Electronic Supplementary Information

Studies on an Iron(III)-Peroxo Porphyrin. Iron(III)-Peroxo or Iron(II)-Superoxo?

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Supporting Figures.

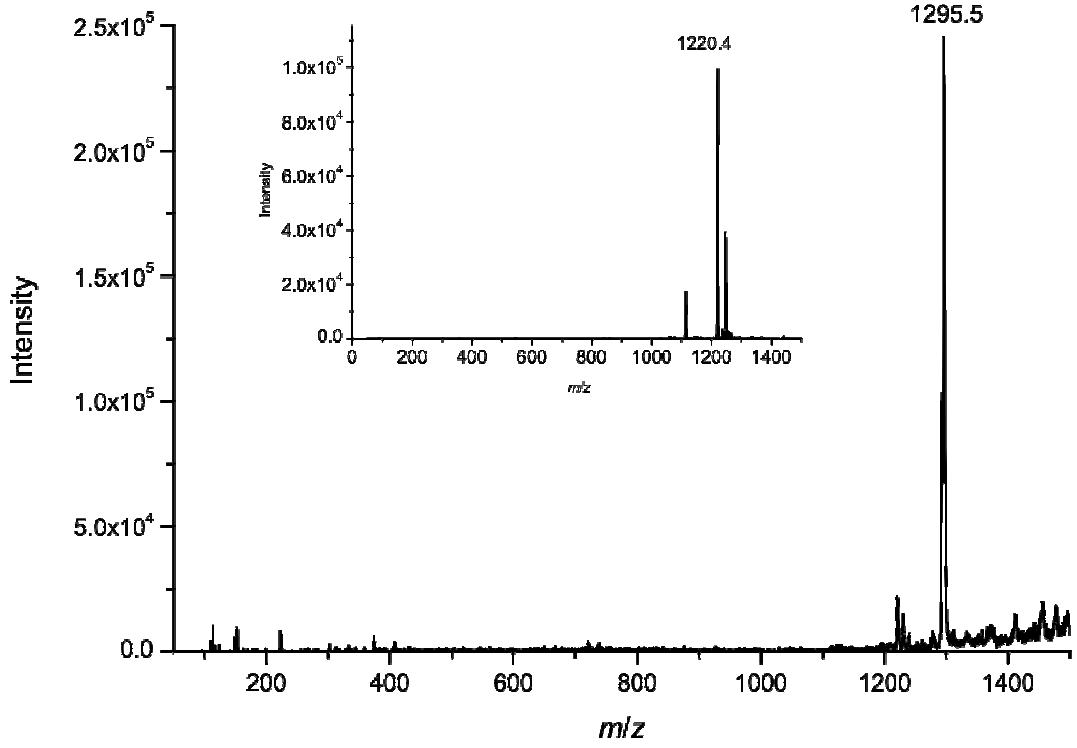

Fig. S1 Mass spectrum of $\{K^+ + KFe^{III}(Porph)(^{18}O_2^{2-})\}$. Inset: MS/MS of *m/z* = 1295.5.

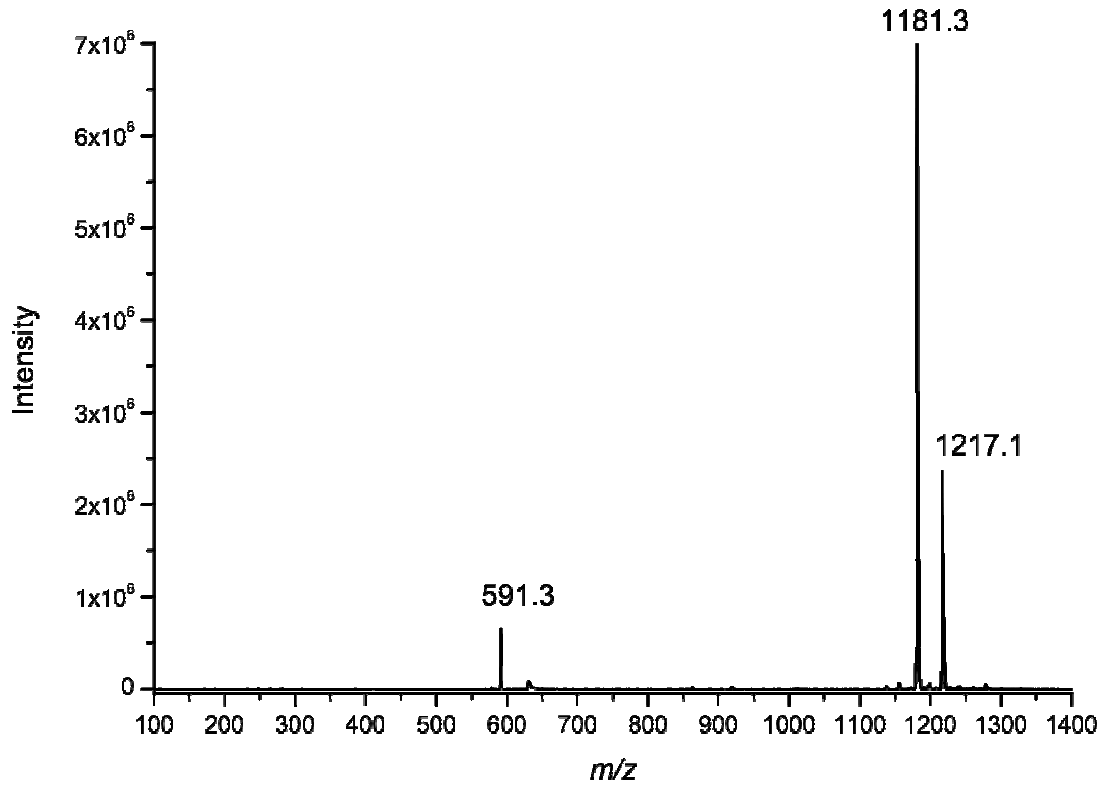

Fig. S2 Mass spectrum of [Fe^{III}(Porph)Cl] in DMSO. Peak at *m/z* = 591.3 is {H^+ + [Fe^{III}(Porph)]$^+$}, peak at *m/z* = 1181.3 is [Fe^{III}(Porph)]$^+$, peak at *m/z* = 1217.1 is {H^+ + [Fe^{III}(Porph)Cl]}.

