Supplementary Information for

Efficient epoxidation of olefins by H_2O_2 catalyzed by iron "helmet" phthalocyanine

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Materials

Solvents and chemicals were obtained from Alfa Aesar and Sigma-Aldrich and used without purification. Aqueous 35 % hydrogen peroxide solution was purchased from Sigma-Aldrich.

Preparation of 14,28-[1,3-diiminoisoindolinato]phthalocyaninatoiron(III) complex (hPcFe) and 14,28-[1,3-diimino-6-tert-butylisoindolinato]tetra-tert-butylphthalocyaninatoiron(III) complex (hPc^{t}Bu$_4$Fe). The complexes were synthesized and purified according to the protocol adapted from ref. S1. Metal iron (300 mg) was dissolved in deoxygenated mixture of 1 mL AcOH and 9 mL H_2O under argon atmosphere. After dissolving of iron, 1 mL of the resulting solution was placed into Schlenk tube and was dried in vacuum at room temperature to obtain 100 mg of white solid $Fe(OAc)_2$ x $4H_2O$. Iron(II) acetate tetrahydrate was dissolved in 2 mL of deoxygenated MeOH and placed into the glass autoclave filled up with Ar. The solution of 1,2-dicyanobenzene (500 mg in 6 mL MeOH) or the solution of 4-*tert*-butyl-1,2-dicyanobenzene (620 mg in 6 mL MeOH) was added to autoclave to obtain hPcFe or hPc^{t}Bu$_4$Fe, respectively. The autoclave was heated at 130^o C during 1 week. The target products were purified by flash column chromatography as described [S1]. The product yields were 19-22%. EPR technique showed the presence of low spin Fe(III) with g factors of 2.192, 2.091, 1.948 for hPcFe and 2.193, 2.148, 1.927 for hPc^{t}Bu$_4$Fe, respectively.

Preparation of oxo species The high-valent oxo complexes hPc^{t}Bu$_4$Fe=O and hPcFe=O were prepared from 10^{-6} M hPc^{t}Bu$_4$Fe and hPcFe solutions by addition of 1000 equiv H_2O_2 at -60°C. The resulting mixtures were incubated at low temperature for 2-3 min and MS analysis was rapidly performed. Among several solvents tested for this preparation

(CH_2Cl_2, CH_3CN, CH_3OH, DMF, acetone and their mixtures) the mixture of MeOH/acetone (8:2, v/v) was found to be the optimal for the formation of hydroperoxo and oxo species accompanied by the lesser protonation.

Equipment and Methods

The mass spectra were recorded in a positive ion mode on a hybrid quadrupole time-of-flight mass spectrometer (MicroTOFQ-II Bruker Daltonics, Bremen) with a Cold Spray Ionization (CSI) ion source. The spray gas pressure was 0,6 bar and dry gas flow was 5 L/min. The CSI temperatures conditions for the analyses were -40°C for the spray gas and 2°C for the dry gas. These conditions permit to keep intact labile complex in the gas phase. The capillary voltage was +4,5 kV. The solutions were infused at 180 µL/h. The mass range of the analysis was 50-1500 m/z and the calibration was done with sodium formate. The UV-vis spectra of solutions were obtained with Agilent 8453 diode-array spectrophotometer. Low temperature UV-vis studies were carried out using liquid nitrogen cooled cryostat and a C Technologies immersion probe (5 mm path length) and fiber-optic cable. EPR spectra were recorded on a Bruker ER-200D in 3 mm quartz tube; conditions : -196°C, microwave frequency 9.3-9.4 GHz, modulation frequency 100 kHz, modulation amplitude 5 G.

The reaction products were identified by GC-MS method (Hewlett Packard 5973/6890 system ; electron impact ionization at 70 eV, He carrier gas, 30m x 0.25 mm HP-INNOWax capillary column, polyethylene glycol (0.25 µm coating) or DB-5MS 50 m capillary column (0.250 mm x 0.25 µm).

