0.5310166723
C7	5.2658805489	2.0875172201	-0.1106955104
C8	4.2475834184	1.2612231019	-0.7211637597
C9	4.4874000109	0.1436193079	-1.5208186924
C10	3.5241981996	-0.6273268239	-2.1722232283
C11	3.8315550803	-1.7422756801	-3.0395976657
C12	2.6404102708	-2.2357170709	-3.4750009812
C13	1.6097514045	-1.4212258772	-2.8720923756
C14	-2.1946968958	-1.0107776770	-2.8415144037
C15	0.2437290893	-1.6201808004	-3.0705966368
C16	-2.8474461935	-0.0032701785	-2.1969982020
C17	-1.8327381768	0.7798446738	-1.5256757862
C18	-1.3996437612	3.9727319209	0.5215920503
C19	-2.0666325033	1.9440514740	-0.7947308656
C20	-1.0987136811	2.7574804508	-0.2042010652
H21	5.5262200538	-0.1421220329	-1.6728970856
H22	-3.9116407900	0.2042801095	-2.1817082234
H23	-2.3937598666	4.3793942857	0.6717691103
H24	-0.0247717239	5.3679004698	1.5339401556
H25	2.4630970485	4.5766564540	1.3427667648
H26	-0.0403953130	-2.4505891809	-3.7136656211
H27	5.0368143454	3.9183059320	1.0960224564
H28	6.3345222357	1.9158870998	-0.1768167244
H29	4.8309726851	-2.0879735985	-3.2796861471
H30	2.4619295090	-3.0672543823	-4.1473513121
H31	-2.6158547045	-1.7945604789	-3.4617868472
N32	0.2467608690	2.5352370270	-0.2176881402
N33	3.0114868358	1.7592678145	-0.4452470429
N34	2.1723694731	-0.4477970127	-2.0962156914
N35	-0.6012244469	0.2473801551	-1.7528275973
O36	1.1908580900	-0.9180725851	0.5124667082
O37	0.8950093314	0.2279275154	1.2573138245
Fe38	1.1773930064	0.5870833799	-0.5222979715
H39	-3.1024327128	2.2591205028	-0.6867715443

Sextet side-on {Fe^{II}(porphin) + O_2^-}
Total energy: -1261.88561546787
Cartesian coordinates:

C1	1.0081771619	3.4896665042	0.2757878038
C2	0.0143036968	4.4219373321	0.7704503791
C3	-0.7245570945	-0.9238871899	-2.7022939873
C4	2.3900387627	3.6266730702	0.4387759296
C5	3.3838668088	2.7787998588	-0.0612779755
C6	4.8072844973	3.0184578063	0.0472883036
C7	5.4250788990	2.0032002431	-0.6205440579
C8	4.3765551538	1.1471876178	-1.1332092093
C9	4.5836799403	0.0160595856	-1.9295316995
C10	3.6030006496	-0.7829680506	-2.5247888747
C11	3.8669791118	-1.9274649497	-3.3749768295
C12	2.6532836794	-2.4214100622	-3.7463207029
C13	1.6549011276	-1.5753152627	-3.1219054801
C14	-2.1431427880	-1.0677935076	-2.9517195385
C15	0.2723548522	-1.7359049353	-3.2536014984
C16	-2.7600850557	-0.0474972465	-2.2905623751
C17	-1.7153072448	0.7147995955	-1.6399442220
C18	-1.1986782876	3.9316861744	0.3911679371
C19	-1.9202263124	1.8842680377	-0.9001471023
C20	-0.9385702112	2.7022910135	-0.3323509081
H21	5.6191762195	-0.2534622201	-2.1305336676
H22	-3.8202191696	0.1792953024	-2.2498852186
H23	-2.1803011619	4.3530941144	0.5805563420
H24	0.2257150906	5.3263723370	1.3311382921
H25	2.7309990576	4.5034062880	0.9868623802
H26	-0.0643729772	-2.5632694929	-3.8760011954
H27	5.2638640298	3.8617272706	0.5546279816
H28	6.4884547488	1.8483179735	-0.7679754135
H29	4.8514301208	-2.2955351430	-3.6441408986
H30	2.4431217261	-3.2750321715	-4.3817417095
H31	-2.5973179333	-1.8424903092	-3.5604513084
N32	0.3999079813	2.4698892946	-0.3861852922
N33	3.1596953640	1.6344134010	-0.7647591694
N34	2.2620881183	-0.5978364703	-2.3979785752
N35	-0.5029400569	0.1512973661	-1.8967452733
O36	1.5165799010	-1.0652744718	0.4785518751
O37	0.9161522977	-0.0576225827	1.1304503029
Fe38	1.3086341684	0.5496858880	-0.8209219737
H39	-2.9529083327	2.2033608147	-0.7724744135