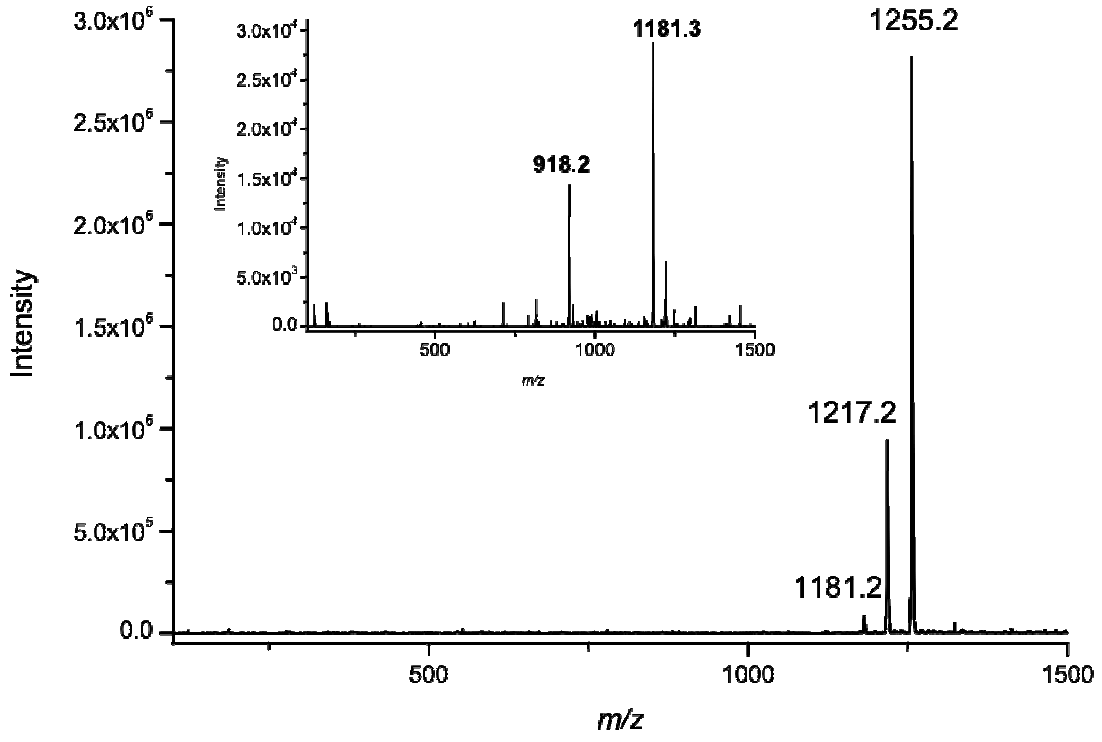

Fig. S3 Mass spectrum of [Fe^{III}(Porph)Cl] in a saturated solution of KCl in DMSO. Peak at *m/z* = 1255.2 is {K^+ + [Fe^{III}(Porph)]Cl}; Inset: MS/MS of {K^+ + Fe^{III}(Porph)Cl}, peak at *m/z* = 1181.3 is [Fe^{III}(Porph)]$^+$, peak at *m/z* = 918.2 is {[Fe^{III}(Porph)]$^+$ - Aza-18-crown-6} (Peak to the right of *m/z* = 1181.3 is peak at *m/z* = 1217.2; {H^+ + [Fe^{III}(Porph)Cl]}).

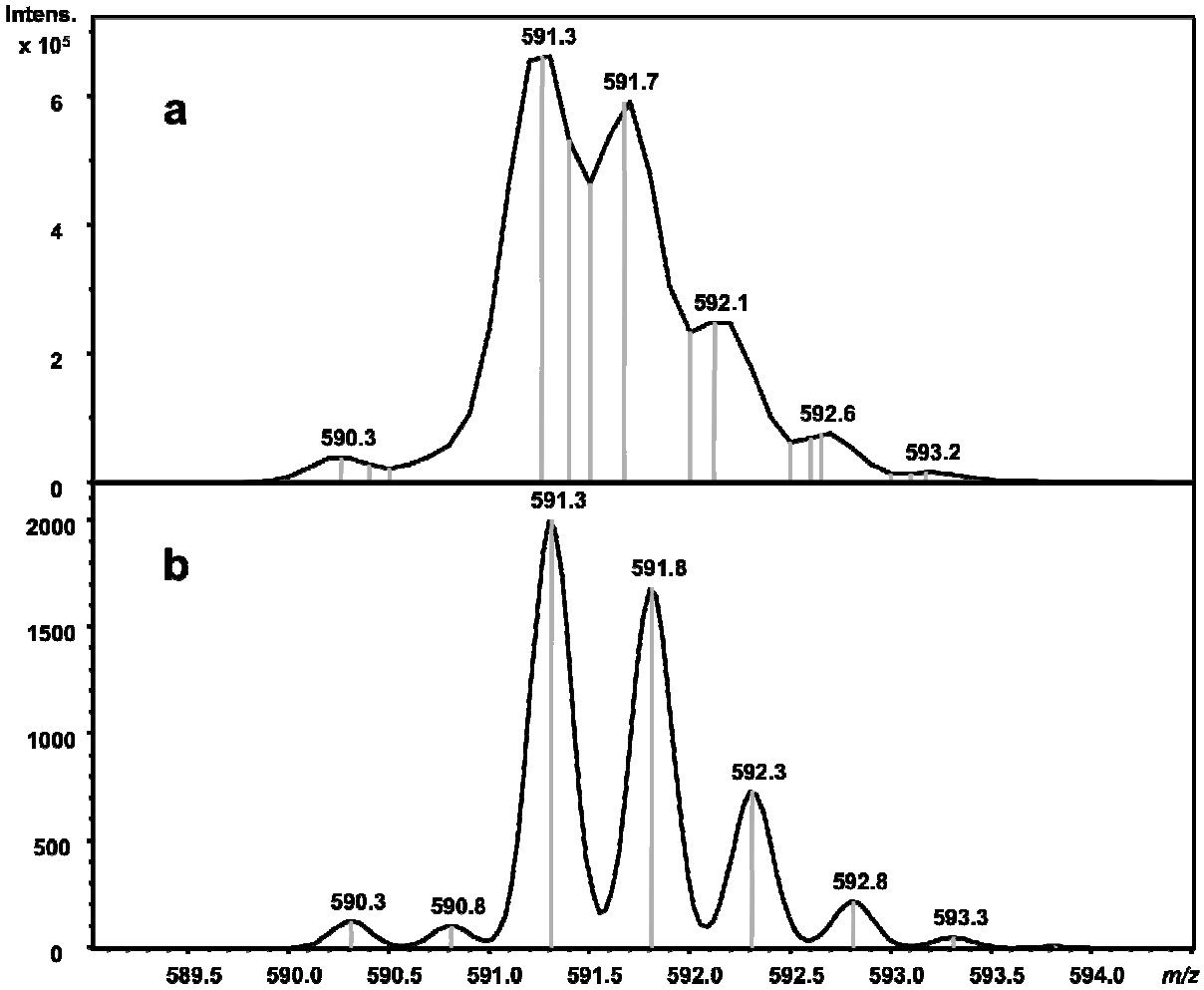

Fig. S4 Comparison of measured and calculated isotopic distribution; a) spectrum of {H^+ + [Fe^{III}(Porph)]$^+$} in Fig. S2, b) calculation of {H^+ + [Fe^{III}(Porph)]$^+$} ($C_{74}H_{88}FeN_5O_5$).

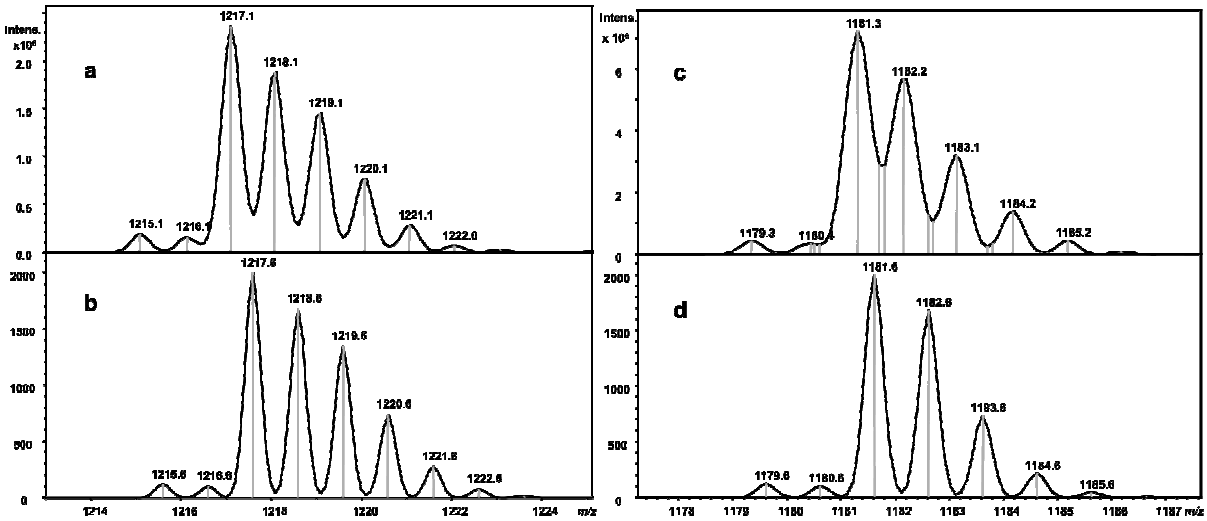

Fig. S5 Comparison of measured and calculated isotopic distribution; a) spectrum of $\{H^+ + [Fe^{III}(Porph)Cl]\}$ in Fig. S2, b) calculation of $\{H^+ + [Fe^{III}(Porph)Cl]\}$ ($C_{74}H_{88}ClFeN_5O_5$), c) spectrum of $[Fe^{III}(Porph)]^+$ in Fig. S2, d) calculation of $[Fe^{III}(Porph)]^+$ ($C_{74}H_{87}FeN_5O_5$).