Computational details. Geometry optimization of hFePc-tBu structure with ***S***=1/2 followed by numerical frequencies calculation was performed with ORCA 2.9.0 program [S2]. Central differences were used in numerical frequencies calculation. All computation were done using BP density functional, TZVP [S3] basis set on iron and VDZP [S2] basis set on other atoms. Relativistic corrections were treated by using the ZORA [S4] approximation. The convergence criteria for the SCF part are chosen to be 10^{-8} Hartree (Eh) in energy, 10^{-7} Eh for the change of elements of the density matrix and $5 \cdot 10^{-7}$ Eh for the maximum element of the direct inversion of iterative subspace (DIIS) error. Geometry is considered to be converged when the change in energy is less than 10^{-6} Eh, the average force is smaller than $3 \cdot 10^{-5}$ Eh·bohr^{-1}, and the maximum force is smaller than 10^{-4} Eh·bohr^{-1}. The optimized Cartesian coordinates in angstroms and vibrational frequencies are presented in Table S1.

Table S1. Optimized Cartesian coordinates and vibrational frequencies calculated for hPc^{t}Bu$_4$Fe.

Atom	X	Y	Z
Fe	3.891564	7.167124	12.672542
N	4.840120	6.021081	11.525362
N	3.022996	5.098965	10.202566
N	2.343572	6.866674	11.683061
N	0.700070	8.073357	13.068998
N	2.859807	7.711016	14.145925

N	4.582823	7.941738	15.843417
N	5.444354	7.501293	13.642773
N	7.136118	6.641801	12.068719
N	1.783454	9.197899	11.237720
N	4.108597	8.742171	11.822461
N	6.529149	8.971977	12.029525
C	6.257981	5.886180	11.501857
C	6.575298	4.747607	10.605380
C	7.797570	4.162709	10.259058
H	8.719280	4.559413	10.704608
C	7.808730	3.082008	9.346895
C	6.567439	2.641243	8.811011
H	6.560768	1.802712	8.097697
C	5.340379	3.235666	9.147606
H	4.393406	2.884999	8.711767
C	5.357246	4.297282	10.060263
C	4.284856	5.153777	10.606425
C	2.139723	6.011174	10.673541
C	0.803805	6.241381	10.089756
C	0.118247	5.564107	9.071256
H	0.599495	4.700488	8.593715
C	-1.166617	6.012267	8.693005

C	-1.704343	7.140970	9.366437
H	-2.705837	7.503940	9.087282
C	-1.008187	7.827008	10.379501
H	-1.447863	8.704285	10.876280
C	0.257156	7.362682	10.734494
C	1.280074	7.901469	11.738416
C	1.458014	7.962675	14.106537
C	1.013250	8.184890	15.504769
C	-0.249746	8.434583	16.040941
H	-1.118024	8.467961	15.366027
C	-0.382902	8.641839	17.438025
C	0.787372	8.595572	18.237142
H	0.707655	8.756670	19.320809
C	2.065292	8.355622	17.695594
H	2.961515	8.335608	18.332931
C	2.165837	8.145318	16.317973
C	3.322643	7.905049	15.431857
C	5.578172	7.841130	14.930996
C	6.991411	8.157465	15.216452
C	7.632941	8.490605	16.417907
H	7.039431	8.530835	17.340727
C	9.018973	8.761789	16.403778

C	9.700512	8.687918	15.160164
H	10.781928	8.893550	15.129463
C	9.051274	8.365635	13.953393
H	9.605379	8.323806	13.004221
C	7.683608	8.100481	13.996055
C	6.688494	7.773041	12.879305
C	3.048327	9.484249	11.279690
C	3.673889	10.699787	10.697976
C	3.121841	11.801612	10.035076
H	2.034191	11.877996	9.890321
C	3.996120	12.795672	9.567135
H	3.564532	13.664846	9.047148
C	5.405784	12.721870	9.737570
C	5.939599	11.599228	10.409838
H	7.017493	11.477928	10.579528
C	5.071585	10.605873	10.877011
C	5.355453	9.354237	11.629147
C	6.298683	13.856586	9.189607
C	-1.990266	5.322479	7.582728
C	9.114608	2.377607	8.919370
C	9.802799	9.134089	17.681904
C	-1.781978	8.912728	18.032819

