

Supporting Information for

Gas-Phase Ion Chemistry of Metalloporphyrin Anions with Molecular Oxygen:
Probing the Influence of the Oxidation and Spin State of the Central Transition
Metal by Experiment and Theory

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S1. Schematic of T-Variable ICR Cell

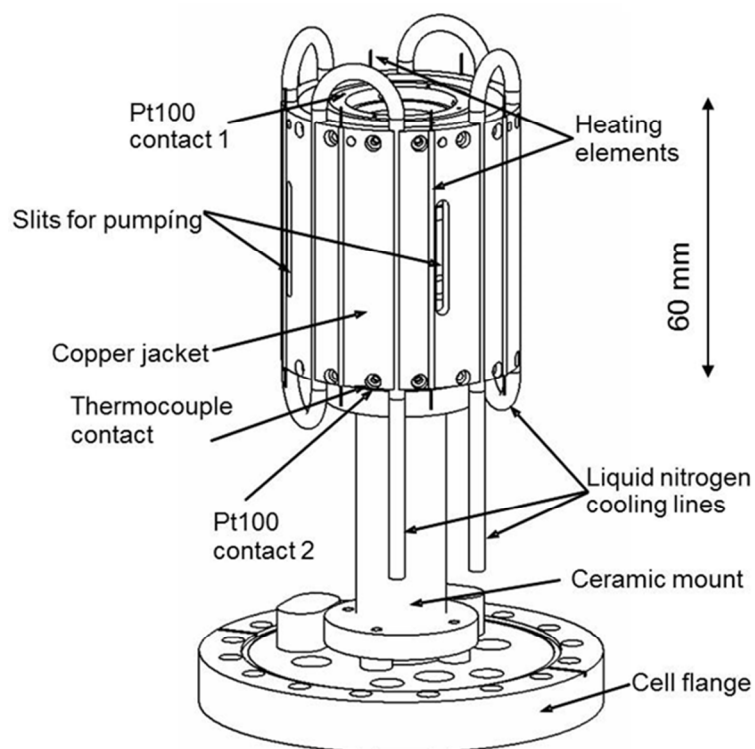


Figure S1: Modified cryo ICR cell capable of being operated over a temperature range of $T=90\text{-}420\text{K}$ by means of liquid nitrogen cooling and coax heating wires (see text for details).

S2. Low temperature hexapole ion trap formation of $[\text{FeTPPS}\cdot\text{O}_2]^{3-}$

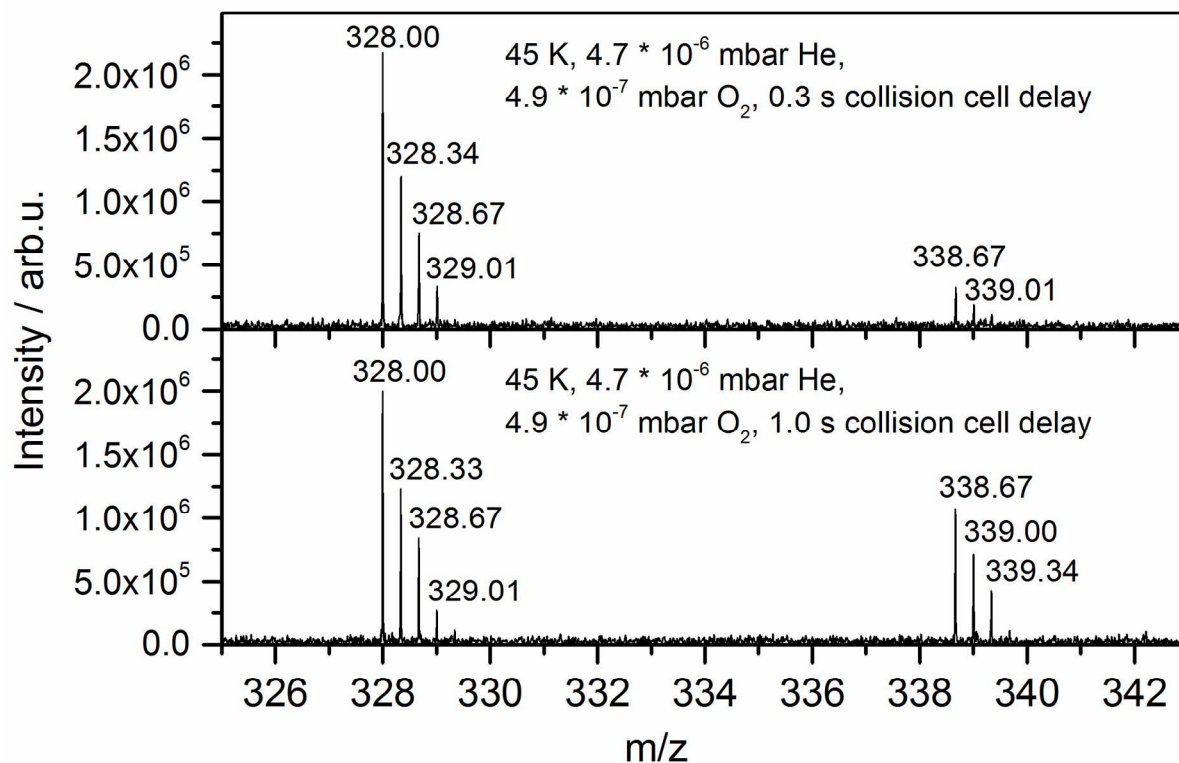


Figure S2: Preliminary measurement series documenting the low temperature reaction of $[\text{FeTPPS}]^{3-}$ with O_2 to form $[\text{FeTPPS}\cdot\text{O}_2]^{3-}$. The reactant ion is injected into a cryogenic hexapole ion trap and held there for a fixed reaction time. Note that the observed mass to charge differences of 10.67 amu per 3 e^- of the triply charge anions corresponds a total mass increase of 32.01 amu.

S3. DFT Geometries

Table S1: Selected geometric parameters of the structures optimized at BP86 level with conductor like screening model (COSMO) Bond lengths in Å, dihedrals in degrees.

		Without O ₂	With O ₂
[Fe ^{II} TPPS] ⁴⁻	Fe-N	1.98	1.98
	Fe-O	-	1.83
	C-C-C-C ^a	15.5	22.3
	N-N-N-N	0.5	0.4
	Fe-N-N-N ^b	0.2	9.2
[Fe ^{III} TPPS] ³⁻	Fe-N	1.95	1.97
	Fe-O	-	1.92
	C-C-C-C ^a	28.5	26.4
	N-N-N-N	2.0	0.3
	Fe-N-N-N ^b	0.1	10.0
[Mn ^{II} TPPS] ⁴⁻	Mn-N	2.00	2.01
	Mn-O	-	1.86
	C-C-C-C ^a	14.1	20.5
	N-N-N-N	0.3	1.4
	Mn-N-N-N ^b	0.4	9.1
[Mn ^{III} TPPS] ³⁻	Mn-N	1.98	1.99
	Mn-O	-	2.04
	C-C-C-C ^a	22.1	23.9
	N-N-N-N	0.5	0.7
	Mn-N-N-N ^b	0.1	7.8

^a Dihedral angle between the four carbons coordinated with the sulphonatophenyl anions.

^b Averaged between the four possible M^{II/III}-N-N-N dihedral angles.

S4. Comparison between Complete 4-sulfonatophenyl and Hydrogen Substituted Models

Table S2: Ground state occupation numbers of full $[\text{Fe}(\text{TPPS})]^{4-}$ system and the $[\text{Fe}(\text{P})]^0$ model system from CASSCF(8,11).

	$\sigma(\text{Fe-N})$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	$3d_z^2$	$\sigma^*(\text{Fe-N})$	$4d_{x^2-y^2}$	$4d_{xy}$	$4d_{xz}$	$4d_{yz}$	$4d_z^2$
$[\text{Fe}(\text{TPPS})]^{4-}$	1.98	1.97	0.99	0.99	1.96	0.04	0.00	0.02	0.01	0.01	0.03
$[\text{Fe}(\text{P})]^0$	1.98	1.97	0.99	0.99	1.96	0.04	0.00	0.02	0.01	0.01	0.03
Model System											

Table S3: Ground state occupation numbers of full $[\text{Fe}(\text{TPPS})]^{3-}$ system and the $[\text{Fe}(\text{P})]^{1+}$ model system from CASSCF(9,13). The holes on the electronic structure after the electron detachment are shown with bold font.

	$\sigma(\text{Fe-N})$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	$3d_z^2$	$\sigma^*(\text{Fe-N})$	$\pi(\text{por})$
$[\text{Fe}(\text{TPPS})]^{3-}$	1.95	1.97	1.00	1.00	0.99	0.07	1.93
	$\sigma(\text{Fe-N})$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	$3d_z^2$	$\sigma^*(\text{Fe-N})$	$\pi(\text{por})$
$[\text{Fe}(\text{P})]^{1+}$ Model System	1.98	1.97	0.99	0.99	1.96	0.04	1.00

	$4d_{xy}$	$4d_{xz}$	$4d_{yz}$	$4d_z^2$	$4d_{x^2-y^2}$	$\pi^*(\text{por})$
$[\text{Fe}(\text{TPPS})]^{3-}$	0.02	0.00	0.01	0.01	0.06	0.01
	$4d_{xy}$	$5d_{xy}$	$4d_{xz}$	$4d_{yz}$	$4d_z^2$	$5d_z^2$
$[\text{Fe}(\text{P})]^{1+}$ Model System	0.02	0.00	0.01	0.01	0.03	0.00

S5. Orbitals Included in the Active Space for the $[\text{M}(\text{P})]^{0/1+}$ Complexes

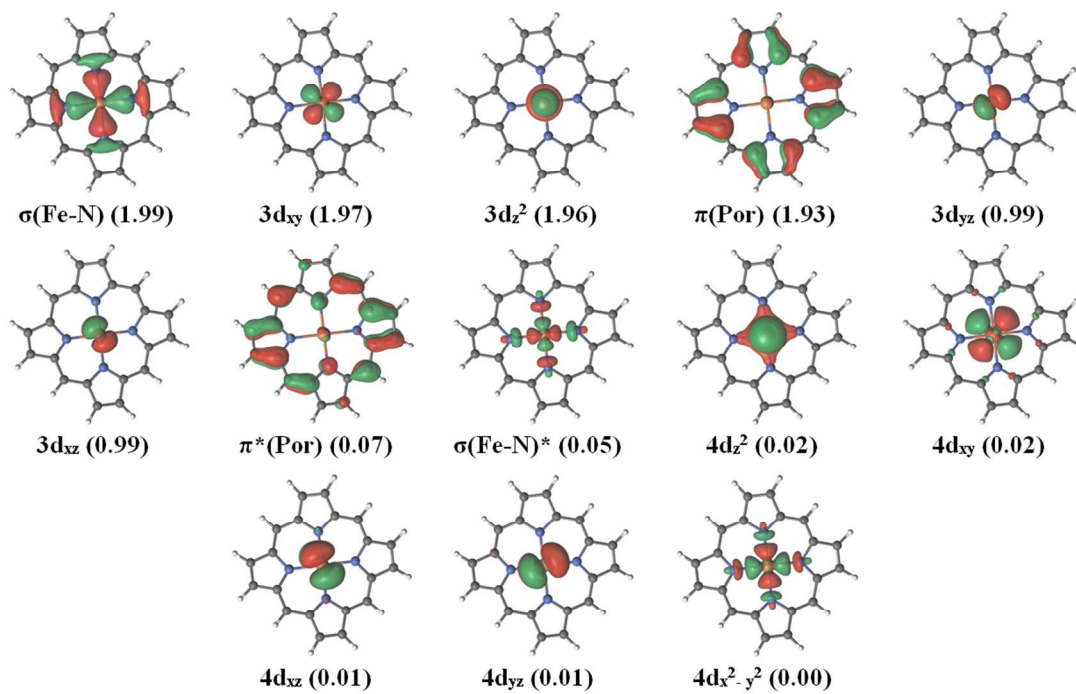


Figure S3: CASSCF(10,13) orbitals for the $[\text{Fe}(\text{P})]^0$ model system.

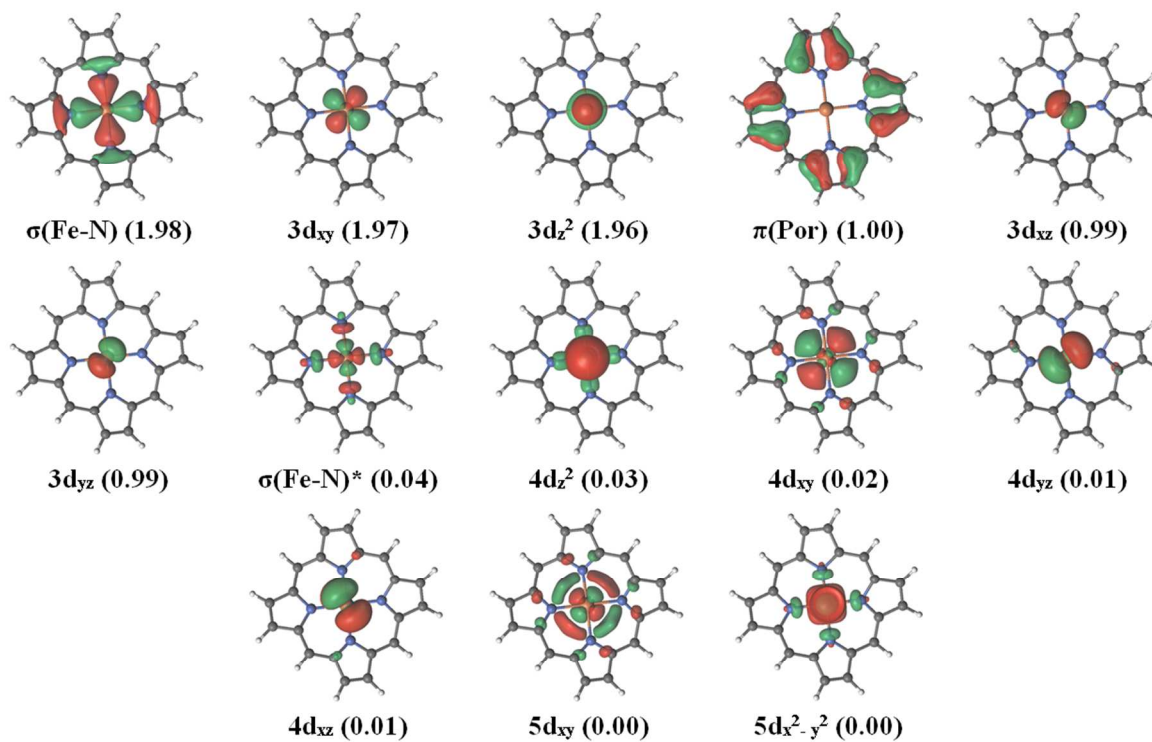


Figure S4: CASSCF(9,13) orbitals for the $[\text{Fe(P)}]^{1+}$ model system.