Doublet end-on {Fe^{II}(porphin) + O_2^- + DMSO}

Total energy: -1814.94784088973

Cartesian coordinates:

C1	5.0455963148	2.3194004187	0.1282364201
C2	5.5765696075	1.3667058415	-0.6815795188
C3	4.4647037668	0.7470967073	-1.3663680022
C4	4.6009264251	-0.2687985450	-2.3018869597
C5	3.5557366440	-0.8681913036	-2.9894777673
C6	3.7277627818	-1.9157282264	-3.9690800652
C7	2.4831018438	-2.2388359049	-4.4102173078
C8	1.5628890793	-1.3833010785	-3.6966918245
C9	-2.1463764758	-0.6089632204	-3.4352295165
C10	0.1856485065	-1.4015576405	-3.8791328661
C11	-2.6797905283	0.3521564894	-2.6318681031
C12	-1.5754825718	0.9745822715	-1.9453951516
C13	-1.7050595451	2.0037380062	-1.0230180339
C14	-0.6556122032	2.6099088693	-0.3445433984
C15	-0.8204146454	3.6835133852	0.6083526794
C16	0.4250183887	3.9958278960	1.0550036224
C17	1.3402691315	3.1110526247	0.3739053296
C18	-0.7191722256	-0.5670820013	-3.2336231634
C19	2.7144180203	3.1162169536	0.5643542014

C20	3.6147016753	2.2733516593	-0.0695030286
H21	5.6082914203	-0.6196530958	-2.5176871288
H22	5.5573517193	2.9982889864	0.8017836875
H23	6.6172214157	1.0933680094	-0.8178607820
H24	4.6822958604	-2.3378659049	-4.2650255114
H25	2.1960446437	-2.9825981795	-5.1461169735
H26	-2.6580538321	-1.2970578864	-4.0998865247
H27	-3.7222947627	0.6195560270	-2.4988523760
H28	-1.7720848856	4.1206442279	0.8905888833
H29	0.7154365030	4.7449278170	1.7837447556
H30	3.1184432971	3.8374106889	1.2720850305
H31	-0.2173978907	-2.1296866100	-4.5806917520
N32	-0.3864064514	0.4118581647	-2.3322723668
N33	0.6651094309	2.2806792785	-0.4767353891
N34	3.2824548465	1.3094701450	-0.9777763775
N35	2.2332399406	-0.5541354380	-2.8401070162
O36	1.1893848973	-0.4803411485	-0.2933098526
O37	1.5657756189	-0.1873335535	0.9193137805
Fe38	1.4493449922	0.8399412282	-1.6022630210
O39	1.8626530223	2.3214518295	-3.1745228902
S40	0.6575237653	2.8334262137	-3.9466841062
C41	1.2299048577	4.4206151698	-4.6338008367
C42	0.6334358508	1.9237795329	-5.5234877141
H43	-0.1495399697	2.3293869997	-6.1736533740
H44	0.4841808334	4.8252907900	-5.3263995350
H45	2.1911197828	4.2718462286	-5.1358327391
H46	1.3611158001	5.1003628721	-3.7880642882
H47	1.6172279685	1.9892874547	-5.9989940294
H48	0.4132892716	0.8827247098	-5.2716882678
H49	-2.7106920649	2.3610904902	-0.8110275939