C	-1.742251	9.115319	19.561494
C	-2.707437	7.707550	17.724243
C	-2.369925	10.193865	17.386599
C	-2.286501	6.343799	6.454636
C	-1.240305	4.123880	6.965992
C	-3.325589	4.807672	8.178144
C	9.041523	0.880590	9.316312
C	9.282184	2.498026	7.382759
C	10.355490	2.998807	9.593066
C	8.895968	9.162688	18.929288
C	10.924963	8.091638	17.919772
C	10.432067	10.539666	17.504869
H	9.494427	9.433499	19.822970
H	8.431901	8.175045	19.126673
H	8.083656	9.911481	18.833760
H	11.640184	8.051684	17.073782
H	10.502452	7.074608	18.051778
H	11.501483	8.345350	18.834073
H	11.005747	10.824801	18.411661
H	11.128277	10.576058	16.643017
H	9.649546	11.307835	17.338045
H	-3.935709	4.314328	7.392634

H	-3.932923	5.630333	8.606193
H	-3.142966	4.069029	8.985223
H	-2.881507	5.867699	5.647229
H	-1.346513	6.727229	6.007898
H	-2.862496	7.215421	6.825175
H	-1.862849	3.656953	6.175702
H	-0.283362	4.431019	6.497297
H	-1.018473	3.341588	7.720000
H	-2.464837	10.097380	16.286630
H	-1.729107	11.075169	17.593592
H	-3.381500	10.401530	17.793861
H	-1.117114	9.985107	19.849474
H	-2.767075	9.305019	19.940350
H	-1.354672	8.220295	20.089656
H	-3.723643	7.886996	18.133362
H	-2.314047	6.775683	18.179320
H	-2.810720	7.533010	16.634675
H	9.971031	0.355239	9.012471
H	8.190423	0.363130	8.829821
H	8.924791	0.764210	10.413092
H	11.269439	2.467155	9.258639
H	10.478439	4.068840	9.329530

H	10.310905	2.919558	10.698173
H	8.439543	2.030555	6.834888
H	9.339767	3.560582	7.070077
H	10.215118	1.993030	7.055862
C	7.794527	13.602939	9.467898
C	5.897512	15.194500	9.862564
C	6.100127	13.969045	7.656098
H	6.383134	13.024975	7.147411
H	5.047991	14.193456	7.388889
H	6.731569	14.783770	7.243860
H	6.526538	16.024094	9.477132
H	4.839000	15.457744	9.664935
H	6.032854	15.143798	10.962214
H	8.008933	13.536549	10.553767
H	8.152746	12.669188	8.989020
H	8.398891	14.438671	9.060138

Vibrational frequencies, cm^{-1}

12.42	380.73	857.00	1188.70	1482.65
16.26	385.49	873.94	1202.68	1484.75
19.10	389.78	898.02	1204.80	1525.18
21.05	395.25	898.53	1222.87	1525.88
24.47	396.67	900.52	1224.79	1587.76

26.07	398.37	901.65	1226.96	1590.15
28.13	406.99	902.01	1235.79	1597.79
32.24	418.89	904.73	1238.21	1598.78
38.82	423.11	904.80	1250.48	1599.71
39.61	424.70	905.03	1251.21	1600.20
50.85	432.17	906.34	1253.39	1619.21
52.87	434.44	906.41	1255.78	1620.22
55.72	437.38	907.61	1256.89	1620.79
57.86	441.92	909.18	1289.01	1620.96
60.89	444.06	911.95	1311.75	1621.15
72.16	444.99	912.26	1314.53	1622.60
77.65	450.93	912.51	1330.74	1649.14
92.22	457.80	913.12	1331.11	1654.25
93.74	462.91	913.33	1331.14	2953.15
97.33	467.20	915.83	1331.27	2953.23
107.34	508.08	918.44	1331.73	2954.03
122.93	515.51	918.67	1333.47	2954.51
128.64	517.63	918.87	1333.94	2954.53
134.86	522.19	919.39	1334.15	2954.55
143.09	523.19	919.86	1335.53	2954.92
147.40	525.82	931.79	1335.81	2955.09
154.17	532.53	946.98	1358.98	2955.44