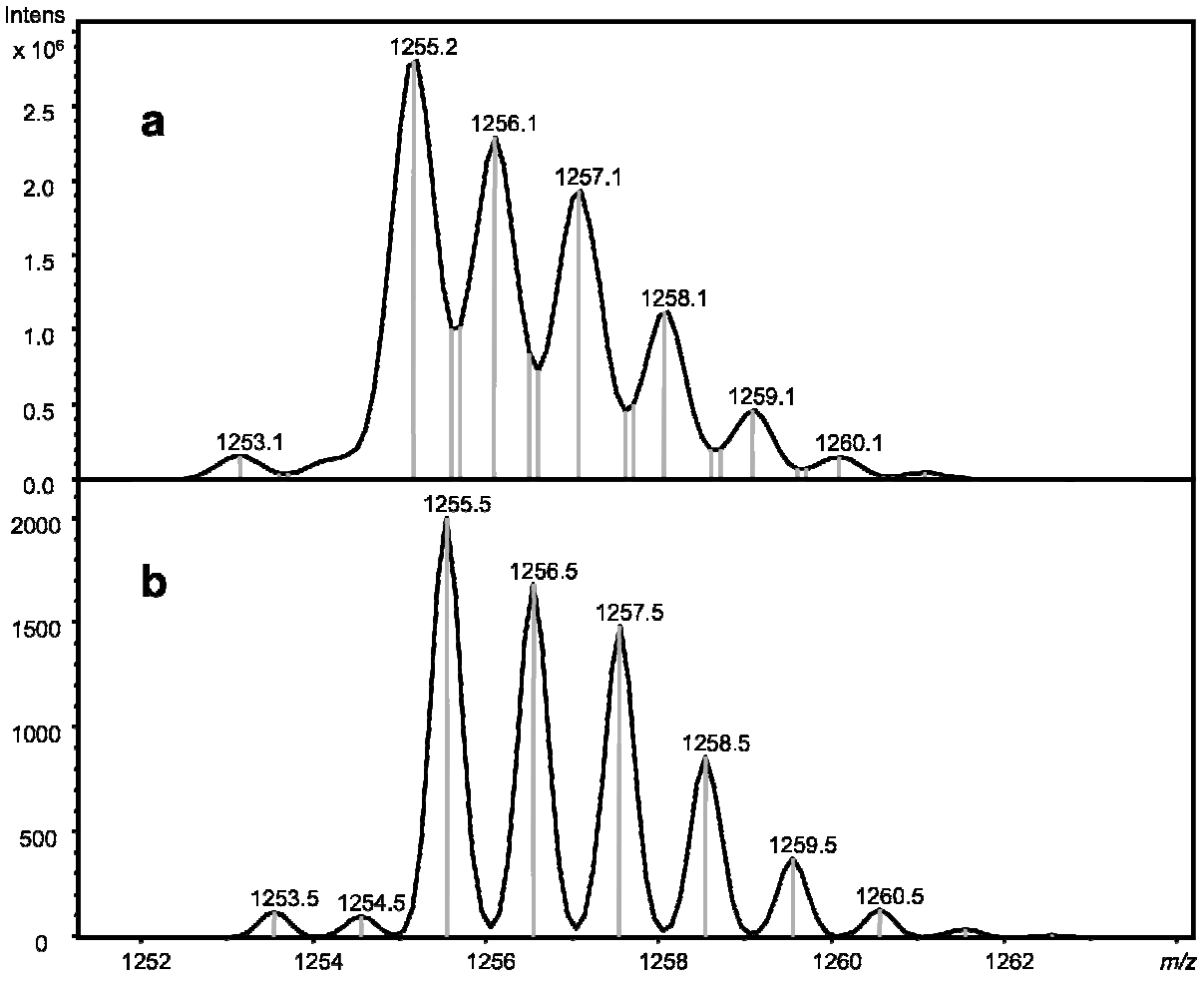

Fig. S6 Comparison of measured and calculated isotopic distribution; a) spectrum of $\{K^+ + [Fe^{III}(Porph)]Cl\}$ in Fig. S3, b) calculation of $\{K^+ + [Fe^{III}(Porph)]Cl\}$ ($C_{74}H_{87}ClFeKN_5O_5$).

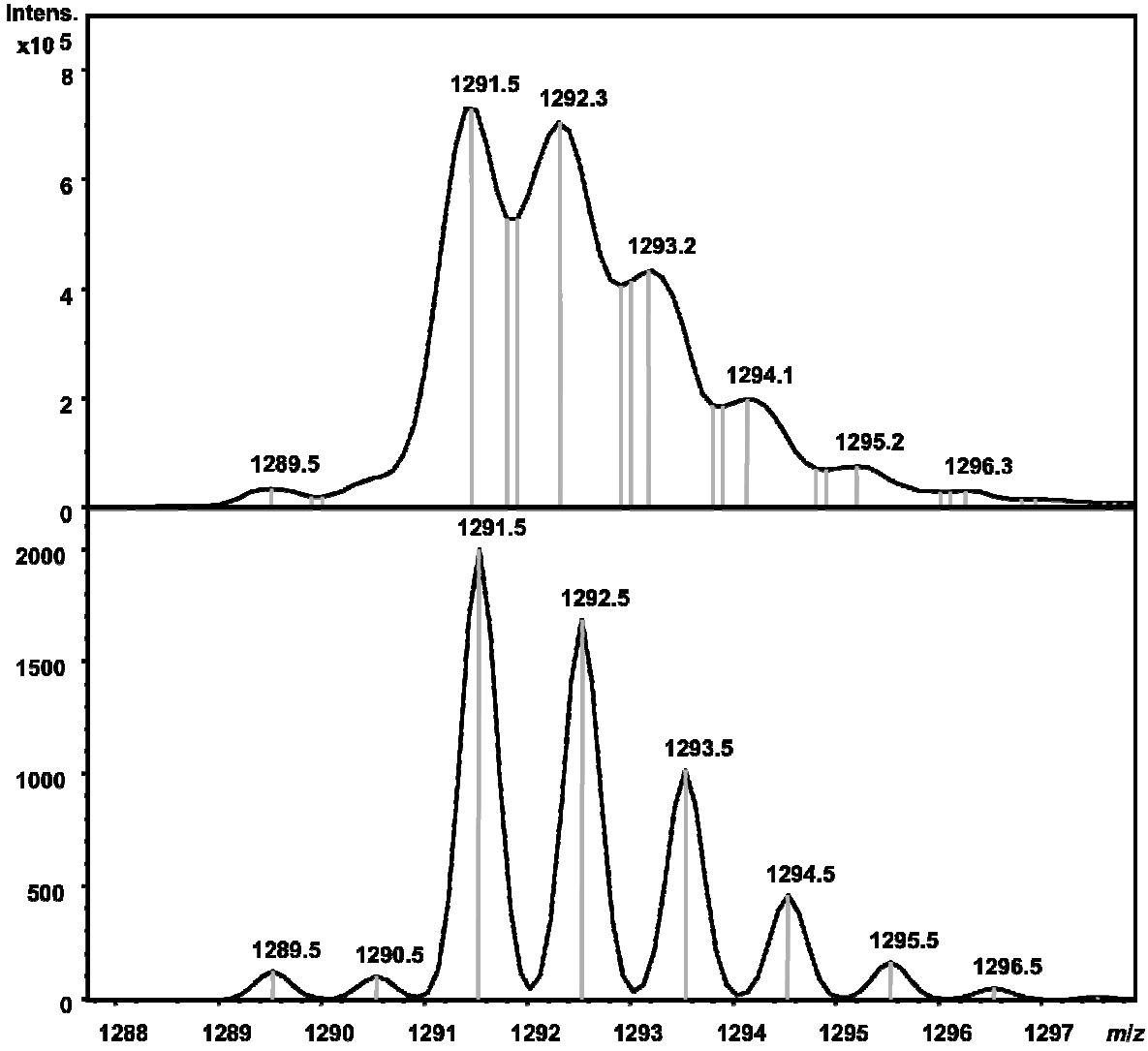

Fig. S7 Comparison of measured and calculated isotopic distribution; a) spectrum of $\{K^+ + KFe^{III}(Porph)(O_2^{2-})\}$ in Fig. 1, b) calculation of $\{K^+ + KFe^{III}(Porph)(O_2^{2-})\}$ ($C_{74}H_{87}FeK_2N_5O_7$).