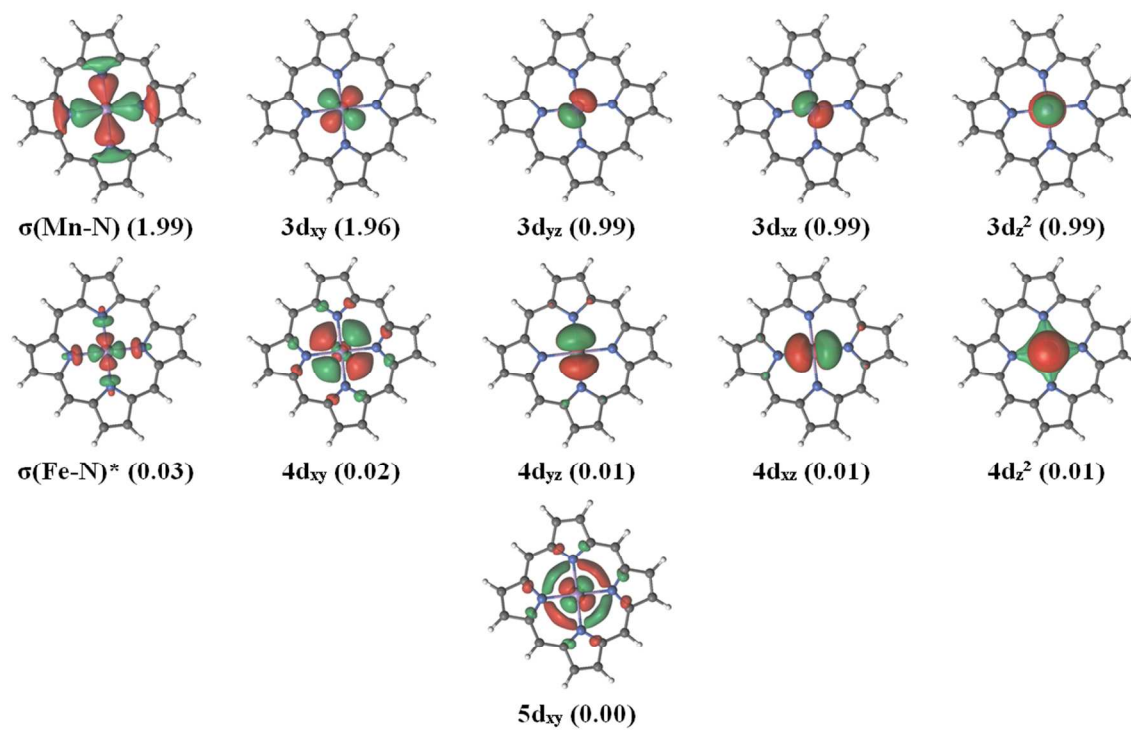


Figure S5: CASSCF(7,11) orbitals for the $[\text{Mn(P)}]^0$ model system.

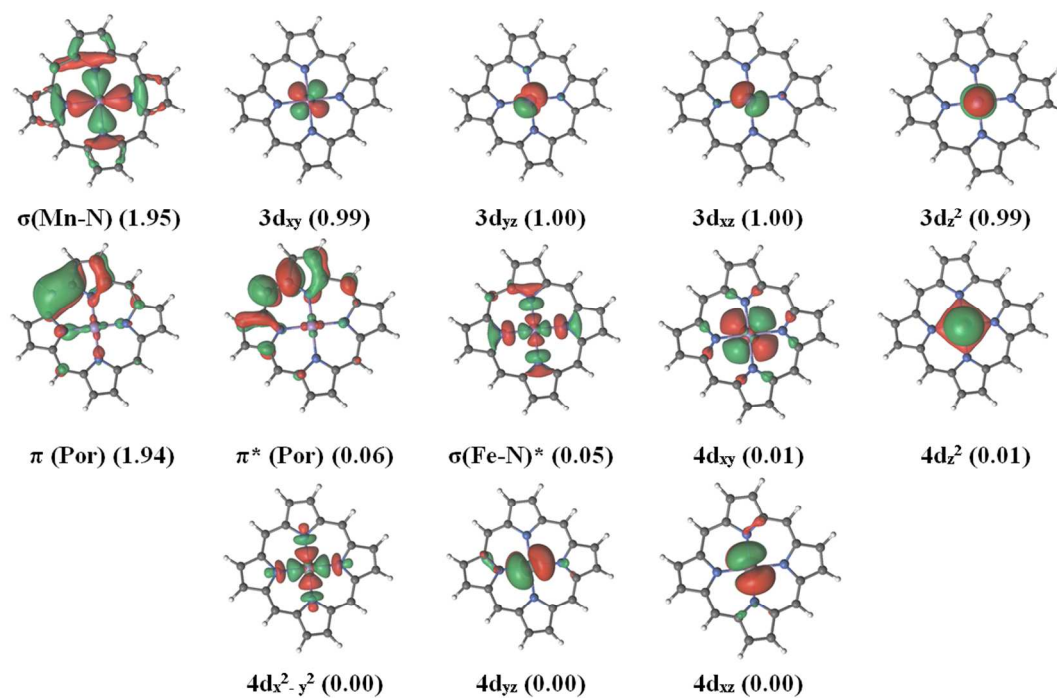


Figure S6: CASSCF(8,13) orbitals for the $[\text{Mn}(\text{P})]^{1+}$ model system.

S6. Relative Energy Differences for $[M(P)]^{0/1+}$ and $[M(P)(O_2)]^{0/1+}$ Complexes

Table S4: Summary of spin states and CASSCF/CASPT2 energies of the $[Fe(P)]^0$ model system.

Active Space	Spin State	CASSCF Energy (a.u.)	CASPT2 Energy (a.u.)
CAS(8,11)	Singlet	-2254.170728	-2258.093223
	Triplet	-2254.224235	-2258.141486
	Quintet	-2254.239426	-2258.147448
CAS(10,13)	Singlet	-2254.178617	-2258.085333
	Triplet	-2254.231979	-2258.133366
	Quintet	-2254.247094	-2258.139105

Table S5: Summary of spin states and CASSCF/CASPT2 energies of the $[Fe(P)]^{1+}$ model system.

Active Space	Spin State	CASSCF Energy (a.u.)	CASPT2 Energy (a.u.)
CAS(9,12)	Quartet	-2253.982852	N/A
CAS(9,13)	Doublet	-2253.999429	-2257.859424
	Quartet	-2254.006373	-2257.857949
	Sextet	-2254.007410	-2257.857938
CAS(11,15)	Quartet	-2253.887222	N/A
	Sextet	-2253.765855	N/A

Table S6: Summary of spin states and CASSCF/CASPT2 energies of the $[Mn(P)]^0$ model system.

Active Space	Spin state	CASSCF Energy (a.u.)	CASPT2 Energy (a.u.)
CAS(7,11)	Doublet	-2140.134113	-2144.036157
	Quartet	-2140.19537726	-2144.091301
	Sextet	-2140.22910113	-2144.113423

Table S7: Summary of spin states and CASSCF/CASPT2 energies of the $[Mn(P)]^{1+}$ model system.

Active Space	Spin State	CASSCF Energy (a.u.)	CASPT2 Energy (a.u.)
CAS(8,13)	Singlet	-2139.914555	-2143.751850
	Triplet	-2139.976758	-2143.818061
	Quintet	-2140.035344	-2143.904389
	Septet	-2139.880378	N/A

Table S8: Summary of spin states and CASSCF/CASPT2 energies of the $[Fe(P)(O_2)]^0$ model system.

Active Space	Spin State	CASSCF Energy (a.u.)	CASPT2 (a.u.)
CAS(14,14)	Triplet	-2403.934353	N/A
	Quintet	-2404.008101	N/A
	Septet	-2404.005074	N/A
CAS(14,15)	Septet	-2403.870744	N/A

Table S9: Summary of spin states and CASSCF/CASPT2 energies of the $[\text{Fe}(\text{P})(\text{O}_2)]^{1+}$ model system.

Active Space	Spin State	CASSCF Energy (a.u.)	CASPT2 Energy (a.u.)
CAS(11,15)	Doublet	-2403.721986	-2408.086583
	Quartet	-2403.765886	-2408.085870
	Sextet	-2403.716792	N/A

Table S10: Summary of spin states and CASSCF/CASPT2 energies of the $[\text{Mn}(\text{P})(\text{O}_2)]^0$ model system.

Active Space	Spin State	CASSCF Energy (a.u.)	CASPT2 Energy (a.u.)
CAS(13,14)	Quartet	-2290.003514	N/A
	Sextet	-2289.888773	-2294.174673
CAS(13,15)	Sextet	-2289.902767	N/A

Table S11: Summary of spin states and CASSCF/CASPT2 energies of the $[\text{Mn}(\text{P})(\text{O}_2)]^{1+}$ model system.

Active Space	Spin State	CASSCF Energy (a.u.)	CASPT2 Energy (a.u.)
CAS(10,15)	Triplet	-2289.639237	N/A
	Quintet	-2289.665834	N/A
	Septet	-2289.704963	N/A

S7. B3LYP Spin Densities for the $[M\text{-TPPS}]^{3-}$ Species

Figure S7 a. $[\text{Fe-TPPS}]^{3-}$, $S = 3/2$

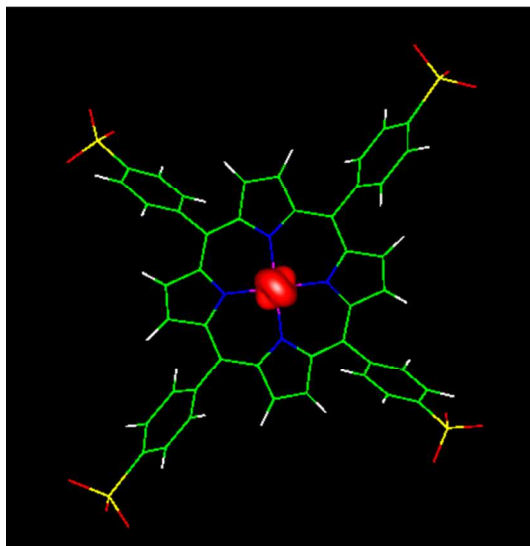
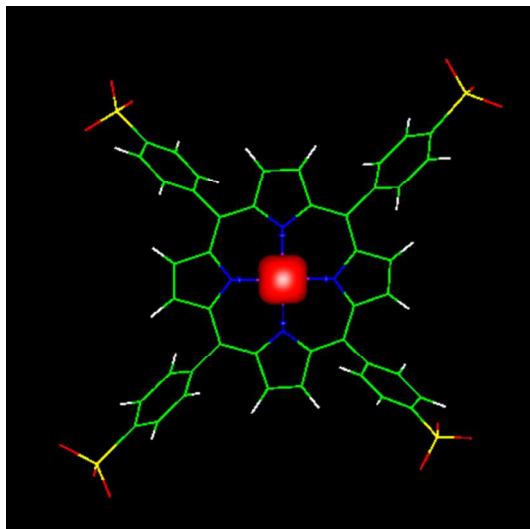


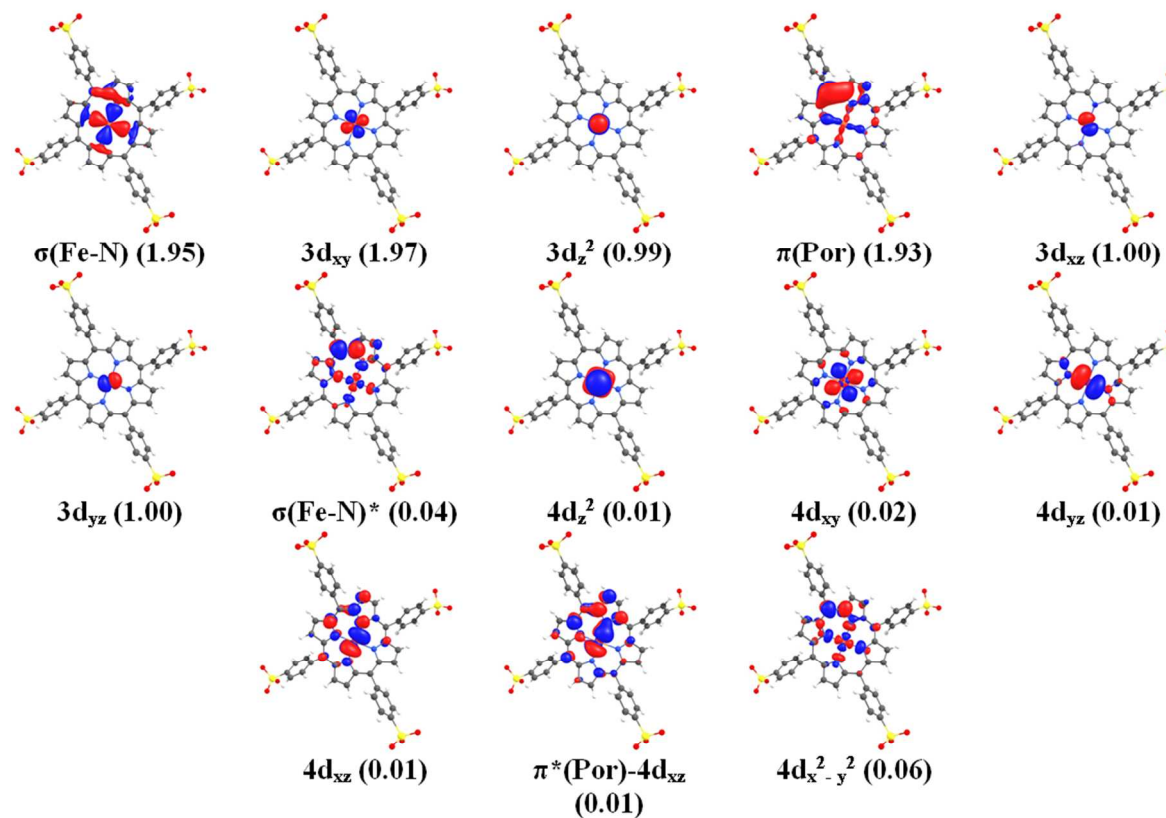
Figure S7 b. $[\text{Mn-TPPS}]^{3-}$, $S = 2$