161.75	533.03	948.88	1361.23	2955.79
175.26	538.33	949.36	1362.51	2959.99
178.66	552.29	956.96	1362.58	2960.03
181.43	563.24	959.79	1362.79	2960.29
190.20	570.57	960.97	1363.12	2960.86
201.43	582.12	960.98	1364.07	2961.19
205.73	586.51	972.62	1367.19	3038.24
207.13	596.22	992.62	1369.06	3038.32
220.40	599.94	997.62	1369.20	3039.22
222.66	609.74	998.97	1371.29	3039.23
223.57	612.45	999.41	1375.06	3039.41
225.52	615.29	999.69	1404.47	3040.09
228.99	622.85	1000.03	1404.51	3040.34
231.65	646.32	1001.59	1404.76	3040.36
235.11	653.80	1001.77	1404.80	3040.59
235.32	664.57	1001.79	1404.93	3040.96
240.10	671.11	1001.95	1410.19	3043.89
244.03	673.38	1002.04	1410.31	3043.94
248.78	676.09	1010.17	1410.34	3044.98
254.55	686.48	1031.18	1410.57	3045.14
256.27	689.92	1042.16	1410.67	3045.23
266.77	690.99	1048.68	1411.80	3045.66

269.52	696.71	1057.31	1412.28	3046.73
269.82	699.63	1065.56	1412.54	3047.02
270.68	710.82	1069.72	1412.61	3048.20
272.25	712.68	1071.35	1412.85	3048.26
274.07	733.45	1085.99	1427.38	3049.96
280.60	737.27	1090.64	1428.55	3049.98
283.22	745.19	1092.47	1428.72	3050.67
288.53	748.12	1099.59	1428.90	3050.89
301.52	754.14	1100.72	1429.10	3051.12
309.82	755.35	1114.92	1429.74	3051.33
313.13	756.98	1116.45	1430.62	3051.86
318.48	769.40	1133.27	1431.50	3052.02
320.53	777.79	1137.60	1431.72	3052.42
321.50	780.89	1143.40	1431.81	3054.07
322.08	788.42	1158.35	1432.10	3099.38
322.30	791.24	1170.76	1432.24	3099.42
322.99	799.36	1172.90	1432.30	3102.54
324.21	803.27	1174.86	1436.23	3103.54
328.09	805.43	1176.78	1440.89	3117.46
333.42	808.42	1178.68	1441.24	3122.04
339.96	819.49	1182.09	1441.70	3126.29
342.17	823.23	1182.71	1445.01	3126.33

344.69	825.35	1182.91	1445.45	3128.25
346.00	832.48	1183.79	1445.84	3128.35
349.36	833.43	1184.07	1453.31	3137.06
358.08	834.07	1185.15	1453.58	3141.95
366.01	834.41	1185.32	1463.44	3142.01
369.14	840.86	1185.42	1464.32	3143.98
375.55	844.20	1185.63	1466.66	3144.08

The geometry of the iron coordination sphere computed for hPc^{t}Bu$_4$Fe is close to those obtained for unsubstituted hFePc complex by X-ray structural determination [S1]. Thus, the lengths of the Fe-N bonds in the distorted phthalocyanine ring according to X-ray data are 1.906, 1.903, 1.873 and 1.870 Å while computed values are 1.879, 1.879, 1.861 and 1.861 Å, respectively. The length of the bond between iron and fifth nitrogen of the isoindole fragment is 1.866 Å from X-ray data in non-substituted complex and 1.803 Å from the computation for the helmet phthalocyanine bearing *tert*-butyl substituents. Such a big difference might occur, most probably, because of the presence of methanol ligand in hPcFe crystal and the absence of the sixth ligand in the model structure of hPc^{t}Bu$_4$Fe.

References

S1. H. M. Kieler, M. J. Bierman, I. A. Guzei, P. J. Liska and R. W. McGaff, *Chem. Commun.* 2006, 3326-3328.

S2. ORCA, Version 2.9.0, January 2012, An ab initio, DFT and semiempirical SCF-MO package – written by F. Neese, with contributions from U. Becker, D. Bykov, D.

Ganyushin, A. Hansen, R. Izsak, D.G. Liakos, C. Kollmar, S. Kossmann, D.A. Pan-tazis, T. Petrenko, C. Reimann, C. Riplinger, M. Roemelt, B. Sandhöfer, I. Schapiro, K. Sivalingam, F. Wennmohs, B. Wezisla and contributions from our collabora-tors: M. Kállay, S. Grimme, E. Valeev. http://www.thch.uni-bonn.de/tc/orca/

S3. A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.* 1992, 97, 2571.

S4. M. Filatov, *Chem. Phys. Lett.* 2002, 365, 222.