Quartet end-on {Fe^{II}(porphin) + O_2^- + DMSO}

Total energy: -1814.93361477866

Cartesian coordinates:

C1	5.0530743761	2.3909360212	0.1040025256
C2	5.6064114587	1.3610600039	-0.5912934597
C3	4.5181148518	0.6892879415	-1.2617025413
C4	4.6644212851	-0.4169567465	-2.0879732851
C5	3.6322540684	-1.0519385008	-2.7661604729
C6	3.8133194131	-2.1748112419	-3.6547436591
C7	2.5846104664	-2.4771838266	-4.1523270925
C8	1.6572886507	-1.5414299371	-3.5590098244
C9	-2.0544243300	-0.6915576021	-3.5357113385
C10	0.2948719194	-1.5243314248	-3.8297342719
C11	-2.6185192009	0.2875598294	-2.7714904997
C12	-1.5396315953	0.9310735673	-2.0672962738
C13	-1.6908458900	1.9843870114	-1.1713341363
C14	-0.6558098835	2.6135157915	-0.4935502921
C15	-0.8360152602	3.7412813500	0.3889420187
C16	0.4039644155	4.0976933750	0.8195422211
C17	1.3354598151	3.1803132498	0.2063949740
C18	-0.6350479843	-0.6449013580	-3.2835557545
C19	2.7101030472	3.2235071190	0.4028042834
C20	3.6303043782	2.3362650802	-0.1407951056
H21	5.6698271502	-0.8082776927	-2.2275973409
H22	5.5459297613	3.1236846343	0.7342141649
H23	6.6492701994	1.0703970500	-0.6544339634
H24	4.7651707069	-2.6497944157	-3.8656535342
H25	2.3117527760	-3.2592796367	-4.8525560747
H26	-2.5467313405	-1.4026280258	-4.1905296727
H27	-3.6660902637	0.5544403290	-2.6819516137
H28	-1.7926004667	4.1905621881	0.6330653231

H29	0.6802541120	4.8991096100	1.4966859067
H30	3.0953064962	4.0052350218	1.0546271924
H31	-0.0813367133	-2.2771424666	-4.5198276132
N32	-0.3412646407	0.3618495892	-2.4058902969
N33	0.6724725479	2.2851508834	-0.5884531199
N34	3.3293186779	1.2961287373	-0.9717699349
N35	2.3146467343	-0.6876822561	-2.7155151503
O36	0.9118819590	-0.8225673578	-0.1635194364
O37	1.5458633000	-0.2431176703	0.8088300583
Fe38	1.4927734928	0.7498840541	-1.5993190688
O39	1.8998163206	2.3267589226	-3.5733598498
S40	0.6719719720	3.1819555046	-3.7753378939
C41	1.2755054602	4.7476988212	-4.5029156793
C42	-0.1540901956	2.5762903556	-5.2818215869
H43	-0.9765655612	3.2479956809	-5.5496917863
H44	0.4308446888	5.3860961488	-4.7900200207
H45	1.9139736377	4.5318684338	-5.3656742712
H46	1.8666228712	5.2425925396	-3.7274924144
H47	0.5723926176	2.5003603354	-6.0959310327
H48	-0.5452633062	1.5850179489	-5.0393227490
H49	-2.7001277739	2.3490612705	-0.9913657460

Doublet end-on {Fe^{II}(porphin) + O_2^- + K^+}

Total energy: -1290.03343319176

Cartesian coordinates:

C1	-0.6474445400	-0.6292251160	-3.2673514919
C2	2.7535578782	3.4717621674	0.0839545627
C3	3.6400784330	2.8499437450	-0.7794423132
C4	5.0507562810	3.1499520042	-0.8389123859
C5	5.5711263501	2.3663353284	-1.8163947994
C6	4.4775022222	1.5843323655	-2.3421061173
C7	4.6106135919	0.6338451923	-3.3415274315
C8	3.5782831480	-0.1461816916	-3.8390720361
C9	3.7380567751	-1.1436395910	-4.8697515566
C10	2.5156878863	-1.7014438313	-5.0607632153
C11	1.6138688856	-1.0345675468	-4.1523372924
C12	-2.0702482189	-0.8401216566	-3.2977305373
C13	0.2585982653	-1.3102311132	-4.0676300005
C14	-2.6198874002	0.0670873915	-2.4422350467
C15	-1.5264419877	0.8199472134	-1.8838171160
H16	5.6011440995	0.4834977426	-3.7623590982
C17	-1.6694302018	1.8248813883	-0.9313984551
C18	-0.6172385433	2.5413323534	-0.3719491846
C19	-0.7795698963	3.5656036581	0.6315031901
O20	1.9007147550	-0.2970183904	-0.7448087856
C21	0.4696860631	4.0070123255	0.9360403500
C22	1.3848666266	3.2597285354	0.1112562697
H23	5.5552989439	3.8745667261	-0.2112039455
H24	6.5959566401	2.3053192515	-2.1614249447
H25	4.6713324644	-1.3721932417	-5.3701052854
H26	2.2286869919	-2.4826559351	-5.7544635985
H27	-2.5758145291	-1.5669213496	-3.9227484127
H28	-3.6671705437	0.2384035504	-2.2214657744
H29	-1.7313451109	3.9034090895	1.0251954922
H30	0.7586105074	4.7834645499	1.6344984944
K31	-0.3182630256	-0.6003630822	0.5263031433
N32	-0.3222000338	0.3747392436	-2.3849885710
N33	0.7118042710	2.3593815461	-0.6737854048
N34	3.3070016722	1.8992518249	-1.7064082539
N35	2.2774569505	-0.0867457596	-3.4176318816
O36	2.2260436937	0.0521082073	0.4873670423
Fe37	1.5474590265	1.0388264702	-1.9483022865

H38	3.1579196143	4.2161241588	0.7648723246
H39	-0.1364147849	-2.0852998819	-4.7193308349
H40	-2.6789609416	2.0873556290	-0.6234774887

Sextet side-on {Fe^{II}(porphin) + O_2^- + K^+}

Total energy: -1290.05417492550

Cartesian coordinates:

C1	1.1807515726	3.8000500248	0.0024601802
C2	0.2040145084	4.6796173418	0.6117068291
C3	-0.6362993661	-0.5910579606	-2.9552826326
C4	2.5644645291	3.9554131014	0.1007349757
C5	3.5352604720	3.1393487093	-0.4786364151
C6	4.9586909596	3.3824363616	-0.4235184017
C7	5.5529529075	2.4014707629	-1.1563464621
C8	4.4932242869	1.5576664409	-1.6597811007
C9	4.6785448718	0.4640388441	-2.5048234574
C10	3.6788225289	-0.3270013703	-3.0732584529
C11	3.9152600303	-1.4515183350	-3.9554909413
C12	2.6955517183	-1.9689674554	-4.2605431514
C13	1.7171621709	-1.1575934689	-3.5649083659
C14	-2.0585231186	-0.8092849983	-3.0395749717
C15	0.3395811933	-1.3700140860	-3.5915799020
C16	-2.6575078182	0.1808684102	-2.3029191091
C17	-1.5990442503	1.0019223109	-1.7708658322
C18	-1.0196734398	4.1708780198	0.3079723603
C19	-1.7843487491	2.1441626541	-0.9812231816
C20	-0.7865074603	2.9822686079	-0.4868470750
H21	5.7053761850	0.2137590229	-2.7596496590
H22	-3.7183031263	0.3631311912	-2.1718037340
H23	-1.9936188700	4.5567383006	0.5855376836
H24	0.4372304240	5.5647635685	1.1916360457
H25	2.9222715591	4.8091938642	0.6707220130
H26	-0.0177322869	-2.2030950247	-4.1925584249
H27	5.4296173427	4.2073836846	0.0977682027
H28	6.6086580403	2.2613332751	-1.3560678510
H29	4.8895211712	-1.7888966784	-4.2890531549
H30	2.4675361452	-2.8147640350	-4.8986574382
H31	-2.5383162942	-1.5875130415	-3.6228028111
K32	-0.7170054341	-1.4002366056	0.0887345608
N33	-0.3855392799	0.4964219628	-2.1595937497
N34	0.5520301875	2.7960443101	-0.6660638755
N35	3.2858518678	2.0206526272	-1.2209662871
N36	2.3433656311	-0.1658506216	-2.8700170504
O37	1.7218907976	-0.6914859978	-0.1987164433
O38	1.0816998450	0.3516440897	0.5769095786
Fe39	1.4945415713	0.9370341557	-1.2225991902
H40	-2.8127626744	2.4193622860	-0.7584523623