S8. Orbitals Included in the Active Space for $[\text{Fe-TPPS}]^{3-}$

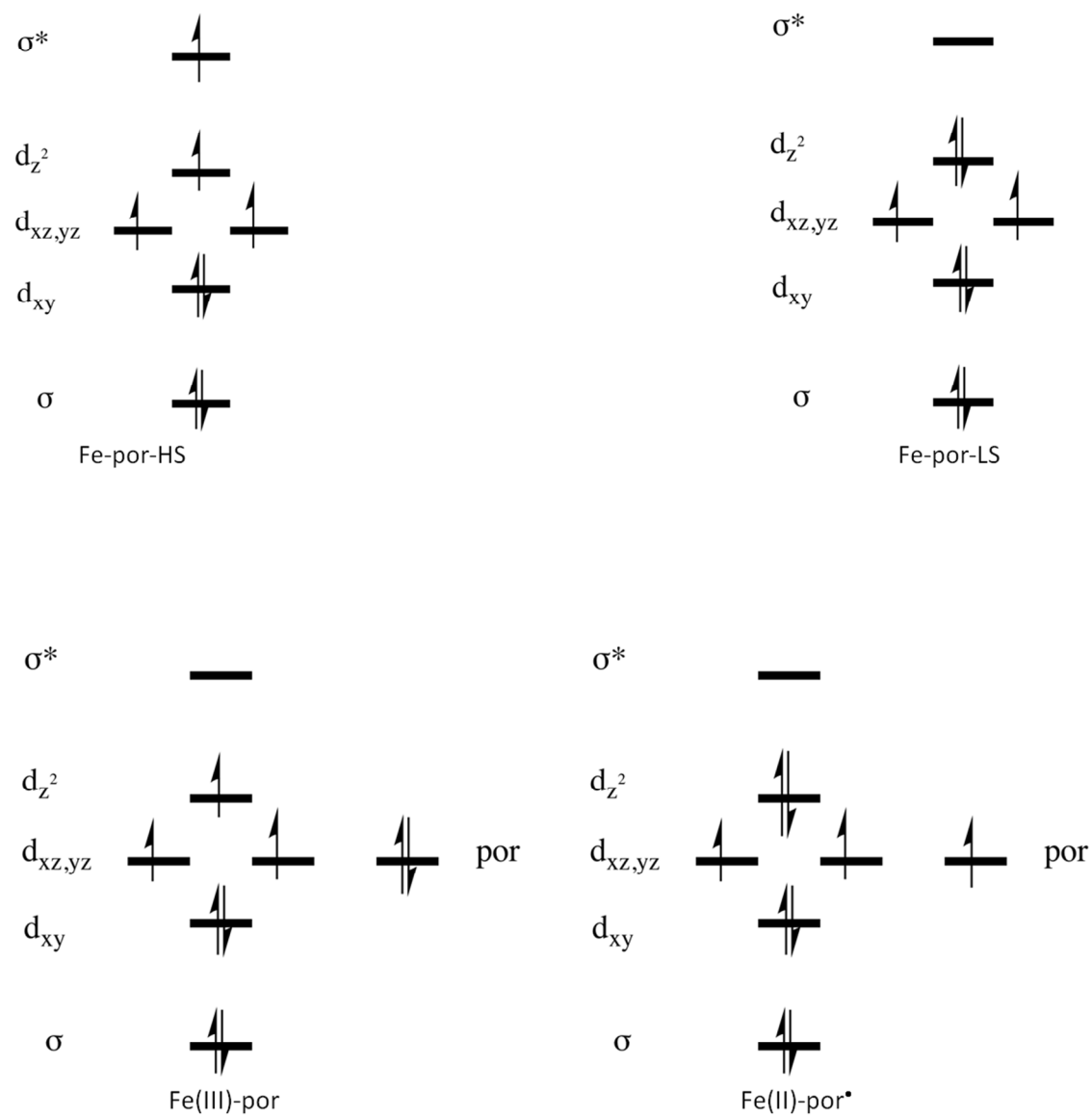
Figure S8

Orbitals Included in the Active Space for $[\text{Fe-TPPS}]^{3-}$



S9. Molecular Orbital Diagrams for $[\text{Fe(P)}]^0$ Complexes

Figure S9 Molecular Orbital Diagrams for $[\text{Fe(P)}]^0$ Complexes



S10. Molecular Orbital Diagrams for $[\text{Fe}(\text{P})(\text{O}_2)]^0$ and $[\text{Mn}(\text{P})(\text{O}_2)]^0$ Complexes

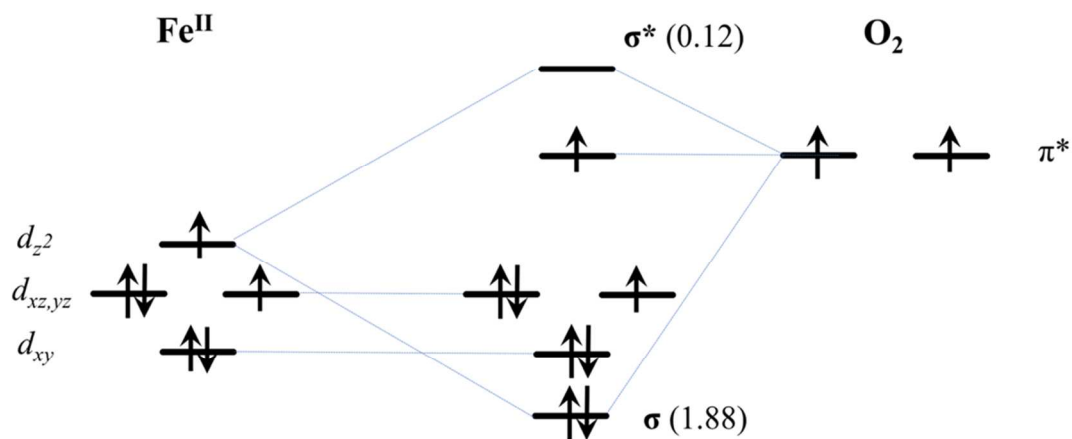


Figure S10: Molecular orbital diagram of $[\text{Fe}(\text{P})(\text{O}_2)]^0$ obtained from CASSCF(14,14).

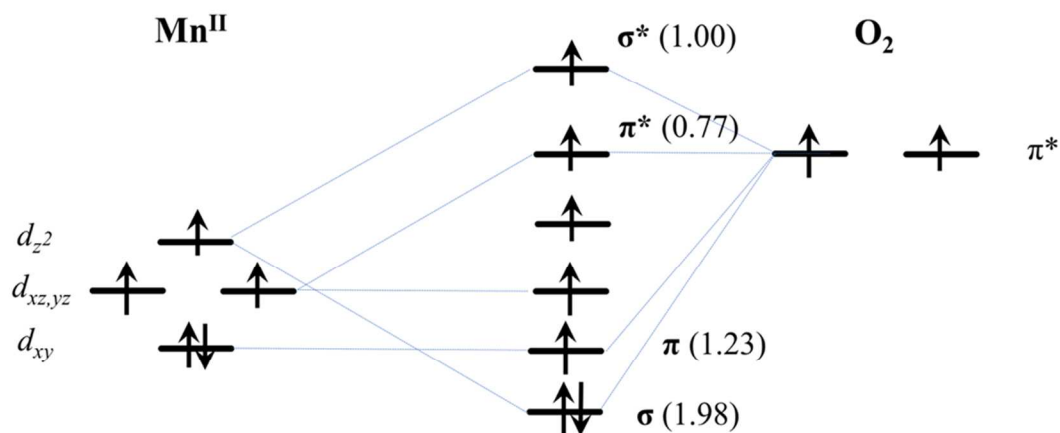


Figure S11: Molecular orbital diagram of $[\text{Mn}(\text{P})(\text{O}_2)]^0$ obtained from CASSCF(13,14).

S11. Total energies, relative stabilities Δ of the 4-/3- complexes, and binding energies (BE)

Table S12:

Total energies (in Hartree)

Relative stabilities Δ of the 4-/3- complexes (B3LYP and BP, both without conductor like screening model, in eV)

Binding energies (BE, in kJ/mol)

	Mn	Mn-O ₂	BE kJ/mol	Fe	Fe-O ₂	BE kJ/mol
Spin	4-:S=3/2 3-:S=2	4-:S=3/2 3-:S=1		4-:S=1 3-:S=3/2	4-:S=1 3-:S=1/2	
B3LYP						
4-	-5552.128632	-5702.289317	-41.3	-5664.845000	-5814.985751	+11.0
3-	-5552.172540	-5702.324259	-17.8	-5664.864214	-5815.008401	+2.0
Δ	1.19	0.95		0.52	0.61	
O ₂	-150.1449386					
BP86						
4-	-5554.612040	-5704.866291	-74.3	-5667.347137	-5817.597727	-64.7
3-	-5554.662531	-5704.913030	-64.5	-5667.392826	-5817.644053	-66.0
Δ	1.37	1.27		1.24	1.26	
O ₂	-150.2259376					

S12. M-O and O-O bond distances

Table S13:

All M-O/O-O bond distances in Å

Functional	Mn 4-	Mn 3-	Fe 4-	Fe 3-	O ₂
BP/COSMO	1.86/1.30	1.95/1.25	1.83/1.28	1.92/1.25	1.22
BP	1.88/1.29	1.87/1.28	1.83/1.28	1.78/1.27	1.22
B3LYP	1.97/1.29	2.29/1.22	1.95/1.26	2.08/1.24	1.20

S13. Zero-point energies, enthalpies and entropies calculated with BP86

Table S14:

All frequencies are scaled by a scaling factor of 0.9914, values for 298.15K and for the measurement temperatures.

	ZPE	T	H	S	multiplicity
	kJ mol^{-1}	K	kJ mol^{-1}	$\text{kJ mol}^{-1}\text{K}^{-1}$	
MnII	1527	195	1594.24	1.02427	4
MnIII	1530	130	1563.2	0.83728	5
FeII	1532	130	1564.75	0.82185	3
FeIII	1531	120	1560.5	0.80893	4
MnII-O ₂	1543	195	1614.73	1.08336	4
MnIII-O ₂	1543	130	1578.8	0.87183	3
FeII-O ₂ triplet	1546	130	1581.76	0.88896	3
FeII-O ₂ singlet	1548	130	1582.54	0.83935	1
FeIII-O ₂ doublet	1543	120	1573.73	0.81461	2
FeIII-O ₂ quartet	1543	120	1574.79	0.83948	4
O ₂	9.5	120	12.96	0.1697	3
O ₂	9.5	130	13.25	0.17203	3
O ₂	9.5	195	15.14	0.18383	3

	ΔZPE	T	ΔH	ΔS	$\Delta\text{S}_{\text{Spin}}$
	kJ mol^{-1}	K	kJ mol^{-1}	$\text{kJ mol}^{-1}\text{K}^{-1}$	$\text{kJ mol}^{-1}\text{K}^{-1}$
MnII-O ₂	6.5	195	5.35	-0.12474	-0.13387
MnIII-O ₂	3.5	130	2.35	-0.13748	-0.15086
FeII-O ₂ triplet	4.5	130	3.76	-0.10492	-0.11405
FeII-O ₂ singlet	6.5	130	4.54	-0.15453	-0.17279
FeIII-O ₂ doublet	2.5	120	0.27	-0.16402	-0.17891
FeIII-O ₂ quartet	2.5	120	1.33	-0.13915	-0.14828

S14. Vibrational frequencies for O2 bound systems, BP functional

Remaining negative force constants belong to rotations of SO₃- groups

All frequencies are unscaled



mode	wave number cm ^{**} (-1)	IR intensity km/mol
1	-13.70	0.00000
2	0.00	0.00000
3	0.00	0.00000
4	0.00	0.00000
5	0.00	0.00000
6	0.00	0.00000
7	0.00	0.00000
8	5.37	0.00484
9	13.05	0.10881
10	15.58	6.79327
11	16.03	4.72507
12	16.97	0.76658
13	18.33	1.38166
14	19.14	4.99834
15	19.34	4.30920
16	21.32	0.10860
17	28.47	0.20439
18	29.21	0.19225
19	34.77	0.60435
20	36.53	0.02555
21	38.24	0.48289
22	40.69	1.00439
23	60.37	0.12916
24	69.10	0.17773
25	73.73	1.15393
26	78.34	0.16823
27	79.99	4.79520
28	89.25	0.58837
29	90.82	4.65968
30	93.72	2.61777
31	105.94	1.24367
32	109.28	1.05530
33	111.13	0.93828
34	113.65	0.24247
35	120.30	0.21466
36	127.52	1.93281
37	140.39	10.77991
38	149.18	14.33938

39	152.19	7.49820
40	163.03	0.80439
41	166.23	1.19065
42	170.48	0.72228
43	201.11	0.41747
44	209.85	0.04806
45	212.18	0.26033
46	217.38	0.34542
47	225.41	0.67681
48	231.47	0.11857
49	238.19	0.09764
50	244.60	0.68815
51	247.80	0.65036
52	248.77	1.04637
53	256.04	1.65134
54	275.63	0.09572
55	284.22	2.18032
56	289.21	2.23626
57	290.22	0.69857
58	299.87	1.49387
59	304.46	0.13010
60	305.86	0.63475
61	318.01	9.78723
62	319.35	9.30245
63	323.38	0.67999
64	340.08	6.62930
65	347.21	2.43349
66	347.54	0.79258
67	354.82	0.50591
68	356.50	1.01301
69	357.47	0.80420
70	359.32	0.61973
71	369.75	0.06879
72	396.37	0.84300
73	398.79	0.10840
74	399.57	0.65835
75	400.37	4.57184
76	400.61	2.01323
77	402.95	0.32522
78	418.90	17.30308
79	421.18	21.92725
80	435.69	1.07407
81	449.40	3.88463
82	456.55	0.12600
83	458.31	10.16483
84	460.53	14.10281