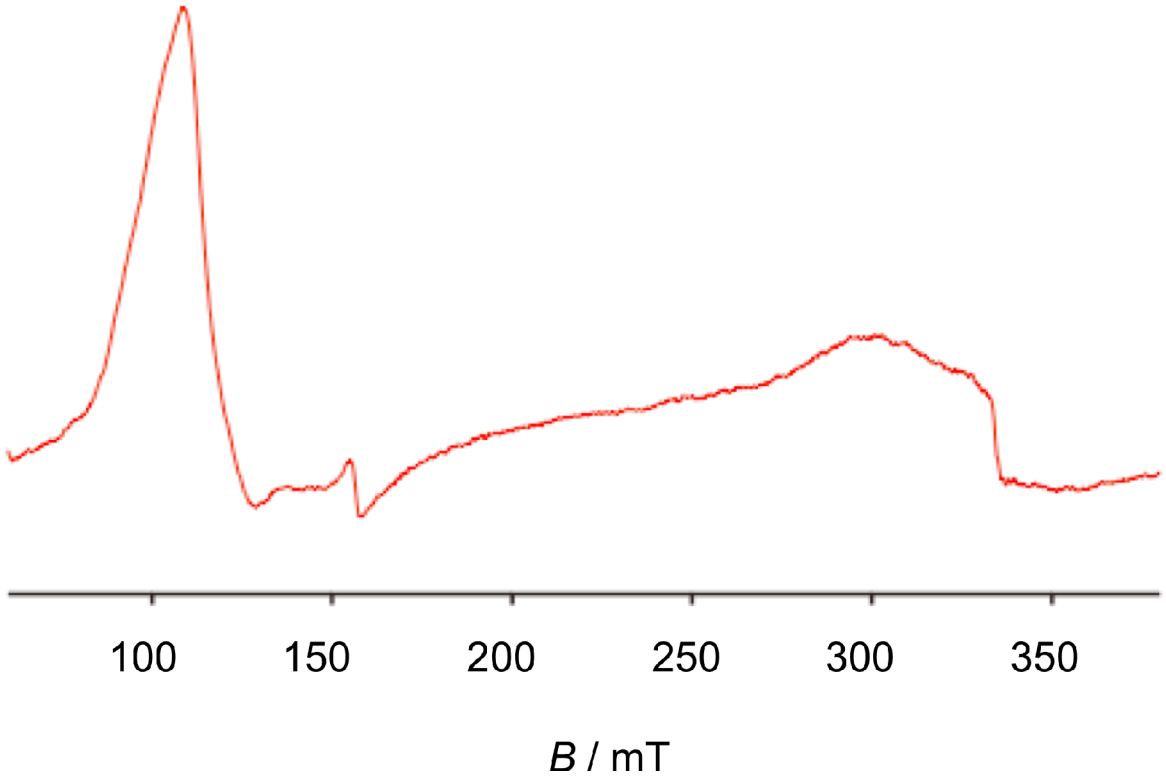

Fig. S8a X-band EPR spectra of $[NaFe^{III}(Porph)OH]^+$ (rhombic impurity at ca. $g = 4$) at $T =$ 10 K, modulation amplitude 0.1 mT, MW frequency 9.376 GHz and MW power 2 mW.

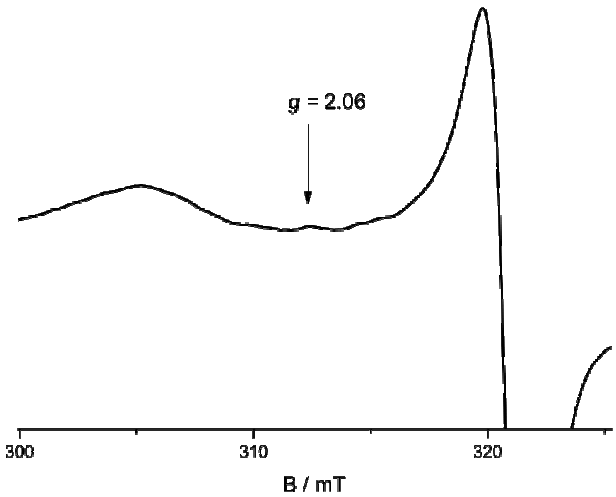

Fig. S8b X-band EPR spectra in DMSO at 6 K; $[Zn^{II}(Porph)]$ with excess of KO_2, microwave frequency was 8.977674 GHz, $P = 0.2$ mW; Mod. width = 0.5 mT, sweep width 200 mT.

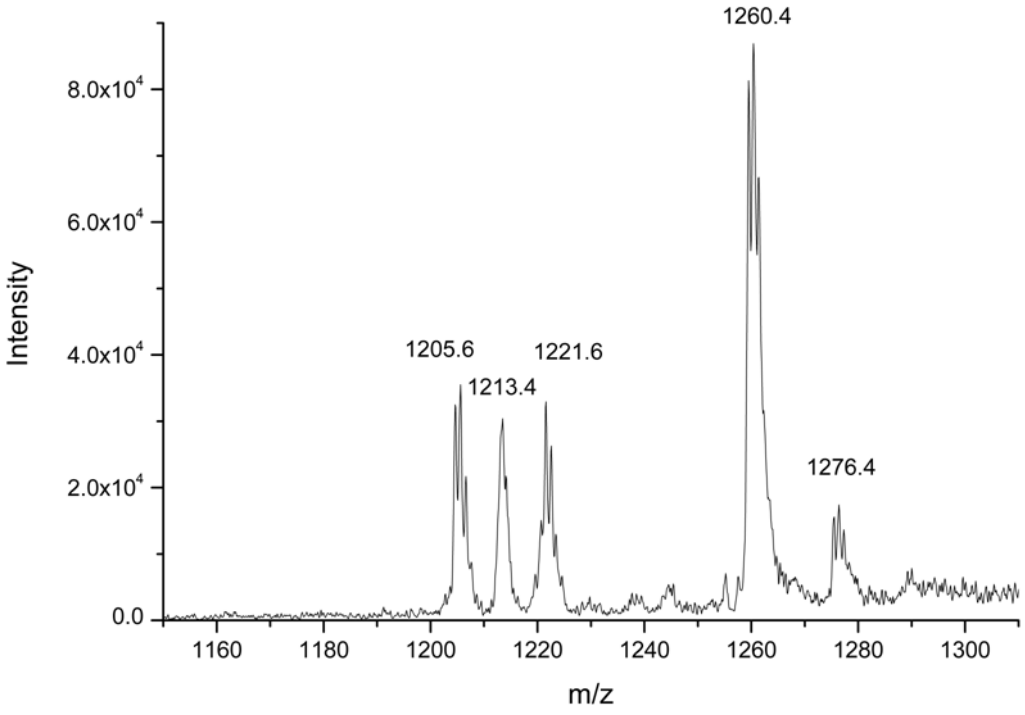

Fig. S9 ESI mass spectrum of reaction product of the complex with Na_2O_2 in DMSO. (The spectrum also confirms replacement of the two potassium cations by sodium. The fact that the di-sodiated su(peroxo) prophyrin is accompanied by additional products indicates an overall greater lability compared to its di-potassiated counterpart.)