Doublet end-on {Fe^{II}(porphin) + O_2^-+ DMSO + K^+}

Total energy: -1843.12784180470

Cartesian coordinates:

C1	5.0101210244	2.3764299073	0.0844686519
C2	5.5560565551	1.4242630310	-0.7120501186
C3	4.4559713103	0.7965227225	-1.4125201144
C4	4.5988501694	-0.2442429815	-2.3191778050
C5	3.5566076587	-0.8764191424	-2.9834183001
C6	3.7252499309	-1.9774579755	-3.9057309506
C7	2.4810434149	-2.3285143277	-4.3185116432
C8	1.5602611131	-1.4359711443	-3.6486783938
C9	-2.1558040038	-0.6599860133	-3.4425718829
C10	0.1821701253	-1.4778164329	-3.8155173408

C11	-2.6996138146	0.3572114775	-2.7138664044
C12	-1.6049556307	1.0079612534	-2.0382172956
C13	-1.7420755986	2.0872621011	-1.1655279448
C14	-0.6917054258	2.6988201743	-0.4821741271
C15	-0.8559104033	3.8003630075	0.4384161655
C16	0.3853334501	4.0870181270	0.9184370956
C17	1.2981322854	3.1653978050	0.2874621827
C18	-0.7344562845	-0.6226109172	-3.2134974159
C19	2.6713925464	3.1654313340	0.4903690306
C20	3.5806901602	2.3269230562	-0.1371576922
H21	5.6066964858	-0.6011011435	-2.5161261360
H22	5.5077962314	3.0574658095	0.7647831537
H23	6.5988185738	1.1525028362	-0.8255474241
H24	4.6777122496	-2.4138792335	-4.1824161713
H25	2.1925727401	-3.1131553639	-5.0083038466
H26	-2.6615765661	-1.3654659974	-4.0920659302
H27	-3.7392418276	0.6577493771	-2.6473611346
H28	-1.7977981897	4.2877937472	0.6644780574
H29	0.6719084834	4.8584206034	1.6239687637
H30	3.0689455271	3.8937031886	1.1931599637
H31	-0.2147429023	-2.2368106288	-4.4857435238
N32	-0.4116350776	0.3939528594	-2.3469274121
N33	0.6270381233	2.3206586275	-0.5554789819
N34	3.2697211866	1.3623049896	-1.0500334663
N35	2.2365367128	-0.5601460232	-2.8472069881
O36	1.3088052378	-0.4599222286	-0.3343572579
O37	1.6102031362	-0.1239515768	0.9125378967
Fe38	1.4704717412	0.8529006207	-1.6748231763
O39	1.7980302050	2.2251474475	-3.2439533748
S40	0.6031266939	2.9421929473	-3.8740301403
C41	1.2905063136	4.5351180408	-4.4039103051
C42	0.4033652247	2.2095201054	-5.5241679996
H43	-0.3618218949	2.7583253535	-6.0828458510
H44	0.5517851695	5.0803731396	-4.9999743509
H45	2.2073205317	4.3627713755	-4.9754749499
H46	1.5236346662	5.0962330055	-3.4957072268
H47	1.3629119946	2.2234772862	-6.0498509317
H48	0.0836797918	1.1766207286	-5.3659540058
H49	-2.7393814711	2.4992841193	-1.0277908169
K50	-0.9919692177	-0.2355978639	0.7067062144

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