85	471.37	3.47644
86	486.31	33.64735
87	487.15	30.24590
88	498.37	0.29002
89	500.89	8.88723
90	501.01	24.42819
91	501.27	9.23188
92	501.65	3.54957
93	536.39	15.05925
94	541.50	3.67702
95	542.86	3.51673
96	544.54	0.16266
97	558.33	14.91391
98	562.72	6.86374
99	563.20	2.31150
100	570.01	0.48389
101	585.04	1.49689
102	589.46	425.52923
103	590.34	413.40117
104	591.75	40.86749
105	624.23	0.22518
106	624.87	0.55160
107	625.33	0.05539
108	626.75	0.77942
109	649.03	0.03381
110	659.03	3.35886
111	661.13	2.72356
112	662.36	0.30943
113	684.73	0.08867
114	695.16	136.99330
115	695.56	118.17682
116	708.00	9.32635
117	708.90	22.42337
118	716.62	23.34039
119	717.11	20.16605
120	721.51	16.18744
121	721.61	2.23325
122	731.66	0.63532
123	732.19	0.54593
124	744.26	0.00796
125	780.75	0.11678
126	789.49	11.58788
127	791.58	0.25810
128	792.40	5.48656
129	796.32	16.93502
130	796.80	3.54639

131	798.91	25.56935
132	800.23	34.36626
133	820.14	2.15634
134	824.05	4.67497
135	825.84	3.53636
136	827.63	3.18691
137	836.42	3.97165
138	838.53	1.89619
139	841.08	0.35218
140	851.20	4.05856
141	854.25	0.95377
142	868.20	7.47523
143	869.21	8.61251
144	871.82	0.28892
145	899.85	0.00809
146	900.58	0.14825
147	901.22	1.29444
148	902.02	0.79898
149	935.40	2.05127
150	936.29	0.50515
151	939.57	2.52513
152	942.56	4.89803
153	954.71	4.28964
154	954.98	91.38584
155	955.35	465.66841
156	955.41	531.76348
157	956.61	59.09234
158	958.03	11.33271
159	958.74	3.84502
160	961.96	1.14023
161	994.09	0.24838
162	996.53	1.85651
163	996.62	2.31496
164	998.08	0.08445
165	1002.90	0.13598
166	1003.58	0.84625
167	1007.81	15.35771
168	1010.21	29.16461
169	1017.42	2.24340
170	1018.33	6.46232
171	1020.32	20.08084
172	1026.73	0.30887
173	1043.42	6.04774
174	1044.99	11.22342
175	1045.86	4.19400
176	1051.75	4.23948

177	1062.48	27.11412
178	1062.55	16.12746
179	1062.77	27.60954
180	1063.47	34.10119
181	1064.22	25.53481
182	1067.55	13.64280
183	1068.06	11.91109
184	1068.25	30.14007
185	1135.21	11.89026
186	1136.73	11.59075
187	1137.51	12.20048
188	1138.39	10.13063
189	1161.73	2.50557
190	1168.17	185.55878
191	1170.28	186.52521
192	1170.87	191.76835
193	1171.64	197.63619
194	1176.66	133.12461
195	1177.42	165.74699
196	1177.97	61.79346
197	1178.13	366.18469
198	1189.57	5.86212
199	1192.11	6.36974
200	1207.96	209.68445
201	1220.99	5.84047
202	1222.15	3.63284
203	1230.64	46.90188
204	1235.56	45.02554
205	1247.62	2.64871
206	1249.54	2.10148
207	1250.13	0.57869
208	1250.44	2.86238
209	1255.97	6.30667
210	1288.23	0.61100
211	1297.39	5.80494
212	1303.48	8.12263
213	1322.78	0.05827
214	1327.03	3.52205
215	1328.28	0.47190
216	1331.15	14.00712
217	1332.63	1.33951
218	1348.85	77.88117
219	1354.59	71.42905
220	1358.64	2.88941
221	1361.93	7.86082
222	1380.48	6.10919

223	1380.91	4.27238
224	1381.36	5.00961
225	1381.88	4.59907
226	1446.20	3.23573
227	1447.73	19.88850
228	1450.50	27.72711
229	1458.40	0.96750
230	1466.39	2.63144
231	1467.97	0.51479
232	1471.52	0.01126
233	1482.65	0.82481
234	1496.25	0.07770
235	1511.84	60.78510
236	1522.11	4.34123
237	1527.73	1.55329
238	1534.36	1.43022
239	1537.03	1.37246
240	1552.97	4.78230
241	1554.12	0.78230
242	1559.23	1.16871
243	1559.89	4.04994
244	1560.30	1.69965
245	1566.75	1.50180
246	1589.31	23.06010
247	1589.64	15.33765
248	1590.07	14.73790
249	1590.81	12.57330
250	3087.98	9.56441
251	3089.21	9.03867
252	3090.70	9.30454
253	3091.50	10.19911
254	3093.65	6.09958
255	3093.81	8.61265
256	3094.70	8.86055
257	3101.12	2.29742
258	3113.43	9.12930
259	3114.15	10.02172
260	3115.12	12.06659
261	3115.59	11.71222
262	3116.79	4.85065
263	3117.13	3.09606
264	3117.71	4.70959
265	3118.28	3.44516
266	3177.32	0.06828
267	3177.50	0.11179
268	3177.88	0.12469

269	3177.92	0.06140
270	3194.11	1.03585
271	3194.72	0.98265
272	3194.91	1.65163
273	3194.97	0.54374

[Mn(TPPS)(O₂)]³⁻

mode wave number IR intensity

	cm ^{**} (-1)	km/mol
1	0.00	0.00000
2	0.00	0.00000
3	0.00	0.00000
4	0.00	0.00000
5	0.00	0.00000
6	0.00	0.00000
7	6.24	0.02725
8	7.53	0.14780
9	12.09	0.87537
10	13.89	8.73076
11	16.91	0.61518
12	18.35	4.02130
13	18.68	3.12192
14	22.55	0.02806
15	23.47	0.00977
16	27.00	0.01888
17	29.14	0.07601
18	29.46	0.07798
19	37.27	0.02955
20	50.64	0.23880
21	52.57	0.29845
22	54.48	0.15638
23	71.87	0.48333
24	75.31	0.16250
25	77.61	1.83931
26	77.88	2.66471
27	81.39	3.92111
28	90.95	0.54771
29	92.44	2.68513
30	95.97	1.75197
31	110.27	0.61576
32	113.43	1.30365
33	114.19	2.09246
34	115.53	0.94439
35	123.32	0.14095
36	128.65	1.30216
37	143.20	4.76411

38	149.04	11.48844
39	151.17	7.80053
40	163.77	0.21915
41	167.48	1.66470
42	169.82	2.83218
43	203.91	2.04887
44	210.88	0.35973
45	211.42	0.33795
46	217.79	2.03196
47	222.19	0.05401
48	231.97	4.93512
49	240.89	0.16714
50	245.70	0.25808
51	248.14	0.51787
52	252.79	4.45119
53	260.16	4.17414
54	273.53	4.33688
55	285.07	4.15561
56	288.42	1.84586
57	290.97	0.13585
58	299.55	0.97118
59	309.32	6.72027
60	311.62	8.22293
61	322.59	0.23009
62	324.53	1.28222
63	328.42	4.12227
64	336.44	5.02680
65	343.38	13.61360
66	345.42	3.70903
67	347.13	15.14188
68	352.08	1.41937
69	355.13	0.45667
70	357.79	0.45083
71	362.26	2.72814
72	367.04	1.21510
73	400.34	0.03359
74	401.74	0.07483
75	402.79	0.14933
76	403.42	0.07807
77	408.26	7.35832
78	420.91	11.83956
79	423.07	2.51950
80	434.16	1.78812
81	443.77	1.12937
82	448.65	1.11224
83	449.01	10.49341

84	451.58	8.83707
85	452.23	8.92897
86	473.02	7.52147
87	473.97	2.91258
88	475.16	4.99452
89	476.35	11.98793
90	478.86	2.35448
91	481.18	3.84635
92	491.03	0.59465
93	531.29	15.94717
94	535.44	37.99846
95	536.92	47.68882
96	540.06	5.96124
97	560.51	133.32034
98	562.55	151.75609
99	564.47	17.27809
100	565.93	63.92304
101	568.86	151.06502
102	570.37	37.91436
103	571.10	78.20533
104	576.33	0.08003
105	622.69	1.10575
106	623.61	0.76164
107	623.66	1.11737
108	625.51	0.20751
109	651.22	1.06784
110	660.20	0.11354
111	660.32	0.27452
112	660.83	0.02421
113	682.19	2.75861
114	695.29	15.70944
115	696.26	11.64719
116	708.57	1.44893
117	709.75	12.98499
118	715.01	0.49414
119	715.80	0.20931
120	719.23	3.72713
121	725.03	21.37785
122	733.27	0.56628
123	734.47	0.23805
124	745.35	8.23538
125	784.74	0.16596
126	793.08	5.20389
127	794.91	1.95533
128	797.84	4.32346
129	799.99	16.47063

130	801.50	10.28179
131	803.78	29.74428
132	804.88	14.62576
133	821.70	1.92285
134	827.20	1.17728
135	829.52	1.37771
136	830.39	0.39535
137	836.89	1.05106
138	839.40	2.41123
139	839.69	2.99407
140	852.28	3.30810
141	856.05	0.74884
142	870.64	1.43052
143	871.22	1.55251
144	872.67	8.61542
145	905.25	0.09831
146	906.27	0.05575
147	906.67	0.05493
148	907.20	0.18502
149	940.51	0.84684
150	944.44	3.12721
151	945.39	0.86878
152	947.36	1.40563
153	956.90	11.51190
154	957.48	38.59257
155	957.60	42.35289
156	959.40	0.74713
157	959.79	5.25667
158	960.86	0.35408
159	961.52	0.23654
160	962.07	0.91359
161	996.20	14.66767
162	996.88	18.81473
163	997.02	4.42817
164	997.49	5.23963
165	1004.85	7.40901
166	1007.34	32.87055
167	1009.74	24.01113
168	1013.12	16.96797
169	1021.87	8.62378
170	1022.79	9.12025
171	1026.64	1.96785
172	1031.36	2.16275
173	1043.31	33.30269
174	1044.62	46.21973
175	1047.03	20.27909

176	1052.01	0.65678
177	1064.63	12.23304
178	1068.00	9.90055
179	1069.14	9.28130
180	1069.67	3.08839
181	1071.48	21.74165
182	1072.16	17.58105
183	1073.46	38.33315
184	1075.33	15.60653
185	1123.80	127.69638
186	1125.44	114.40754
187	1127.27	132.04658
188	1131.13	112.02109
189	1136.31	81.16238
190	1137.44	105.35939
191	1138.13	76.36506
192	1138.55	127.18579
193	1140.78	60.75153
194	1142.97	35.85354
195	1144.74	128.84759
196	1144.97	28.70341
197	1163.34	0.75987
198	1190.76	3.34890
199	1192.60	2.00433
200	1221.25	65.86772
201	1223.85	46.42782
202	1236.11	23.62140
203	1238.56	7.25977
204	1240.68	492.57685
205	1250.07	0.98140
206	1251.48	2.37423
207	1252.45	0.45833
208	1254.04	0.67303
209	1261.49	1.05349
210	1282.08	0.43329
211	1295.28	0.81120
212	1298.93	2.92195
213	1320.48	0.33938
214	1329.72	1.48429
215	1329.98	1.36467
216	1335.30	7.50197
217	1336.23	0.05623
218	1353.04	1.47490
219	1355.56	2.37428
220	1362.29	5.46240
221	1364.89	10.63197

222	1385.25	6.86606
223	1385.70	5.09278
224	1387.37	5.04137
225	1387.65	5.16200
226	1444.67	0.13137
227	1447.38	0.30317
228	1448.31	0.67417
229	1459.99	0.87555
230	1467.41	9.67653
231	1467.65	11.93385
232	1472.26	0.64690
233	1481.91	1.47840
234	1497.01	0.29163
235	1506.64	7.57453
236	1509.35	1.55429
237	1519.91	1.02409
238	1528.22	0.99506
239	1528.76	0.37650
240	1546.39	19.17893
241	1552.92	1.78093
242	1559.86	1.19332
243	1560.88	0.50822
244	1561.68	0.31685
245	1571.33	1.02230
246	1588.67	29.41495
247	1589.58	50.75841
248	1590.29	60.51629
249	1591.33	20.70146
250	3097.84	4.80870
251	3098.37	3.28111
252	3098.68	3.42968
253	3098.97	1.96764
254	3099.75	5.72970
255	3099.93	4.93054
256	3101.11	3.19923
257	3106.51	1.94117
258	3122.07	2.43673
259	3122.09	4.02472
260	3122.13	7.63950
261	3122.37	6.83533
262	3123.04	9.23012
263	3123.10	7.11443
264	3123.74	6.01130
265	3124.99	3.81171
266	3181.43	0.14625
267	3181.66	0.01730

268	3181.91	0.01521
269	3182.06	0.01320
270	3197.80	0.06774
271	3198.05	0.06068
272	3198.17	0.10536
273	3198.45	0.05402

[Fe(TPPS)(O₂)]⁴⁻

mode	wave number cm ⁻¹	IR intensity km/mol
1	0.00	0.00000
2	0.00	0.00000
3	0.00	0.00000
4	0.00	0.00000
5	0.00	0.00000
6	0.00	0.00000
7	1.90	0.57332
8	4.46	0.01293
9	11.62	0.07238
10	14.14	11.97063
11	17.91	0.18904
12	18.56	2.91803
13	19.52	4.62512
14	19.75	3.03315
15	23.15	0.09567
16	24.99	0.02794
17	28.34	0.23290
18	29.74	0.19786
19	37.21	0.08453
20	42.27	0.17540
21	42.73	1.64257
22	44.65	0.41882
23	66.56	0.13469
24	70.78	0.16272
25	80.88	5.39010
26	81.40	0.75826
27	87.19	1.37119
28	91.05	0.25958
29	92.86	4.86081
30	97.85	2.24774
31	109.17	1.24320
32	111.74	1.87640
33	112.62	0.73140
34	115.08	0.21864
35	121.70	0.15440