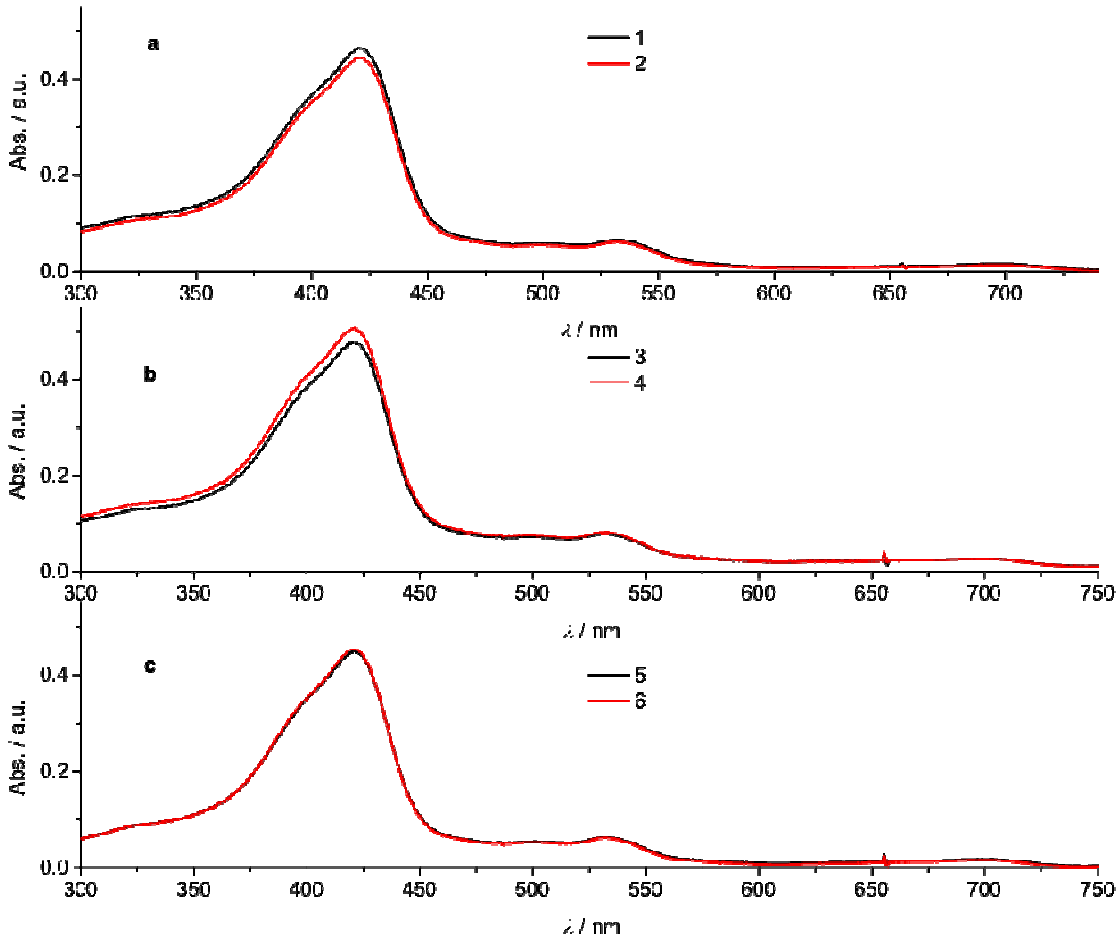

Fig. S10 UV/vis spectra of [Fe^{III}(Porph)Cl] in DMSO (5 x 10^{-6} M) and PF_6-salts (2 mM) in tandem cuvette; 1: KPF_6 before mixing; 2: KPF_6 after mixing; 3: NH_4PF_6 before mixing; 4: NH_4PF_6 after mixing; 5: Bu_4NPF_6 before mixing; 6: Bu_4NPF_6 after mixing.

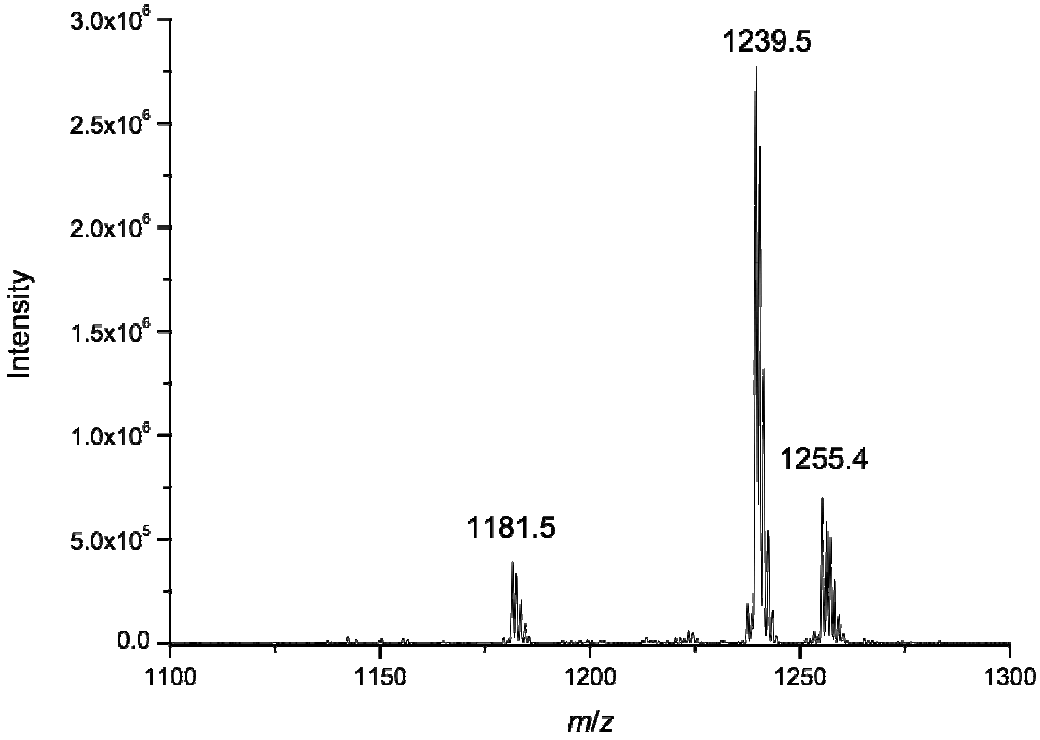

Fig. S11 ESI mass of [Fe^{III}(Porph)Cl] in DMSO with an excess of KPF_6.

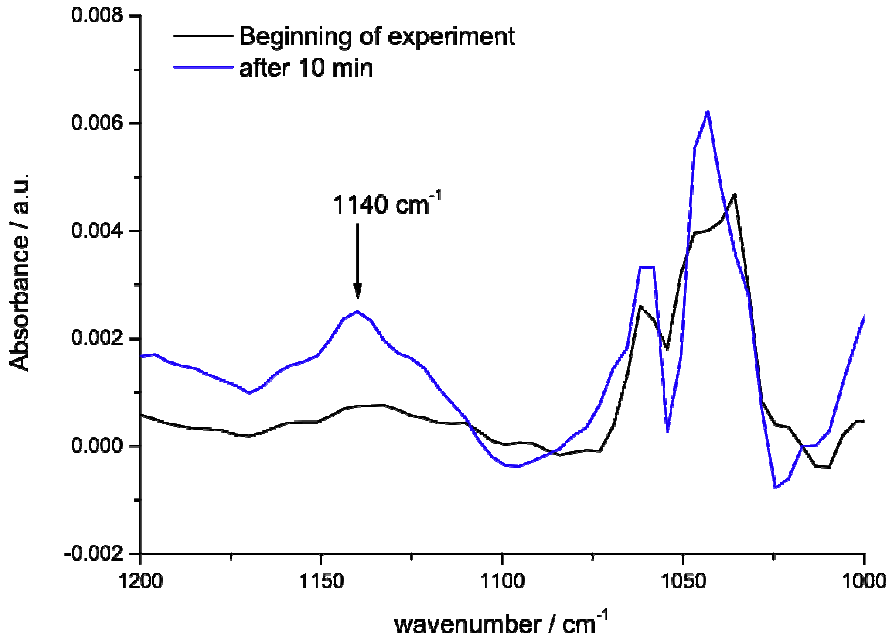

Fig. S12 ReactIR spectra of KO_2 in DMSO. Starting spectra was taken as background.