36	127.68	1.48271
37	146.92	16.90079
38	149.53	12.97927
39	158.73	0.80922
40	162.23	0.23807
41	166.89	2.25764
42	173.88	1.18538
43	205.59	0.09961
44	213.46	0.03664
45	216.02	0.65893
46	219.58	0.52926
47	230.75	0.26627
48	239.13	0.19398
49	247.31	1.32668
50	251.62	0.74027
51	255.80	0.86171
52	258.52	1.97692
53	263.21	2.62615
54	274.50	0.79913
55	289.56	1.74839
56	293.41	0.20661
57	296.30	3.01791
58	301.11	1.46630
59	306.84	1.05091
60	321.00	5.41695
61	323.60	4.03893
62	326.24	7.74973
63	334.94	3.47234
64	342.71	2.84500
65	346.73	2.79584
66	348.71	4.15206
67	354.73	0.38293
68	356.37	0.55722
69	357.95	1.10215
70	361.90	3.66864
71	370.83	0.17314
72	399.38	1.01750
73	401.01	3.25841
74	402.16	1.65856
75	402.87	2.86331
76	405.26	0.59427
77	418.44	9.31270
78	420.62	17.10659
79	421.80	8.54086
80	437.27	1.69836
81	453.95	5.94770

82	458.71	0.03986
83	466.40	3.01820
84	467.89	1.55382
85	471.15	4.13507
86	492.71	26.44442
87	493.70	37.92623
88	499.20	0.61273
89	501.23	25.85541
90	501.35	16.00546
91	501.65	18.47259
92	502.87	0.32630
93	536.41	20.01414
94	540.99	0.64068
95	542.53	3.89682
96	542.84	0.65191
97	561.87	14.42372
98	565.25	3.24685
99	565.63	5.78342
100	574.75	0.11544
101	584.59	1.15467
102	590.01	418.91520
103	590.89	363.68708
104	591.88	94.49917
105	623.72	0.28046
106	624.54	0.76573
107	624.70	0.53630
108	626.59	0.65961
109	654.60	0.11162
110	662.08	5.57346
111	663.08	5.63232
112	664.45	0.67292
113	684.31	0.59177
114	695.84	127.80850
115	696.44	108.95484
116	708.30	32.03419
117	710.45	14.06270
118	717.24	27.06853
119	717.81	13.62351
120	721.85	1.76984
121	722.14	17.65287
122	732.30	1.89304
123	733.33	0.16464
124	746.05	0.29089
125	779.95	0.11351
126	790.14	13.98261
127	791.95	3.75044

128	793.40	1.06008
129	797.25	9.74002
130	797.97	10.36170
131	800.12	23.84725
132	800.97	28.59706
133	819.98	3.51276
134	825.09	3.49761
135	827.02	4.98126
136	828.18	4.14211
137	836.41	5.83963
138	837.85	3.55992
139	840.43	0.42149
140	850.57	3.86334
141	853.51	1.53770
142	868.13	9.07628
143	868.76	8.40484
144	872.62	0.49112
145	898.61	0.19879
146	899.23	0.27753
147	900.18	1.69363
148	900.82	0.62634
149	936.24	2.48779
150	939.62	3.76975
151	940.29	0.29960
152	944.16	2.65658
153	954.88	81.65571
154	955.20	501.82587
155	955.32	519.99779
156	956.30	1.00545
157	957.01	45.87965
158	957.89	6.18159
159	958.21	1.52041
160	961.47	1.60296
161	993.27	0.17092
162	995.87	1.61705
163	996.76	1.60828
164	997.94	0.59360
165	1002.29	1.47853
166	1003.71	1.58403
167	1004.64	9.95626
168	1008.29	27.84588
169	1017.52	1.70166
170	1021.57	4.32069
171	1024.20	10.00200
172	1029.37	0.22172
173	1042.69	4.28949

174	1044.22	5.93271
175	1044.91	3.86597
176	1052.16	2.77671
177	1062.86	11.76126
178	1063.61	0.30274
179	1063.89	34.47864
180	1064.25	40.37946
181	1064.55	34.52728
182	1065.15	12.05648
183	1065.97	23.00404
184	1067.25	27.73187
185	1134.70	7.04389
186	1135.14	29.86920
187	1135.50	3.36730
188	1138.10	11.76630
189	1161.67	3.15086
190	1168.27	181.63708
191	1169.73	180.75352
192	1170.09	206.89660
193	1170.78	194.64619
194	1176.52	67.99629
195	1176.68	229.13014
196	1177.22	190.14656
197	1177.68	254.61478
198	1188.77	3.63100
199	1192.56	2.33615
200	1220.36	0.28693
201	1222.01	0.09006
202	1233.88	47.17472
203	1238.98	42.52553
204	1247.32	4.55841
205	1247.88	2.54325
206	1248.00	6.53165
207	1249.85	16.57547
208	1255.75	176.34544
209	1258.69	3.05723
210	1284.52	0.45610
211	1295.64	5.52155
212	1302.79	9.15164
213	1320.84	0.36885
214	1326.37	2.00992
215	1326.55	0.76805
216	1330.42	13.14366
217	1331.96	0.05440
218	1351.49	82.58112
219	1355.61	84.20678

220	1362.24	10.75827
221	1365.17	11.26073
222	1379.95	7.88627
223	1380.35	3.87434
224	1380.56	5.66550
225	1381.78	5.18219
226	1448.74	0.19218
227	1451.00	24.91819
228	1452.49	30.06664
229	1458.47	1.70829
230	1467.76	0.15338
231	1469.21	1.69073
232	1474.13	0.11433
233	1488.46	1.19571
234	1502.10	0.18398
235	1518.99	68.08347
236	1527.51	6.25537
237	1528.75	1.47673
238	1538.41	0.01522
239	1539.16	0.81825
240	1553.99	4.70564
241	1557.46	0.04768
242	1558.42	1.19901
243	1558.76	3.16159
244	1558.98	4.38709
245	1576.82	0.69102
246	1588.32	24.17221
247	1588.97	22.88072
248	1589.11	24.45569
249	1589.29	18.98286
250	3090.97	8.45268
251	3092.55	9.00720
252	3092.72	8.02679
253	3093.26	7.89807
254	3093.43	9.65774
255	3094.89	6.00259
256	3095.38	8.39862
257	3101.05	2.85218
258	3115.43	11.53505
259	3115.75	9.60499
260	3115.97	13.25267
261	3116.24	12.58233
262	3116.68	1.68342
263	3117.27	1.88522
264	3117.67	3.53933
265	3118.67	3.00328

266	3176.26	0.24376
267	3176.30	0.20398
268	3176.67	0.22767
269	3178.20	0.14197
270	3193.43	1.63415
271	3193.80	1.68648
272	3194.06	1.59549
273	3195.40	1.16501



mode	wave number cm**(-1)	IR intensity km/mol
1	-9.61	0.00000
2	0.00	0.00000
3	0.00	0.00000
4	0.00	0.00000
5	0.00	0.00000
6	0.00	0.00000
7	0.00	0.00000
8	3.79	0.01816
9	12.99	7.95671
10	13.50	0.07063
11	13.68	0.63142
12	17.14	0.09770
13	18.43	2.93723
14	18.53	2.51674
15	21.08	0.00819
16	25.05	0.01287
17	27.64	0.01144
18	28.08	0.02827
19	36.57	0.01387
20	46.02	0.21408
21	48.53	0.06028
22	51.27	0.12420
23	69.33	0.09055
24	74.91	0.73823
25	81.03	4.60661
26	83.14	0.22992
27	86.92	1.04575
28	92.25	0.09713
29	95.34	1.99463
30	99.43	1.99818
31	111.31	1.58393
32	113.81	2.34804
33	113.97	1.39037

34	116.94	0.21202
35	123.51	0.05998
36	129.73	1.51360
37	140.73	4.66986
38	151.51	10.05137
39	152.81	7.85915
40	164.97	0.43388
41	169.31	1.01506
42	171.03	2.05811
43	208.21	0.45907
44	215.03	0.28920
45	217.61	0.43278
46	223.02	0.62617
47	229.59	1.09743
48	242.32	0.01929
49	252.36	0.29067
50	254.51	0.38657
51	259.12	0.08600
52	264.42	0.85595
53	269.62	0.22459
54	278.03	1.91830
55	290.07	0.03544
56	292.96	0.31006
57	300.60	0.37974
58	304.77	0.51296
59	306.00	2.29458
60	326.56	0.62511
61	328.43	0.31431
62	330.67	3.55619
63	332.02	1.50973
64	341.21	0.57010
65	342.47	1.72261
66	345.94	0.54006
67	350.12	0.52978
68	351.73	1.07139
69	353.88	0.14961
70	359.89	2.86013
71	366.30	0.37482
72	399.58	0.24764
73	401.16	0.63850
74	402.57	0.06204
75	403.69	0.31730
76	404.64	0.37287
77	411.51	14.11314
78	413.60	1.02559
79	435.16	5.49876

80	436.09	1.74278
81	441.91	1.86490
82	443.32	10.35887
83	444.16	10.03866
84	453.36	1.29091
85	457.09	3.40847
86	460.43	6.35774
87	460.61	10.38009
88	461.25	7.33247
89	461.68	6.63711
90	481.17	3.34171
91	488.06	2.45736
92	489.23	0.09761
93	530.21	16.19880
94	535.80	44.64557
95	536.75	46.47498
96	538.57	3.03219
97	560.26	144.03265
98	561.47	125.51415
99	565.06	3.81144
100	566.26	41.52045
101	568.50	0.96100
102	569.05	184.60377
103	571.93	159.68440
104	575.22	0.65752
105	623.26	0.03759
106	624.05	0.45136
107	624.32	0.86087
108	626.11	0.10405
109	652.99	0.05709
110	660.57	0.97106
111	663.79	0.20039
112	664.04	0.30525
113	683.97	0.52492
114	697.52	17.03668
115	699.24	14.47351
116	709.90	21.87408
117	711.15	0.02041
118	716.95	0.23346
119	717.83	0.26537
120	721.09	5.75072
121	722.86	16.09707
122	731.92	0.37060
123	733.27	0.14301
124	745.81	0.00302
125	778.83	0.01170

126	788.97	5.37945
127	791.61	0.91938
128	793.96	2.87637
129	798.87	11.31504
130	799.00	6.80880
131	800.95	36.63965
132	802.83	17.37989
133	821.53	1.19293
134	826.33	1.05649
135	828.20	0.86101
136	829.17	0.53780
137	836.78	0.49679
138	838.74	0.77355
139	840.10	3.41514
140	850.86	3.93710
141	854.02	0.03605
142	868.88	0.95541
143	870.37	0.22993
144	873.00	0.33325
145	898.82	0.02894
146	899.95	0.07288
147	900.45	0.04152
148	901.75	0.08457
149	940.74	0.09174
150	942.94	1.92512
151	944.98	1.05400
152	946.07	1.99138
153	958.28	11.72871
154	958.45	20.08294
155	958.65	23.20851
156	959.24	0.35028
157	959.35	1.94517
158	960.11	1.50386
159	960.96	0.57339
160	961.22	0.62622
161	993.68	0.05271
162	995.53	0.63100
163	997.65	3.90306
164	999.08	2.51673
165	1002.19	1.79011
166	1003.93	28.35691
167	1004.39	1.47780
168	1007.77	32.81103
169	1015.73	4.51186
170	1022.40	2.15375
171	1023.82	1.76725

172	1030.79	0.08957
173	1045.40	26.08281
174	1045.92	20.52132
175	1046.78	11.69912
176	1054.63	0.54704
177	1068.71	2.07686
178	1069.07	18.75999
179	1069.53	29.96125
180	1070.22	53.35101
181	1073.07	11.17567
182	1073.42	10.09878
183	1074.94	5.18026
184	1075.28	24.01016
185	1101.15	83.24042
186	1101.88	48.83249
187	1102.10	147.56955
188	1102.54	102.51616
189	1111.96	100.35240
190	1113.14	78.03659
191	1114.30	54.07409
192	1115.02	56.61957
193	1140.42	51.21136
194	1141.22	106.15141
195	1141.54	20.09642
196	1143.36	42.80943
197	1163.54	0.36157
198	1190.78	4.30267
199	1193.86	4.62146
200	1219.47	1.11659
201	1223.69	8.38153
202	1237.68	1.41458
203	1239.93	0.17437
204	1245.29	156.16847
205	1250.38	6.46738
206	1251.33	0.26233
207	1251.89	4.76802
208	1253.79	0.92231
209	1260.93	0.91710
210	1282.00	0.09489
211	1295.82	1.06859
212	1302.32	1.68757
213	1323.50	0.11174
214	1330.13	0.45645
215	1331.20	0.76257
216	1334.80	4.99675
217	1335.91	0.04091

218	1353.03	2.80720
219	1358.23	2.54911
220	1363.56	0.02659
221	1364.29	0.55251
222	1382.97	5.58282
223	1383.24	9.24264
224	1383.57	3.70112
225	1384.59	4.54764
226	1451.83	0.31499
227	1453.31	0.30278
228	1456.41	0.63028
229	1462.30	0.86647
230	1470.59	8.32246
231	1474.24	10.71795
232	1477.39	0.20749
233	1491.55	0.18466
234	1503.72	1.01198
235	1521.74	3.08484
236	1533.75	0.15680
237	1535.83	0.30119
238	1540.19	0.04646
239	1544.42	0.16140
240	1558.47	1.70313
241	1561.13	0.08990
242	1563.53	0.03486
243	1563.81	1.16210
244	1564.68	0.24282
245	1580.48	0.58574
246	1592.80	45.32053
247	1593.39	57.50148
248	1593.88	40.12344
249	1594.53	28.99763
250	3100.55	3.22036
251	3100.77	4.63849
252	3101.50	2.88300
253	3102.21	2.56427
254	3103.64	3.47754
255	3103.93	2.64258
256	3104.74	2.86589
257	3108.79	2.04565
258	3122.86	7.69875
259	3123.76	5.38640
260	3123.86	5.89477
261	3123.97	6.59380
262	3125.48	6.10570
263	3125.62	7.04477

264	3125.81	5.44419
265	3128.03	4.34935
266	3178.20	0.04115
267	3178.45	0.03917
268	3179.09	0.03348
269	3179.42	0.03566
270	3195.84	0.49546
271	3195.96	0.54478
272	3196.40	0.51062
273	3196.70	0.47527