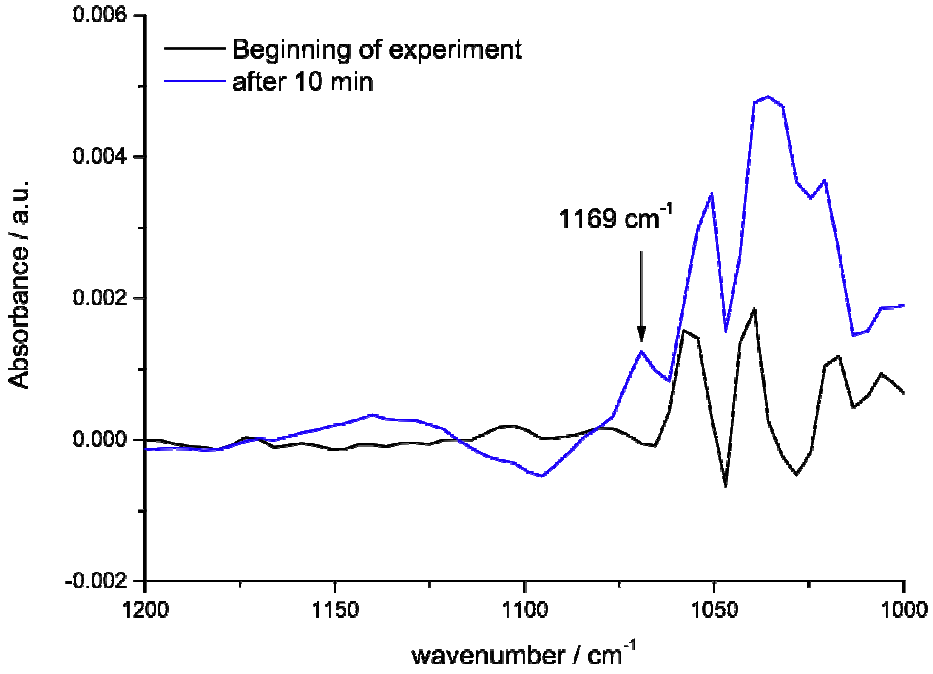

Fig. S13 ReactIR spectra of $K^{18}O_2$ (some traces of $K^{16}O_2$ are present in the sample of $K^{18}O_2$) in DMSO. Starting spectra (not shown) was taken as background.

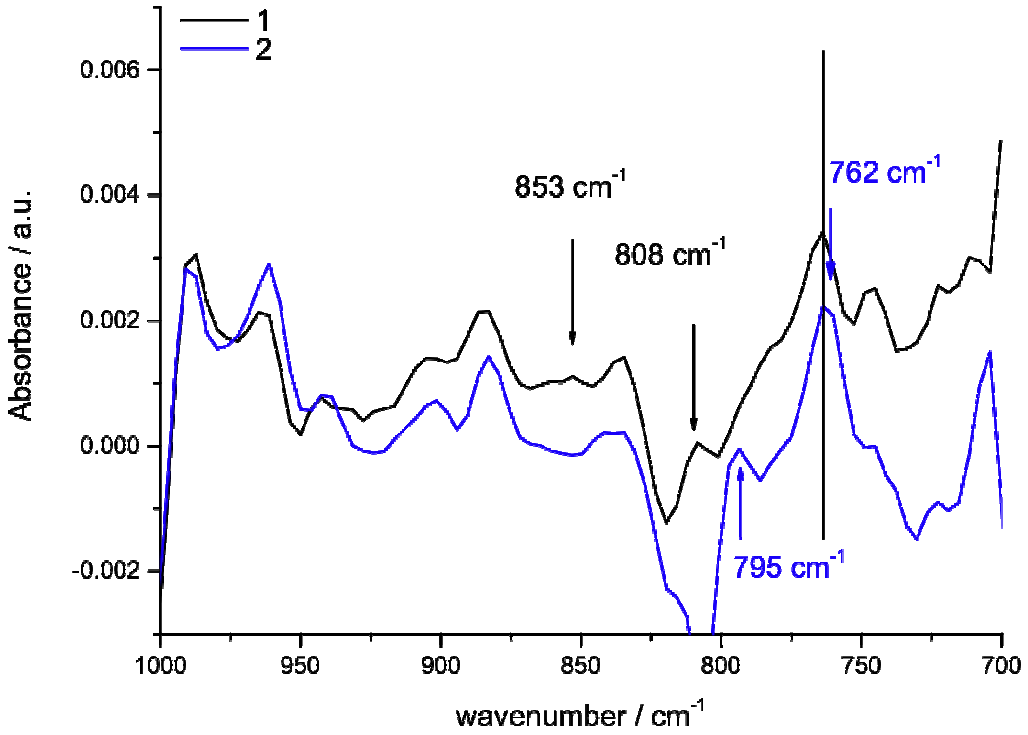

Fig. S14 ReactIR spectra of [Fe^{III}(Porph)Cl] with 1) KO_2, 2) $K^{18}O_2$, in DMSO. The spectrum of the complex in DMSO before respective addition of superoxide (not shown) was taken as background.

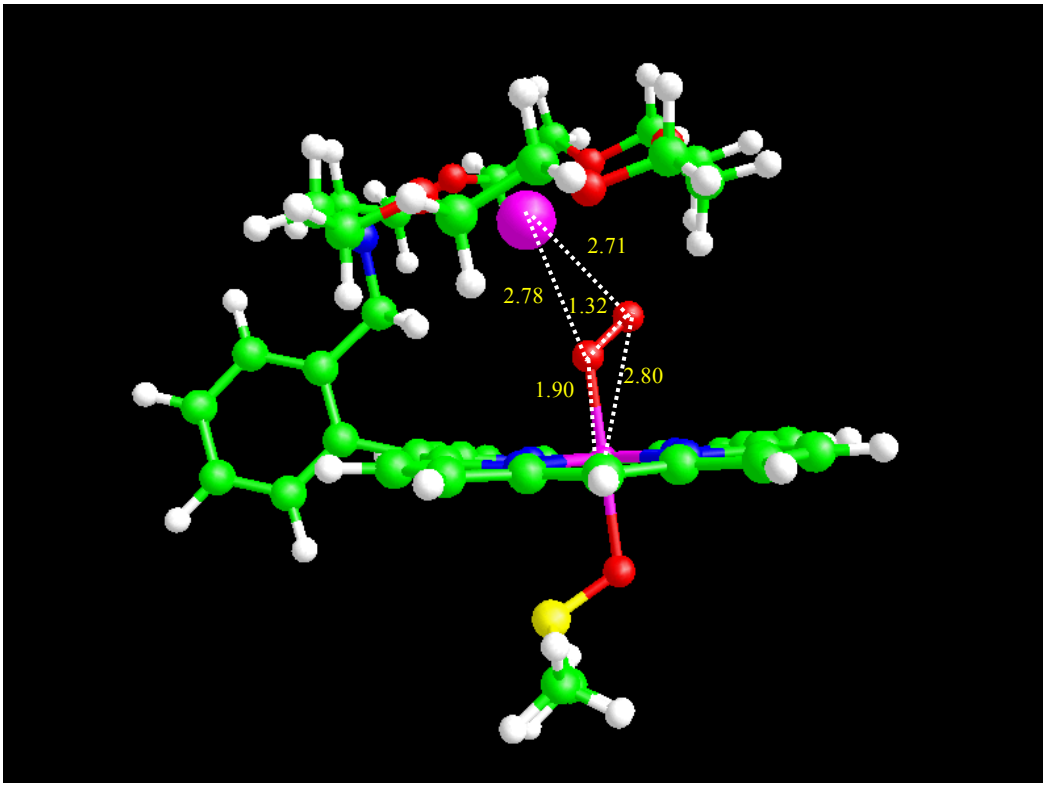

Fig. S14 Lowest energy structure of the optimized end-on doublet complex {$KFe^{II}(por) + O_2^-$} with DMSO.

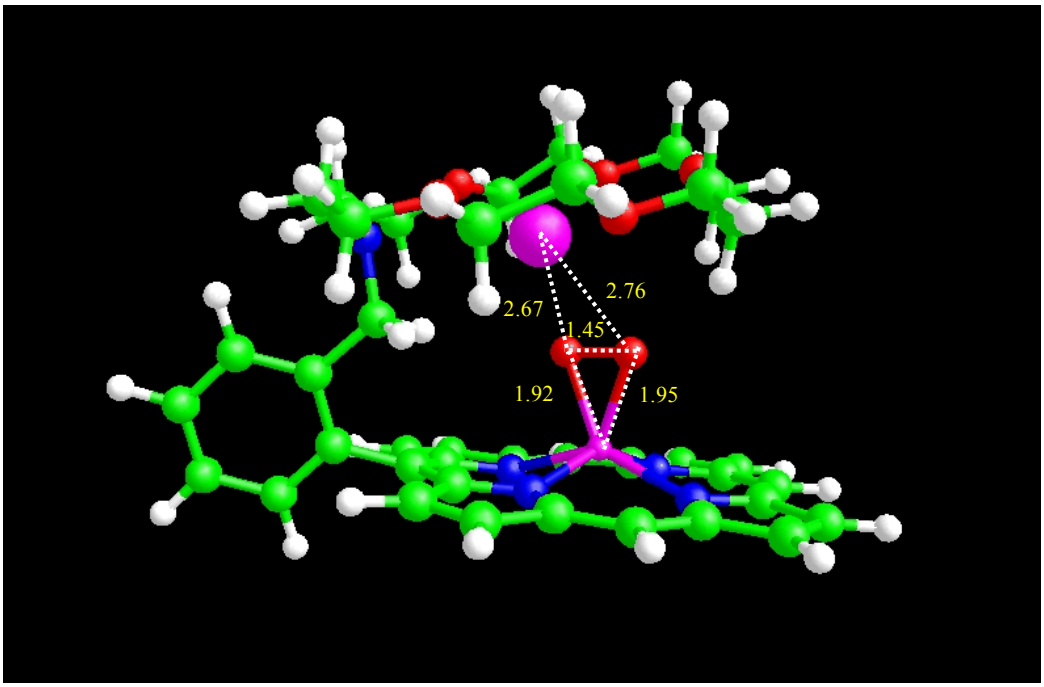

Fig. S15 Lowest energy structure of the optimized side-on sextet complex {$KFe^{II}(por) + O_2^-$} without DMSO.

Supporting Tables.

Table S1 Cartesian coordinates and total energies of the optimized structure of end-on DMSO bound {KFe^{II}(por)(DMSO) + O_2^-} (Calculated at the B3PW91/BSI level).

Total energy: -3014.98592197483 Hartree

C1	-3.8195817885	-2.0419491313	0.8041839848
C2	4.9878773915	2.3383059643	0.1320909612
C3	5.5022099215	1.2685175920	-0.5240612647
C4	4.3844769968	0.5981190145	-1.1520667945
C5	4.5064143542	-0.5236101683	-1.9577898929
C6	3.4602683057	-1.1338320401	-2.6358545574
C7	3.6216341132	-2.2451571205	-3.5454111216
C8	2.3889353848	-2.5132033440	-4.0491844025
C9	1.4824468860	-1.5702101086	-3.4339140470
C10	-2.2105989840	-0.7167241969	-3.2745585262
C11	0.1182844722	-1.5266974653	-3.6827559578
C12	-4.1190901218	-1.3308783512	2.1117815066
C13	-2.7567518985	0.2131968016	-2.4414305147
C14	-1.6563871382	0.8563371800	-1.7636526545
C15	-1.8041855510	1.8735900095	-0.8124241029
C16	-0.7261779798	2.5572286488	-0.2416751575
C17	-2.0387567869	0.5977105177	4.6059277158
C18	-0.8693342255	3.6858775375	0.6516464293
C19	0.3896129990	4.0894313585	0.9690100660
C20	1.2920848709	3.1910880339	0.2940525764
C21	-3.1760610254	2.1616088314	-0.2847077379
C22	-4.0365536116	3.0493247804	-0.9349113393
C23	-1.2912274496	-4.5748353453	-0.0073917553
C24	-3.6038693237	1.5302517126	0.9080282285
C25	-4.8727556437	1.8275017052	1.4112958226
C26	-5.7216793268	2.7158040346	0.7504827156
C27	-5.3057635861	3.3266648418	-0.4276669245

C28	0.1002897863	0.0344344258	5.3869409683
C29	1.0572597683	-1.1206918874	5.5714499529
C30	2.5518008470	-2.4989482040	4.3747956467
C31	2.9622170069	-2.8850685380	2.9728135126
C32	2.1758776453	-3.9355965402	1.0203376177
C33	1.0159534260	-4.7354857330	0.4753191381
C34	-2.3796929402	-3.5566704741	-0.2593717644
C35	-2.6244237993	0.5755597984	1.5821444591
C36	-3.2833159811	0.0497230368	3.9255403857
C37	-0.7856211054	-0.6594749005	-3.0777577899
C38	2.6715953230	3.2240236822	0.4443586569
C39	3.5591286544	2.3042056006	-0.0918048158
H40	-4.7017606770	-2.6518405722	0.5441384080
H41	-2.1071218727	0.0414649379	0.7770036404
H42	-3.6225749061	-0.8140756467	4.5109902454
H43	-4.0676873873	0.8227271212	4.0236385195
H44	5.5035295419	-0.9337026756	-2.0998327824
H45	5.5061980389	3.0888799385	0.7178820210
H46	6.5359364283	0.9523723151	-0.5986942329
H47	4.5642203479	-2.7320213959	-3.7677863138
H48	2.1020913280	-3.2697013527	-4.7707762514
H49	-2.7183556216	-1.3887344887	-3.9575530232
H50	-3.8007695873	0.4681079506	-2.3129401837
H51	-3.6693927231	-1.3266075291	-0.0185834804
H52	-1.6417741775	1.4813795261	4.0813327551
H53	-2.3270570190	0.9309507779	5.6176747717
H54	-1.8119139230	4.1209363443	0.9595459923
H55	0.6929221550	4.9125487191	1.6063676963
H56	-5.2139507512	1.3639802570	2.3321081608
H57	-6.7062323848	2.9283233357	1.1612774351
H58	-5.9613907123	4.0210517726	-0.9479753234
H59	-3.6952881303	3.5299103175	-1.8487853875
H60	3.0846856947	4.0145892198	1.0669960432
H61	-0.2851307756	-2.2533128826	-4.3847287069