S15. Cartesian Coordinates of the $[M(TPPS)]^{4-/3-}$ and $[M(TPPS)(O_2)]^{4-/3-}$ Complexes

$[Fe(TPPS)]^{4-}$ - Triplet

N	-0.6772915	2.0718815	-0.1511714
C	0.3077878	3.0410480	0.0390471
C	-1.8697478	2.7820469	-0.2470053
C	-0.2817171	4.3579467	0.1129577
C	-1.6291730	4.1992973	-0.0940727
C	1.6925122	2.8024396	0.0765127
C	2.2404833	1.5254612	-0.1431842
C	2.6309523	3.9544109	0.2698807
C	2.8187457	4.9206877	-0.7457958
C	3.7238729	5.9785948	-0.5707299
C	4.4483205	6.0860326	0.6291990
C	4.2720190	5.1371793	1.6506074
C	3.3704461	4.0767862	1.4684648
C	3.6500053	1.2921480	-0.3581648
C	3.7918959	-0.0442603	-0.6358599
C	2.4771719	-0.6373835	-0.5387484
N	1.5214252	0.3377352	-0.2641591
C	2.2329292	-2.0192789	-0.6336610
C	0.9636520	-2.5771692	-0.3895291
C	3.3683089	-2.9485545	-0.9369909
C	4.4107821	-3.1644636	-0.0070928
C	5.4600874	-4.0524718	-0.2980340
C	5.4801590	-4.7318122	-1.5267351
C	4.4551386	-4.5234754	-2.4681754
C	3.4058970	-3.6418443	-2.1708459
C	0.7385257	-3.9954768	-0.2269794
C	-0.5856697	-4.1572972	0.0947676
C	-1.1812485	-2.8407007	0.0791791
N	-0.2165319	-1.8690470	-0.1869117
C	-2.5586899	-2.6038892	0.2329989
C	-3.1227065	-1.3252480	0.0708079
C	-3.4720845	-3.7635127	0.4886066
C	-4.1283169	-3.8975300	1.7354109
C	-4.9812461	-4.9828246	1.9849103
C	-5.1915875	-5.9494676	0.9841431
C	-4.5577758	-5.8265748	-0.2625508
C	-3.7025057	-4.7398414	-0.5069076
C	-4.5447836	-1.0914091	-0.0277233
C	-4.7091554	0.2477960	-0.2790964
C	-3.3910908	0.8419101	-0.2826929
C	-3.1557169	2.2253534	-0.3863252
C	-4.3141241	3.1535413	-0.5862709
C	-4.4434797	3.8767310	-1.7933477
C	-5.5217381	4.7548388	-1.9941532
C	-6.4808042	4.9246118	-0.9836843
C	-6.3648840	4.2192591	0.2288713
C	-5.2905456	3.3394834	0.4226545
N	-2.4161879	-0.1353039	-0.0966945
H	0.2693304	5.2877136	0.2881727
H	-2.4034454	4.9735966	-0.1129569
H	4.4269655	2.0631417	-0.3314252
H	4.7121575	-0.5869564	-0.8762081
H	-1.1172926	-5.0893789	0.3114623
H	1.5092341	-4.7681589	-0.3181486
H	-5.3170221	-1.8634927	0.0529001

H	-5.6464460	0.7906346	-0.4401262
H	-3.6936668	3.7425791	-2.5886136
H	-5.6292296	5.3164488	-2.9340870
H	-5.1957158	2.7981497	1.3766509
H	-7.1107698	4.3664938	1.0247991
H	-3.2142686	-4.6407469	-1.4887414
H	-4.7493659	-6.5846480	-1.0362535
H	-3.9602714	-3.1434131	2.5200876
H	-5.4893658	-5.0778012	2.9567405
H	4.3933466	-2.6400318	0.9606987
H	6.2732282	-4.2252484	0.4223454
H	2.6061271	-3.4763266	-2.9092966
H	4.4867051	-5.0437165	-3.4375724
H	3.2370946	3.3299310	2.2666958
H	4.8559427	5.2263069	2.5791757
H	3.8893905	6.7152706	-1.3712532
H	2.2634710	4.8293669	-1.6921989
S	5.5759521	7.4941242	0.8829210
S	-7.8928501	6.0495332	-1.2299231
S	-6.2521106	-7.3887268	1.3342331
S	6.7998571	-5.9328087	-1.8952188
O	6.1390001	-7.2793284	-1.7577192
O	7.2242506	-5.6204599	-3.3056468
O	7.8748638	-5.6874751	-0.8709077
O	-5.4463289	-8.2324797	2.2867739
O	-6.4917843	-8.0506435	0.0035895
O	-7.4967463	-6.8134025	1.9558645
O	-7.6589973	6.7166612	-2.5588803
O	-7.8374682	6.9961355	-0.0600132
O	-9.1045380	5.1556798	-1.2118072
O	4.7064348	8.5883442	1.4456457
O	6.1250553	7.8124790	-0.4825213
O	6.6153418	6.9993693	1.8530745
Fe	-0.4476699	0.1012976	-0.1848325

[Fe(TPPS)]³⁻ - Quartet

N	-0.6665137	1.9985165	-0.2996073
C	0.2727215	2.9507757	0.0913522
C	-1.8351972	2.7049679	-0.5619666
C	-0.3332495	4.2566709	0.1211473
C	-1.6228057	4.1119886	-0.3375398
C	1.6474029	2.6987803	0.2824219
C	2.2143458	1.4442369	-0.0313103
C	2.5519475	3.8103554	0.6973628
C	2.7421363	4.9507790	-0.1200829
C	3.5812003	5.9937923	0.2964550
C	4.2307975	5.9142995	1.5413683
C	4.0674273	4.7801683	2.3558977
C	3.2413676	3.7283715	1.9309772
C	3.6170280	1.2415464	-0.2860037
C	3.7525743	-0.0274839	-0.8027664
C	2.4464300	-0.6346057	-0.7767748
N	1.5017490	0.2894707	-0.3347731
C	2.1902840	-2.0031687	-1.0069249
C	0.9394636	-2.5793970	-0.6910376
C	3.2973152	-2.9053078	-1.4388335
C	4.4400478	-3.1017192	-0.6280442
C	5.4675778	-3.9636329	-1.0405236
C	5.3686982	-4.6309764	-2.2722950
C	4.2384004	-4.4468591	-3.0910973
C	3.2044206	-3.5981576	-2.6715085

C	0.7406960	-3.9897887	-0.4750610
C	-0.5130351	-4.1407000	0.0738385
C	-1.1173666	-2.8340237	0.1075282
N	-0.2072803	-1.8769167	-0.3371135
C	-2.4735571	-2.5807508	0.4023073
C	-3.0599185	-1.3236527	0.1346556
C	-3.3572077	-3.6778954	0.8921135
C	-3.9712218	-3.5528137	2.1633948
C	-4.8093201	-4.5633789	2.6528026
C	-5.0604806	-5.7041838	1.8682267
C	-4.4782151	-5.8321952	0.5962466
C	-3.6264651	-4.8267313	0.1122528
C	-4.4771462	-1.1202903	-0.0230426
C	-4.6482767	0.1532328	-0.5177058
C	-3.3441418	0.7614596	-0.5734794
C	-3.1050175	2.1330881	-0.8000380
C	-4.2348986	3.0493540	-1.1286221
C	-4.2154066	3.7919093	-2.3322657
C	-5.2555147	4.6857121	-2.6353649
C	-6.3119363	4.8623480	-1.7275409
C	-6.3425994	4.1357162	-0.5219646
C	-5.3146279	3.2314602	-0.2280063
N	-2.3706354	-0.1663589	-0.2076125
H	0.1621729	5.1796625	0.4383327
H	-2.3816869	4.8916406	-0.4578074
H	4.3986928	1.9948826	-0.1431360
H	4.6697421	-0.5091106	-1.1562040
H	-0.9863832	-5.0683914	0.4110146
H	1.4874061	-4.7679666	-0.6636476
H	-5.2473830	-1.8755123	0.1643277
H	-5.5876081	0.6370494	-0.8038387
H	-3.3847043	3.6585533	-3.0420313
H	-5.2533452	5.2605946	-3.5731132
H	-5.3271833	2.6857365	0.7273420
H	-7.1645399	4.2885278	0.1932428
H	-3.1902119	-4.9205148	-0.8937387
H	-4.7087152	-6.7180214	-0.0138919
H	-3.7752853	-2.6605825	2.7773716
H	-5.2814019	-4.4632601	3.6416332
H	4.5133156	-2.5944953	0.3456518
H	6.3561372	-4.1254407	-0.4130271
H	2.3235038	-3.4507053	-3.3146162
H	4.1738720	-4.9604311	-4.0621428
H	3.1102930	2.8428433	2.5713292
H	4.5968716	4.7250185	3.3186308
H	3.7468910	6.8701713	-0.3474448
H	2.2463136	5.0084837	-1.1007322
S	5.2185885	7.3286633	2.1312980
S	-7.6566027	6.0396956	-2.0822369
S	-6.1090670	-7.0366535	2.5390085
S	6.6810248	-5.7849046	-2.7927659
O	6.0686611	-7.1496270	-2.6207576
O	6.9589177	-5.4336427	-4.2293158
O	7.8390111	-5.5231908	-1.8687893
O	-5.2321395	-7.7284466	3.5491413
O	-6.4695290	-7.9000818	1.3612756
O	-7.2856310	-6.3307120	3.1571560
O	-7.2999674	6.6917294	-3.3903699
O	-7.6449408	6.9839813	-0.9099674
O	-8.8965364	5.1886123	-2.1470048
O	4.2126146	8.2264023	2.8030794
O	5.8248392	7.9319050	0.8936989

O	6.2281794	6.7445879	3.0815757
Fe	-0.4354715	0.0613358	-0.2967679

[Mn(TPPS)]⁴⁺ - Quartet [Mn def2-SVP]

N	-0.6604528	2.0845953	-0.1754988
C	0.3345791	3.0444302	0.0131435
C	-1.8595414	2.7942986	-0.2452005
C	-0.2541086	4.3567618	0.1085030
C	-1.6099135	4.2019079	-0.0779380
C	1.7239111	2.7966053	0.0268947
C	2.2691904	1.5183912	-0.1882447
C	2.6586505	3.9536658	0.2082186
C	2.8030528	4.9408039	-0.7948228
C	3.6701546	6.0291596	-0.6133380
C	4.4048211	6.1451459	0.5795477
C	4.2861895	5.1667426	1.5815633
C	3.4203096	4.0779539	1.3931747
C	3.6778961	1.2753955	-0.4116708
C	3.8179428	-0.0660787	-0.6650459
C	2.5062841	-0.6623681	-0.5555804
N	1.5516980	0.3252967	-0.2915708
C	2.2571309	-2.0429485	-0.6268324
C	0.9831639	-2.6067744	-0.3994844
C	3.3946968	-2.9793442	-0.9008079
C	4.4207000	-3.1872594	0.0488112
C	5.4664384	-4.0897525	-0.2094755
C	5.5004507	-4.7906207	-1.4257779
C	4.4937380	-4.5879527	-2.3879841
C	3.4474422	-3.6927272	-2.1225467
C	0.7473295	-4.0169527	-0.2328297
C	-0.5863061	-4.1744884	0.0724473
C	-1.1788923	-2.8605519	0.0510058
N	-0.2036938	-1.8979736	-0.2117072
C	-2.5606999	-2.6132345	0.1920252
C	-3.1220027	-1.3329566	0.0417342
C	-3.4795760	-3.7722351	0.4312206
C	-4.1345184	-3.9214352	1.6770103
C	-4.9948614	-5.0039821	1.9121868
C	-5.2139116	-5.9539842	0.8975127
C	-4.5808146	-5.8173958	-0.3481884
C	-3.7184302	-4.7328208	-0.5776165
C	-4.5446145	-1.0900526	-0.0604544
C	-4.7060099	0.2526748	-0.2934400
C	-3.3900568	0.8500625	-0.2883998
C	-3.1484040	2.2316897	-0.3696320
C	-4.3065978	3.1651606	-0.5459018
C	-4.4450348	3.9033058	-1.7429026
C	-5.5210399	4.7884873	-1.9223113
C	-6.4684435	4.9512482	-0.8997096
C	-6.3444571	4.2295954	0.3023952
C	-5.2729657	3.3414468	0.4740523
N	-2.4164202	-0.1381961	-0.1103730
H	0.2987078	5.2855342	0.2821594
H	-2.3804263	4.9803319	-0.0747078
H	4.4555185	2.0461691	-0.4035664
H	4.7380254	-0.6122804	-0.8989288
H	-1.1234869	-5.1056623	0.2791128
H	1.5138284	-4.7952056	-0.3122211
H	-5.3186432	-1.8616303	0.0059846
H	-5.6430753	0.7979668	-0.4486001
H	-3.7036826	3.7753644	-2.5470638
H	-5.6358771	5.3616101	-2.8543916

H	-5.1720114	2.7863024	1.4194757
H	-7.0821306	4.3696659	1.1072856
H	-3.2302502	-4.6231256	-1.5584586
H	-4.7791711	-6.5624243	-1.1328835
H	-3.9598758	-3.1798985	2.4722661
H	-5.5023893	-5.1100889	2.8832163
H	4.3919685	-2.6461746	1.0071953
H	6.2655797	-4.2578768	0.5275547
H	2.6609108	-3.5332551	-2.8764212
H	4.5364808	-5.1245682	-3.3480186
H	3.3243591	3.3143705	2.1810526
H	4.8792286	5.2609208	2.5039614
H	3.7929089	6.7887464	-1.4001265
H	2.2338632	4.8487383	-1.7328997
S	5.4416923	7.6157542	0.8645624
S	-7.8752437	6.0882709	-1.1191389
S	-6.2827026	-7.3903702	1.2309478
S	6.8101401	-6.0159003	-1.7488110
O	6.1300787	-7.3505246	-1.5896964
O	7.2584520	-5.7425815	-3.1600851
O	7.8743030	-5.7609017	-0.7155380
O	-5.4719207	-8.2605006	2.1551629
O	-6.5463811	-8.0238428	-0.1091362
O	-7.5138686	-6.8169977	1.8809992
O	-7.6517982	6.7654450	-2.4448736
O	-7.7997198	7.0244606	0.0579646
O	-9.0932490	5.2031620	-1.0949851
O	4.5065405	8.6190808	1.4885602
O	5.9356750	8.0308574	-0.4957299
O	6.5360678	7.1614006	1.7932308
Mn	-0.4317278	0.0933183	-0.1873713