H62	-5.1022852486	-0.8427894825	1.9845476208
H63	-0.1786122344	0.4240281951	6.3807665654
H64	0.5997138537	0.8437029388	4.8307997740
H65	1.9050845381	-0.7737141898	6.1864014518
H66	0.5593206261	-1.9415074905	6.1147966474
H67	2.2297574728	-3.3936779079	4.9330827089
H68	3.4197409550	-2.0637478699	4.8974787340
H69	3.1704060185	-1.9839675450	2.3804792217
H70	3.8823099782	-3.4922752342	3.0302760379
H71	3.0939966516	-4.5407995978	0.9305140711
H72	2.3053822897	-3.0073912540	0.4467435625
H73	-4.2416489404	-2.0940555748	2.8913165554
H74	1.2698607237	-5.0985396912	-0.5337397532
H75	0.8283953036	-5.6100204067	1.1205369130
H76	-1.6202716551	-5.3072055580	0.7494318641
H77	-1.1044519940	-5.1198552751	-0.9479292020
H78	-2.0564091793	-2.8415844284	-1.0300978137
H79	-3.2722684304	-4.0865126091	-0.6337369255
H80	-1.8344242690	1.1739962088	2.0512243527
K81	-0.2671278933	-1.6906418833	2.0922472828
N82	-3.0761510789	-0.4129260075	2.5586145953
N83	-0.4617956879	0.3196035664	-2.1741844788
N84	0.5991366528	2.2772095747	-0.4521337618
N85	3.2147557179	1.2394619176	-0.8715233364
N86	2.1528722573	-0.7445766425	-2.5759197082
O87	-2.6850398002	-2.8769358801	0.9465128528
O88	0.9872583334	-0.3963888795	-0.0271038445
O89	1.9124552088	-0.6368173803	0.8855956412
O90	-1.0483151654	-0.4080382165	4.6911220431
O91	-0.1288027534	-3.9089571080	0.4221659598
O92	1.5015489111	-1.5541447012	4.3088679769
O93	1.9163349296	-3.6341268627	2.3824555367
Fe94	1.3847201416	0.7448945676	-1.4889752459
O95	1.8050927505	2.0129079225	-3.1290871700

S96	0.6427905047	2.8487033969	-3.6653545605
C97	1.4272453997	4.4058395298	-4.1698843473
C98	0.3062855878	2.2043997526	-5.3291806505
H99	-0.4384977267	2.8340409301	-5.8272374670
H100	0.7033568752	5.0355129495	-4.6970988784
H101	2.2947981797	4.1905367426	-4.8007512904
H102	1.7537180569	4.9020454595	-3.2526123585
H103	1.2372270285	2.1644268548	-5.9027235774
H104	-0.0877376153	1.1945923868	-5.1910956858

Table S2 Cartesian coordinates and total energies of the optimized structure of side-on {KFe^{II}(por) + O_2^-} (Calculated at the B3PW91/BSI level).

Total energy: -2461.91329013658 Hartree

C1	-4.0606177502	-2.4275016207	0.9817094101
C2	-5.3356053651	3.5142647334	-0.4540347050
C3	-5.8125760018	2.6401993195	0.5168684420
C4	-5.0057115955	1.5969070088	0.9718391375
C5	-3.7145072972	1.4069032157	0.4732703473
C6	-2.7938230754	0.2791009927	0.9312196947
C7	-3.0353735613	0.3276744003	3.3935750817
C8	-4.0499178392	3.3381205479	-0.9635615364
C9	-3.2313362855	2.2981960210	-0.5152278788
C10	1.1281468384	3.8221335745	-0.1233428477
C11	0.1605404594	4.6667190515	0.5393217201
C12	-4.1046616134	-1.4686573225	2.1580047463
C13	0.8083487696	-4.9561560085	0.1426358764
C14	-0.6463753266	-0.4152922887	-3.2462013023
C15	2.5102886367	3.9708871786	-0.0108703925
C16	3.4852264919	3.1299502774	-0.5444665749
C17	4.9079627080	3.3529233932	-0.4402621938
C18	5.5135549422	2.3401559929	-1.1196901927
C19	4.4597716686	1.5036246094	-1.6441803045

C20	4.6625361107	0.4023522445	-2.4747293926
C21	3.6697983491	-0.3436472442	-3.1094017928
C22	3.9101409852	-1.4237562828	-4.0418147782
C23	2.0062385560	-4.0659810621	0.3781693666
C24	2.6879821871	-1.8620366886	-4.4505877472
C25	1.7078460461	-1.0514791517	-3.7608178599
C26	-2.0660053809	-0.5940042454	-3.4155816352
C27	0.3267198131	-1.1811269271	-3.8900595785
C28	-2.6769792404	0.3130825097	-2.6003018573
C29	-1.6257796604	1.0609497420	-1.9485489516
C30	-1.0635491677	4.1309525800	0.2833406864
C31	-1.8450104310	2.1233865570	-1.0510386827
C32	-0.8394766012	2.9767808661	-0.5664209204
C33	-1.6948703263	0.9717055582	3.7095746371
C34	3.0316609371	-2.7135220534	2.0105487651
C35	2.8422568043	-2.1807703417	3.4129899265
C36	1.5078893348	-0.5966254299	4.5903364011
C37	-1.5463134739	-4.9254701741	0.0512652745
C38	-2.7278077135	-4.0021563487	-0.1402345660
C39	0.5350168478	0.5204560527	4.2842127469
H40	5.6943599060	0.1327009532	-2.6873997763
H41	-3.7377820323	0.4964137280	-2.4831633959
H42	-1.3647352509	1.6419084585	2.9009781220
H43	-1.8237452404	1.5946763214	4.6115819731
H44	-2.0292437593	4.4875917513	0.6169484676
H45	0.3966447298	5.5442723534	1.1303703337
H46	2.9234873965	-4.6584590771	0.2191015494
H47	3.9884331732	-3.2608005916	1.9587333145
H48	3.0518889863	-1.8777677801	1.2951920519
H49	3.7408244721	-1.6106172708	3.7013787096
H50	2.7187488726	-3.0120826701	4.1272268296
H51	0.9261713445	-5.4853706808	-0.8172380620
H52	1.1212228410	-1.2344971161	5.4027999520
H53	2.4553628526	-0.1469817450	4.9310670726

H54	0.9244620309	1.1188716597	3.4471464412
H55	0.4443263313	1.1696298856	5.1721814135
H56	-2.7236542603	-0.4532219482	0.1182705034
H57	-1.7786870902	0.6912988973	0.9931118476
H58	0.7448871324	-5.7094068344	0.9447664542
H59	-3.6375214948	-4.6192007148	-0.2312309582
H60	-2.6113717451	-3.4251878184	-1.0711884557
H61	-1.5112460624	-5.6263939235	-0.8001659174
H62	-3.7941999650	1.1306587166	3.4028711260
H63	-5.3938845476	0.9302718462	1.7354157460
H64	-6.8128151698	2.7661576567	0.9253321159
H65	-5.9582024226	4.3291465192	-0.8157083548
H66	-3.6647708874	4.0122848268	-1.7249727456
H67	2.8641246946	4.8265610614	0.5596223983
H68	-0.0328752038	-1.9548655746	-4.5648050121
H69	-1.6770791636	-5.5183049307	0.9720332250
H70	-3.9886012600	-2.0601084644	3.0760563270
H71	-5.1309686355	-1.0562637291	2.1836369443
H72	-4.2138721236	-1.8991419277	0.0274044827
H73	-3.2789527629	-0.3504573926	4.2210185663
H74	-4.8972344751	-3.1381294775	1.0918713885
H75	2.0040653447	-3.2284861728	-0.3346044459
H76	5.3715308086	4.1880494639	0.0718808267
H77	6.5735982524	2.1786138578	-1.2774463999
H78	4.8873476947	-1.7801102967	-4.3467924082
H79	2.4607745543	-2.6502006766	-5.1592757207
H80	-2.5294659591	-1.3069346524	-4.0882210452
K81	-0.2754326947	-1.6956447038	1.5139332620
N82	-0.4088876481	0.5970706744	-2.3589153937
N83	0.4943119401	2.8300468743	-0.8074386500
N84	3.2425343489	1.9946711425	-1.2639503535
N85	2.3316766454	-0.1415918397	-2.9622148687
N86	-3.0544484706	-0.4569420457	2.1645516999
O87	1.9522445234	-3.5847208559	1.7077911364

O88	-0.3642891862	-4.1636261912	0.1201325155
O89	1.5700165535	-0.6686976843	-0.2403746425
O90	-0.7254633577	-0.0304977593	3.9490492454
O91	0.9353503482	0.4235407827	0.4667806120
O92	-2.8313676981	-3.1281693048	0.9672942119
O93	1.7078681581	-1.3434346896	3.4144858136
Fe94	1.4090125610	0.9354597965	-1.3279132316

Table S3 Cartesian coordinates and total energies of the optimized structure of free DMSO (Calculated at the B3PW91/BSI level).

Total energy: -553.07635583763

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