[Mn(TPPS)]³⁻ - Quintet

N	-0.6566189	2.0359684	-0.2835776
C	0.3154302	2.9880893	0.0268315
C	-1.8490616	2.7399867	-0.4393197
C	-0.2911112	4.2910553	0.1144856
C	-1.6192528	4.1435302	-0.2144317
C	1.6992627	2.7428675	0.1221736
C	2.2560851	1.4805609	-0.1649249
C	2.6181073	3.8714409	0.4665594
C	2.7966074	4.9715520	-0.4050757
C	3.6369371	6.0362912	-0.0461740
C	4.3039856	6.0139866	1.1914296
C	4.1549189	4.9174129	2.0580933
C	3.3218782	3.8486063	1.6935052
C	3.6533610	1.2603564	-0.4314308
C	3.7905782	-0.0524251	-0.8223135
C	2.4888973	-0.6624073	-0.7287432
N	1.5459284	0.2973213	-0.3582136
C	2.2403405	-2.0430299	-0.8611497
C	0.9845464	-2.6091983	-0.5583968
C	3.3647286	-2.9594636	-1.2261262
C	4.4705720	-3.1398219	-0.3636657
C	5.5186760	-4.0045038	-0.7176704
C	5.4737874	-4.6934135	-1.9407137
C	4.3805452	-4.5246743	-2.8106028
C	3.3299931	-3.6678169	-2.4516300
C	0.7716673	-4.0144811	-0.3266167
C	-0.5252310	-4.1635163	0.1107353
C	-1.1359936	-2.8597504	0.0814361

N	-0.1912959	-1.9061342	-0.3024163
C	-2.5073466	-2.6123689	0.2882269
C	-3.0832802	-1.3487741	0.0424271
C	-3.4151045	-3.7257519	0.7052620
C	-4.0537829	-3.6631110	1.9681812
C	-4.9255840	-4.6807088	2.3797518
C	-5.1789281	-5.7712070	1.5272464
C	-4.5610959	-5.8433727	0.2679267
C	-3.6817733	-4.8264189	-0.1404393
C	-4.4970946	-1.1297974	-0.1193576
C	-4.6647367	0.1827018	-0.4988533
C	-3.3609213	0.7941146	-0.5009772
C	-3.1247603	2.1755005	-0.6453880
C	-4.2710033	3.0993201	-0.9029069
C	-4.3150451	3.8587956	-2.0940371
C	-5.3777917	4.7447030	-2.3374300
C	-6.4002267	4.8861463	-1.3863145
C	-6.3677764	4.1423504	-0.1917850
C	-5.3123117	3.2521765	0.0452811
N	-2.3913267	-0.1653469	-0.2048039
H	0.2326217	5.2144648	0.3814160
H	-2.3887715	4.9209747	-0.2585419
H	4.4322662	2.0276013	-0.3695583
H	4.7065030	-0.5644095	-1.1342742
H	-1.0267511	-5.0886327	0.4130459
H	1.5343173	-4.7917705	-0.4412167
H	-5.2687921	-1.8975196	-0.0017962
H	-5.6020716	0.6929509	-0.7425780
H	-3.5135380	3.7482597	-2.8407362
H	-5.4220019	5.3355469	-3.2643439
H	-5.2783171	2.6869186	0.9890900
H	-7.1631227	4.2693290	0.5579753
H	-3.2151760	-4.8761544	-1.1360690
H	-4.7866722	-6.6937600	-0.3922897
H	-3.8575244	-2.8095886	2.6350407
H	-5.4212464	-4.6239590	3.3604933
H	4.5040579	-2.6085465	0.5996425
H	6.3822278	-4.1489612	-0.0520521
H	2.4790855	-3.5298008	-3.1361887
H	4.3606033	-5.0540866	-3.7750905
H	3.1993802	2.9933519	2.3756210
H	4.6992163	4.9048810	3.0141330
H	3.7893403	6.8856754	-0.7284660
H	2.2813485	4.9864160	-1.3775416
S	5.2932860	7.4541251	1.7119256
S	-7.7936002	6.0225687	-1.6830153
S	-6.2867166	-7.1063108	2.0923787
S	6.8035446	-5.8587867	-2.3865302
O	6.2001417	-7.2195698	-2.1590888
O	7.1019319	-5.5746546	-3.8339426
O	7.9461581	-5.5437071	-1.4595629
O	-5.4854093	-7.8464758	3.1302388
O	-6.5921467	-7.9262271	0.8682669
O	-7.4871619	-6.3990312	2.6620717
O	-7.4706427	6.7453911	-2.9627723
O	-7.8171576	6.9165383	-0.4723249
O	-8.9981221	5.1246727	-1.7823856
O	4.3011374	8.3590703	2.3945183
O	5.8533701	8.0322896	0.4407998
O	6.3398296	6.9046573	2.6433097
Mn	-0.4231042	0.0653288	-0.2904690

[Fe(TPPS)(O₂)]⁴⁺ - Triplet

N	-0.6647438	2.0061627	-0.1826919
C	0.3020826	2.9660778	0.1065262
C	-1.8451506	2.7094163	-0.3553117
C	-0.3037257	4.2747790	0.1921676
C	-1.6281088	4.1214181	-0.1370463
C	1.6855273	2.7293030	0.1901439
C	2.2409206	1.4683374	-0.1012125
C	2.6025762	3.8667223	0.5144882
C	2.7635758	4.9555908	-0.3750058
C	3.6021442	6.0312525	-0.0463895
C	4.2879260	6.0326112	1.1810451
C	4.1573248	4.9489990	2.0665819
C	3.3234006	3.8705603	1.7312101
C	3.6512304	1.2495989	-0.3204802
C	3.7942169	-0.0584184	-0.7137918
C	2.4789402	-0.6562735	-0.6678148
N	1.5260071	0.2961651	-0.3209274
C	2.2275586	-2.0307143	-0.8424470
C	0.9709658	-2.6003372	-0.5523881
C	3.3463225	-2.9456754	-1.2308627
C	4.4450931	-3.1714899	-0.3702508
C	5.4805344	-4.0438378	-0.7433782
C	5.4307871	-4.6974820	-1.9852498
C	4.3463198	-4.4827344	-2.8560699
C	3.3094323	-3.6176036	-2.4768413
C	0.7700270	-4.0172186	-0.3500716
C	-0.5234887	-4.1786592	0.0811035
C	-1.1328356	-2.8682658	0.0755611
N	-0.1983675	-1.9012314	-0.2838477
C	-2.4990169	-2.6305105	0.3197708
C	-3.0758216	-1.3606237	0.1297371
C	-3.3877078	-3.7680906	0.7146805
C	-3.9998323	-3.7727886	1.9917194
C	-4.8313706	-4.8313449	2.3850636
C	-5.0676141	-5.9003517	1.5009870
C	-4.4809107	-5.9049983	0.2249706
C	-3.6455776	-4.8449324	-0.1646169
C	-4.5001549	-1.1373385	0.0415645
C	-4.6763817	0.1761668	-0.3213285
C	-3.3618823	0.7717653	-0.3859635
C	-3.1185932	2.1451605	-0.5756027
C	-4.2421715	3.0770840	-0.8979995
C	-4.2393915	3.7686396	-2.1307362
C	-5.2522440	4.6924789	-2.4371302
C	-6.2743381	4.9409222	-1.5078425
C	-6.2956323	4.2582312	-0.2767570
C	-5.2880576	3.3303597	0.0229214
N	-2.3851921	-0.1803460	-0.1270374
H	0.2202563	5.1991580	0.4553174
H	-2.4038627	4.8928221	-0.1833047
H	4.4298850	2.0130050	-0.2198492
H	4.7163631	-0.5771987	-0.9950186
H	-1.0235065	-5.1085424	0.3703539
H	1.5390417	-4.7863743	-0.4773355
H	-5.2681707	-1.9023448	0.1968340
H	-5.6197477	0.6988627	-0.5109404
H	-3.4334976	3.5765797	-2.8554253
H	-5.2569871	5.2350615	-3.3939446
H	-5.2935954	2.8162932	0.9961119

H	-7.0929858	4.4627097	0.4536586
H	-3.2003250	-4.8443580	-1.1712118
H	-4.6946832	-6.7381850	-0.4606991
H	-3.8121378	-2.9395013	2.6863079
H	-5.3060847	-4.8267726	3.3778443
H	4.4819526	-2.6701796	0.6088668
H	6.3374045	-4.2233939	-0.0775833
H	2.4639400	-3.4463551	-3.1608499
H	4.3215756	-4.9846054	-3.8352044
H	3.2161969	3.0254792	2.4287018
H	4.7153020	4.9557123	3.0148856
H	3.7381253	6.8708029	-0.7443691
H	2.2335124	4.9527064	-1.3396781
S	5.2773334	7.4859387	1.6591681
S	-7.5739158	6.1646696	-1.8709627
S	-6.0992176	-7.3009336	2.0465839
S	6.7396199	-5.8766217	-2.4524352
O	6.1079783	-7.2322909	-2.2752751
O	7.0614145	-5.5540305	-3.8870496
O	7.8783016	-5.6168545	-1.5031732
O	-5.2181836	-8.0783183	2.9887114
O	-6.4532752	-8.0593946	0.7956685
O	-7.2834340	-6.6666373	2.7259552
O	-7.2392765	6.7323813	-3.2243261
O	-7.4673045	7.1682794	-0.7530585
O	-8.8589698	5.3805557	-1.8469470
O	4.2829091	8.4241726	2.2920008
O	5.8577995	8.0138277	0.3748794
O	6.3093245	6.9682048	2.6247601
Fe	-0.4465603	0.0635009	-0.4550556
O	-0.6576811	0.1973274	-2.2668293
O	-1.5487140	0.8847015	-2.8858202

[Fe(TPPS)(O₂)]³⁻ - Doublet

N	-0.6902909	1.9860234	-0.1474290
C	0.2540384	2.9402135	0.2308078
C	-1.8706938	2.6899827	-0.3464963
C	-0.3719972	4.2282220	0.3632336
C	-1.6785352	4.0836182	-0.0491927
C	1.6392529	2.7112878	0.3270929
C	2.1952812	1.4711980	-0.0405623
C	2.5569610	3.8225905	0.7121137
C	2.6571149	4.9982831	-0.0700871
C	3.5376696	6.0262067	0.2974110
C	4.3211841	5.8949207	1.4572854
C	4.2382641	4.7306745	2.2416557
C	3.3672973	3.6972872	1.8664535
C	3.5925431	1.2805546	-0.3283421
C	3.7375099	-0.0063114	-0.7907311
C	2.4414689	-0.6280321	-0.7112605
N	1.4846416	0.2968838	-0.2898832
C	2.2016842	-2.0008645	-0.9031535
C	0.9632403	-2.5737539	-0.5503479
C	3.3016691	-2.8979052	-1.3625039
C	4.4757846	-3.0781404	-0.5951070
C	5.5026983	-3.9194875	-1.0509433
C	5.3706012	-4.5798740	-2.2834299
C	4.2060386	-4.4156485	-3.0562255
C	3.1734267	-3.5888624	-2.5926511
C	0.7864074	-3.9769009	-0.2872504
C	-0.4874648	-4.1343087	0.2075456

C	-1.1199358	-2.8417858	0.1640573
N	-0.2045291	-1.8727589	-0.2610889
C	-2.4882029	-2.6174366	0.4000430
C	-3.0739527	-1.3659828	0.1192064
C	-3.3698130	-3.7248108	0.8678579
C	-4.0766359	-3.5752061	2.0870734
C	-4.9031948	-4.6015657	2.5640061
C	-5.0431898	-5.7877151	1.8213277
C	-4.3715699	-5.9411925	0.5963996
C	-3.5378847	-4.9164681	0.1233064
C	-4.4850223	-1.1752517	-0.0869973
C	-4.6574385	0.1203605	-0.5205186
C	-3.3622245	0.7456397	-0.4894126
C	-3.1256552	2.1234128	-0.6670875
C	-4.2253512	3.0447586	-1.0646203
C	-4.0772385	3.8420388	-2.2247808
C	-5.0876293	4.7364622	-2.6100554
C	-6.2485061	4.8560839	-1.8295539
C	-6.4088679	4.0762121	-0.6682924
C	-5.4061945	3.1740991	-0.2908166
N	-2.3855550	-0.1849979	-0.1338715
H	0.1219172	5.1414794	0.7093018
H	-2.4560571	4.8528256	-0.0967782
H	4.3649275	2.0505233	-0.2323835
H	4.6534884	-0.4919931	-1.1412605
H	-0.9568043	-5.0578254	0.5602554
H	1.5590215	-4.7426158	-0.4123380
H	-5.2487110	-1.9516190	0.0271171
H	-5.5916229	0.6041577	-0.8222123
H	-3.1691942	3.7461358	-2.8389204
H	-4.9870776	5.3496408	-3.5174683
H	-5.5221266	2.5895868	0.6339090
H	-7.3172840	4.1789013	-0.0561548
H	-3.0349929	-5.0305818	-0.8488060
H	-4.5193567	-6.8610326	0.0114874
H	-3.9617910	-2.6505989	2.6730018
H	-5.4506135	-4.4836350	3.5110181
H	4.5780614	-2.5710843	0.3762375
H	6.4178747	-4.0658234	-0.4586908
H	2.2661296	-3.4550380	-3.2012126
H	4.1153001	-4.9247948	-4.0274179
H	3.3027041	2.7865441	2.4810485
H	4.8682066	4.6345541	3.1384107
H	3.6367993	6.9288406	-0.3232900
H	2.0630625	5.0942961	-0.9913537
S	5.4031381	7.2660075	1.9809259
S	-7.5453757	6.0526377	-2.2819731
S	-6.0461302	-7.1535773	2.4931503
S	6.6871992	-5.6957706	-2.8712695
O	6.1268660	-7.0782661	-2.6670820
O	6.8787262	-5.3391059	-4.3207963
O	7.8837415	-5.3954373	-2.0102298
O	-5.1217553	-7.8558640	3.4527348
O	-6.4296660	-7.9935030	1.3056246
O	-7.2133818	-6.4868608	3.1689982
O	-7.1401276	6.6100899	-3.6190382
O	-7.5189370	7.0670311	-1.1692462
O	-8.8128771	5.2423725	-2.3200039
O	4.5348701	8.1074342	2.8782115
O	5.8032799	7.9660478	0.7104038
O	6.5494730	6.6088742	2.7002977
Fe	-0.4614300	0.0647544	-0.4490867

O	-0.5992715	0.1486356	-2.3643411
O	-1.4566849	0.8582989	-2.9315522

[Mn(TPPS)(O₂)]⁴⁻ - Quartet

N	-0.6666671	2.0437889	-0.1302700
C	0.3117267	2.9948954	0.1285678
C	-1.8491373	2.7412758	-0.3035733
C	-0.2872678	4.3112501	0.1848423
C	-1.6177355	4.1581957	-0.1191271
C	1.6944486	2.7423872	0.2146044
C	2.2541281	1.4711612	-0.0328686
C	2.6201489	3.8880725	0.4876198
C	2.8253049	4.9036677	-0.4752798
C	3.6872910	5.9785316	-0.2096054
C	4.3510026	6.0517197	1.0272788
C	4.1678394	5.0448156	1.9908245
C	3.3098504	3.9675134	1.7192714
C	3.6675604	1.2381630	-0.2174778
C	3.8138674	-0.0797967	-0.5801629
C	2.4958608	-0.6717569	-0.5630880
N	1.5478037	0.2913102	-0.2409272
C	2.2343178	-2.0458777	-0.7486389
C	0.9687327	-2.6171583	-0.5057855
C	3.3595173	-2.9580749	-1.1300690
C	4.4053897	-3.2574516	-0.2283824
C	5.4519907	-4.1153376	-0.6058010
C	5.4658568	-4.6775180	-1.8925620
C	4.4328366	-4.3891987	-2.8034517
C	3.3844018	-3.5399977	-2.4204024
C	0.7495076	-4.0366056	-0.3324838
C	-0.5547505	-4.1955582	0.0657242
C	-1.1564046	-2.8792564	0.0799780
N	-0.2045529	-1.9201226	-0.2509296
C	-2.5230953	-2.6325899	0.3175304
C	-3.1020736	-1.3553134	0.1632292
C	-3.4200469	-3.7778604	0.6750468
C	-3.9914929	-3.8477772	1.9686233
C	-4.8320256	-4.9122960	2.3247489
C	-5.1165695	-5.9218313	1.3862464
C	-4.5675805	-5.8621185	0.0953700
C	-3.7232140	-4.7957420	-0.2571904
C	-4.5254631	-1.1194352	0.0891873
C	-4.6967012	0.2041547	-0.2442041
C	-3.3808372	0.7957799	-0.3117743
C	-3.1259325	2.1710349	-0.4940064
C	-4.2532544	3.0986794	-0.8206703
C	-4.2853127	3.7266338	-2.0863090
C	-5.3136331	4.6257138	-2.4139423
C	-6.3153624	4.9119266	-1.4734999
C	-6.2978933	4.2965972	-0.2073365
C	-5.2743835	3.3934959	0.1143329
N	-2.4151533	-0.1711842	-0.0697881
H	0.2470005	5.2388257	0.4148337
H	-2.3887006	4.9339975	-0.1740395
H	4.4490057	1.9980215	-0.1123673
H	4.7413142	-0.6090796	-0.8224498
H	-1.0695759	-5.1271876	0.3221138
H	1.5152588	-4.8098359	-0.4561084
H	-5.2979687	-1.8820287	0.2340935
H	-5.6392007	0.7356196	-0.4132631
H	-3.4969109	3.5003002	-2.8205246

H	-5.3479158	5.1173142	-3.3973664
H	-5.2515079	2.9272050	1.1111445
H	-7.0787553	4.5325279	0.5313978
H	-3.3040870	-4.7453127	-1.2738182
H	-4.8155819	-6.6521356	-0.6287684
H	-3.7653319	-3.0610066	2.7049225
H	-5.2730035	-4.9580632	3.3320559
H	4.3943080	-2.8219531	0.7825006
H	6.2699411	-4.3518170	0.0905413
H	2.5795777	-3.3094308	-3.1354915
H	4.4575936	-4.8197494	-3.8160032
H	3.1642859	3.1805713	2.4755872
H	4.7066263	5.1066602	2.9483322
H	3.8613080	6.7598333	-0.9645016
H	2.3131885	4.8425700	-1.4478572
S	5.3897904	7.4980869	1.4130753
S	-7.6492978	6.0850416	-1.8771189
S	-6.1696644	-7.3261538	1.8785509
S	6.7966793	-5.8236070	-2.3802598
O	6.1470873	-7.1824356	-2.3869763
O	7.2250009	-5.3631651	-3.7479594
O	7.8644050	-5.6722067	-1.3303717
O	-5.3227894	-8.1172948	2.8402502
O	-6.4854367	-8.0678518	0.6073461
O	-7.3736537	-6.6956704	2.5261147
O	-7.3297393	6.6179387	-3.2481703
O	-7.5779601	7.1278770	-0.7927592
O	-8.9087213	5.2612786	-1.8303444
O	4.4364785	8.4975835	2.0142532
O	5.9633411	7.9425495	0.0942801
O	6.4226306	6.9966854	2.3864007
Mn	-0.4513076	0.0720486	-0.3985360
O	-0.5778494	0.2164778	-2.2533587
O	-1.5719944	0.7724640	-2.8793932

[Mn(TPPS)(O₂)]³⁻ - Triplet

N	-0.6799496	2.0331521	-0.1921605
C	0.2786597	2.9879679	0.1409236
C	-1.8655996	2.7290344	-0.3946019
C	-0.3379224	4.2880586	0.2152379
C	-1.6530993	4.1348605	-0.1598025
C	1.6627715	2.7475145	0.2459559
C	2.2275318	1.4907860	-0.0596198
C	2.5918867	3.8658155	0.5883098
C	2.7376212	4.9911879	-0.2581793
C	3.6491996	6.0090411	0.0613209
C	4.4131577	5.9210098	1.2389342
C	4.2761507	4.8120363	2.0916069
C	3.3784167	3.7858695	1.7623041
C	3.6269076	1.2866675	-0.3334020
C	3.7738102	-0.0160763	-0.7503104
C	2.4760579	-0.6358962	-0.6676055
N	1.5267674	0.3062817	-0.2748396
C	2.2328611	-2.0168054	-0.8193623
C	0.9829196	-2.5937440	-0.5045609
C	3.3570469	-2.9188610	-1.2112001
C	4.4988178	-3.0628499	-0.3887904
C	5.5554992	-3.9019736	-0.7750394
C	5.4850444	-4.6004208	-1.9910794
C	4.3530328	-4.4734443	-2.8183084
C	3.2915039	-3.6457441	-2.4253145

C	0.7892009	-3.9978046	-0.2482245
C	-0.4996923	-4.1516597	0.2088321
C	-1.1253997	-2.8543520	0.1631902
N	-0.1943851	-1.8981054	-0.2407448
C	-2.4988729	-2.6164313	0.3811162
C	-3.0843200	-1.3559655	0.1391535
C	-3.3972541	-3.7423957	0.7761978
C	-4.1036007	-3.6798040	2.0028059
C	-4.9736699	-4.7124848	2.3794411
C	-5.1621392	-5.8148617	1.5250218
C	-4.4791532	-5.8852794	0.2995403
C	-3.5970739	-4.8577116	-0.0705166
C	-4.4998318	-1.1461421	-0.0288071
C	-4.6733759	0.1567620	-0.4376487
C	-3.3705756	0.7705865	-0.4527204
C	-3.1309181	2.1496973	-0.6370130
C	-4.2634180	3.0650679	-0.9666363
C	-4.2520950	3.7942179	-2.1776459
C	-5.2970422	4.6808536	-2.4861095
C	-6.3549919	4.8556000	-1.5801956
C	-6.3787336	4.1397008	-0.3682107
C	-5.3431666	3.2457033	-0.0669034
N	-2.3997051	-0.1726200	-0.1246962
H	0.1723549	5.2142787	0.4984123
H	-2.4265868	4.9070147	-0.2228703
H	4.4003284	2.0583472	-0.2650946
H	4.6942906	-0.5136516	-1.0713268
H	-0.9836028	-5.0750254	0.5424573
H	1.5598516	-4.7681869	-0.3549115
H	-5.2683086	-1.9153976	0.0980646
H	-5.6133817	0.6579634	-0.6895958
H	-3.4256173	3.6539423	-2.8909128
H	-5.2993394	5.2482181	-3.4284030
H	-5.3570407	2.6980166	0.8874626
H	-7.2025481	4.2902856	0.3453797
H	-3.0799192	-4.9076452	-1.0406331
H	-4.6610543	-6.7412369	-0.3665682
H	-3.9618537	-2.8149788	2.6687232
H	-5.5146099	-4.6601557	3.3362148
H	4.5528471	-2.5259251	0.5702970
H	6.4467352	-4.0182395	-0.1411892
H	2.4107708	-3.5401744	-3.0769021
H	4.3097583	-5.0117066	-3.7770184
H	3.2814409	2.9114064	2.4235287
H	4.8864585	4.7516858	3.0048298
H	3.7925083	6.8650160	-0.6144644
H	2.1544598	5.0548161	-1.1892361
S	5.5480164	7.2752625	1.6906805
S	-7.7126468	6.0142649	-1.9504503
S	-6.2710217	-7.1695136	2.0389486
S	6.8404040	-5.7151273	-2.4876290
O	6.2740324	-7.0981305	-2.3052736
O	7.1168755	-5.3692942	-3.9258695
O	7.9825318	-5.4041312	-1.5590551
O	-5.4999170	-7.9015753	3.1047401
O	-6.5121954	-7.9872701	0.7990288
O	-7.5045291	-6.4841547	2.5623480
O	-7.3744271	6.6351792	-3.2786167
O	-7.6951548	6.9888807	-0.8030109
O	-8.9474345	5.1543512	-1.9812492
O	4.6991742	8.2339688	2.4830778
O	6.0269211	7.8402512	0.3809802

O	6.6344246	6.6244552	2.5037064
Mn	-0.4462362	0.0717258	-0.3963125
O	-0.5391764	0.1748449	-2.4332524
O	-1.5357517	0.6377035	-3.0152719

S16. Reaction kinetics of $[\text{Mn}^{\text{II}}\text{TPPS}]^{4-}$ with molecular oxygen in a linear-logarithmic plot.

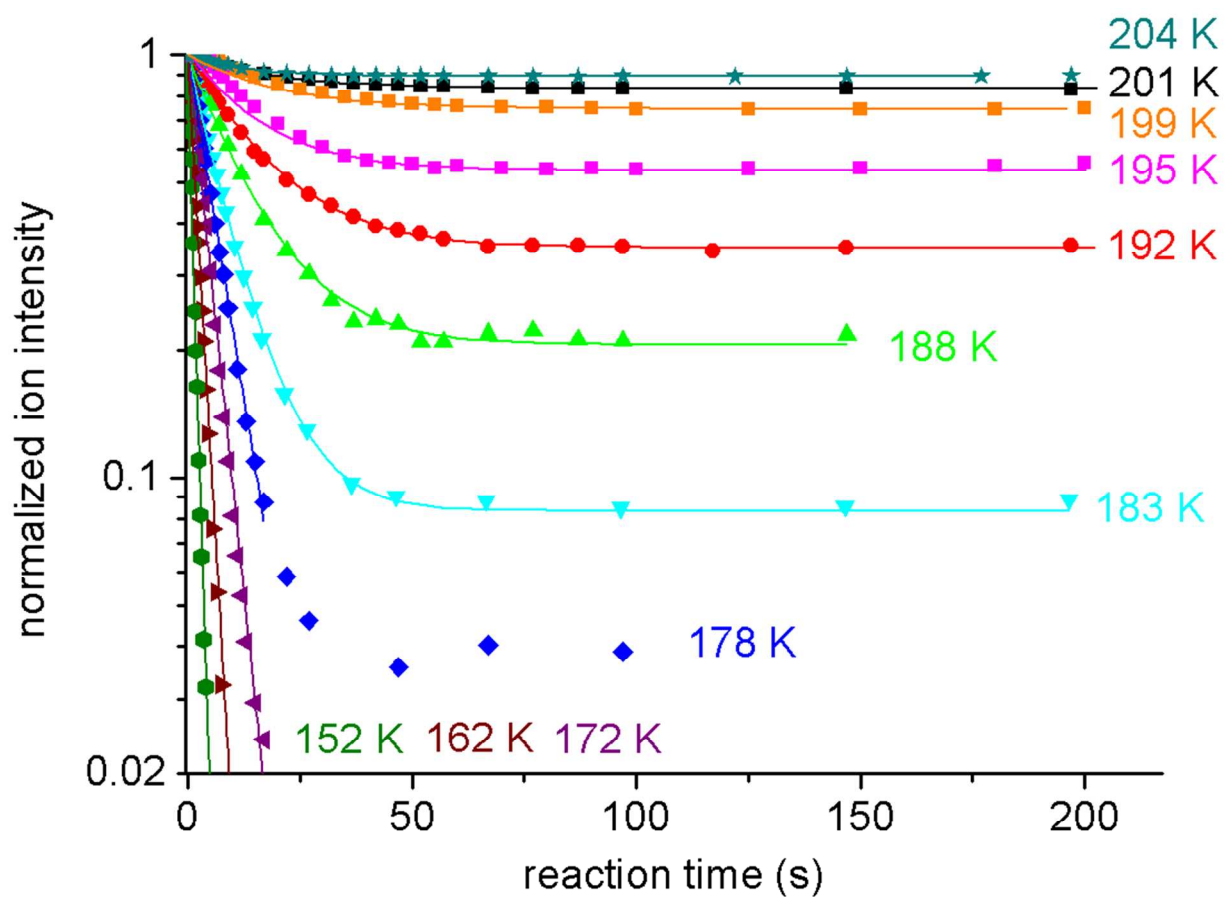


Figure S12: Reaction kinetics of $[\text{Mn}^{\text{II}}\text{TPPS}]^{4-}$ with molecular oxygen in a linear-logarithmic plot (see also figure 4).