A DFT and Multi-configurational Perturbation Theory Study on O_2 Binding to a Model Heme Compound via the Spin-change Barrier

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Electronic Supplementary Information

S1. Search for a DFT Functional to calculate potential energy curves of O_2 binding

In this study, we want to investigate potential energy surface of the O_2 binding over wide reaction coordinate space. For this purpose, DFT is an attractive choice because of the high through-put performance. However, examination of exchange-correlation functionals for this particular case is essential for the DFT studies. One of the criteria would be provided by comparing calculations in previous studies. According to our biblographic knowledge, there is only one paper reporting CASPT2 calculations for the potential energy curve of the O_2 binding.{Ribas-Arino, 2007 #208} They performed single-point CASPT2 calculations with the BP86-optimized structures for the singlet ground state. Therefore, we performed relaxed potential energy scan calculations with the BP86 functional in the same way as this previous study. Next, we performed single-point DFT calculations for singlet and triplet states with various functionals to check if the results are close to the previous CASPT2 results for the singlet and triplet states.

The results are shown in Figure S1. BP86 gives energy minimum at Fe-O distance of 1.8 Å for the singlet state (see Figure S1a). However, BP86 calculation for triplet state shows a discontinuity at around 2.0 – 2.2 Å. Existence of several low-lying triplet states causes a difficulty in following the potential curve. The ωB97XD, M06, BHandH, and PBE0 functionals gave very flat potential curves. On the other hand, B3LYP*, TPSSH, and B97D gave energy minimum at around 1.8 Å in the singlet curve. In the previous CASPT2 curve for the triplet ground state,{Ribas-Arino, 2007 #208} an energy minimum was found at about 2.5 Å. Even though B3LYP* and TPSSH gave very repulsive potential curves for the triplet state, B97D curve have a minimum at 2.2 Å. In this point, although the energy of the singlet ground state is much lower than that of the triplet state, B97D worked better because the energy minimum Fe-O distance was reproduced qualitatively.

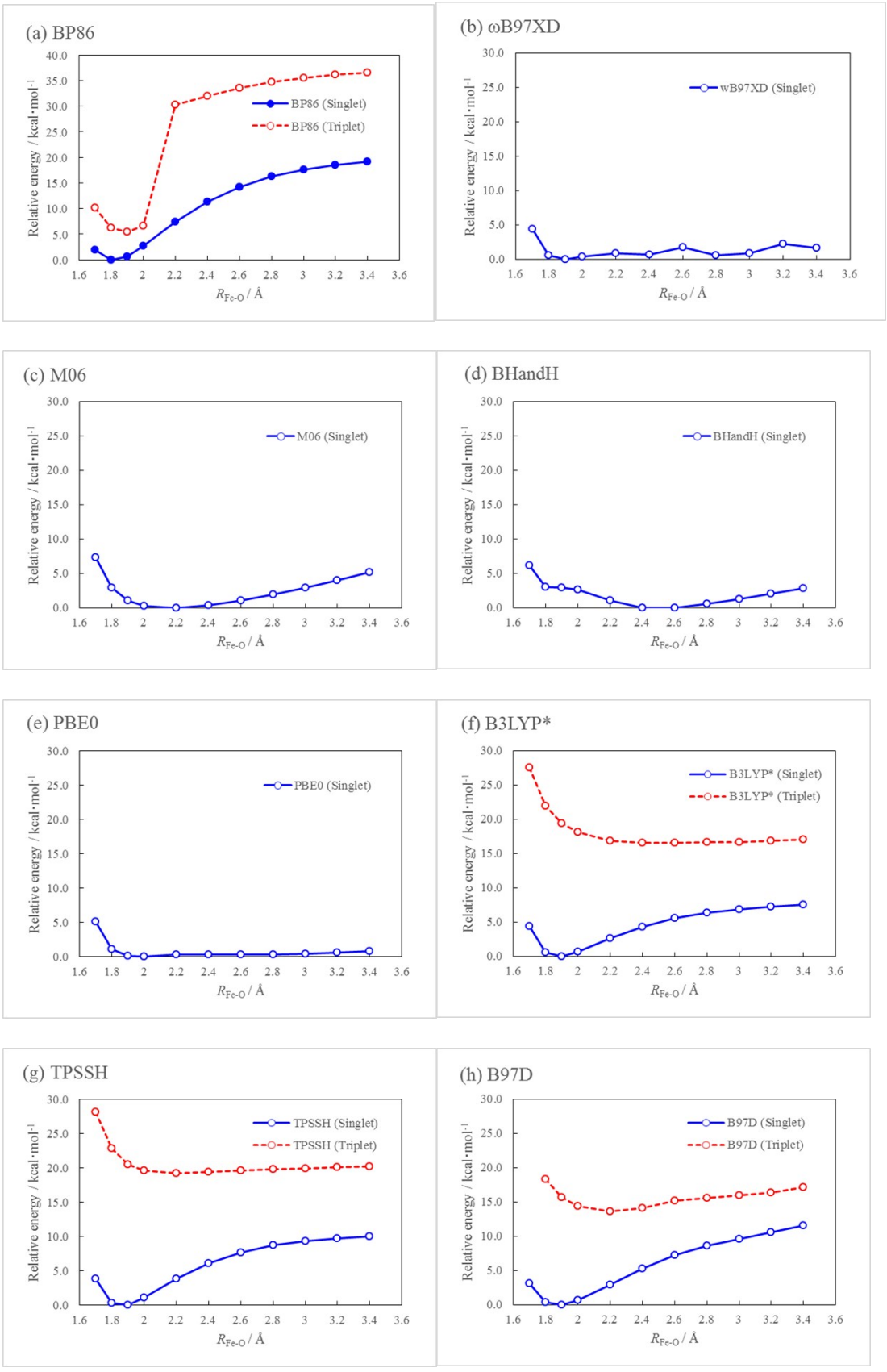

(a) BP86
BP86 (Singlet)
BP86 (Triplet)
(b) ωB97XD
wB97XD (Singlet)
(c) M06
M06 (Singlet)
(d) BHandH
BHandH (Singlet)
(e) PBE0
PBE0 (Singlet)
(f) B3LYP*
B3LYP* (Singlet)
B3LYP* (Triplet)
(g) TPSSH
TPSSH (Singlet)
TPSSH (Triplet)
(h) B97D
B97D (Singlet)
B97D (Triplet)
Relative energy / kcal·mol-1
RFe-O / Å

Figure S1. Potential energy curves for O_2 binding to the FePorIm complex. Relaxed potential energy scan calculations with Fe-O distance as the reaction coordinate.

S2. Two dimensional potential energy surface calculated at the B3LYP/cc-pVDZ level

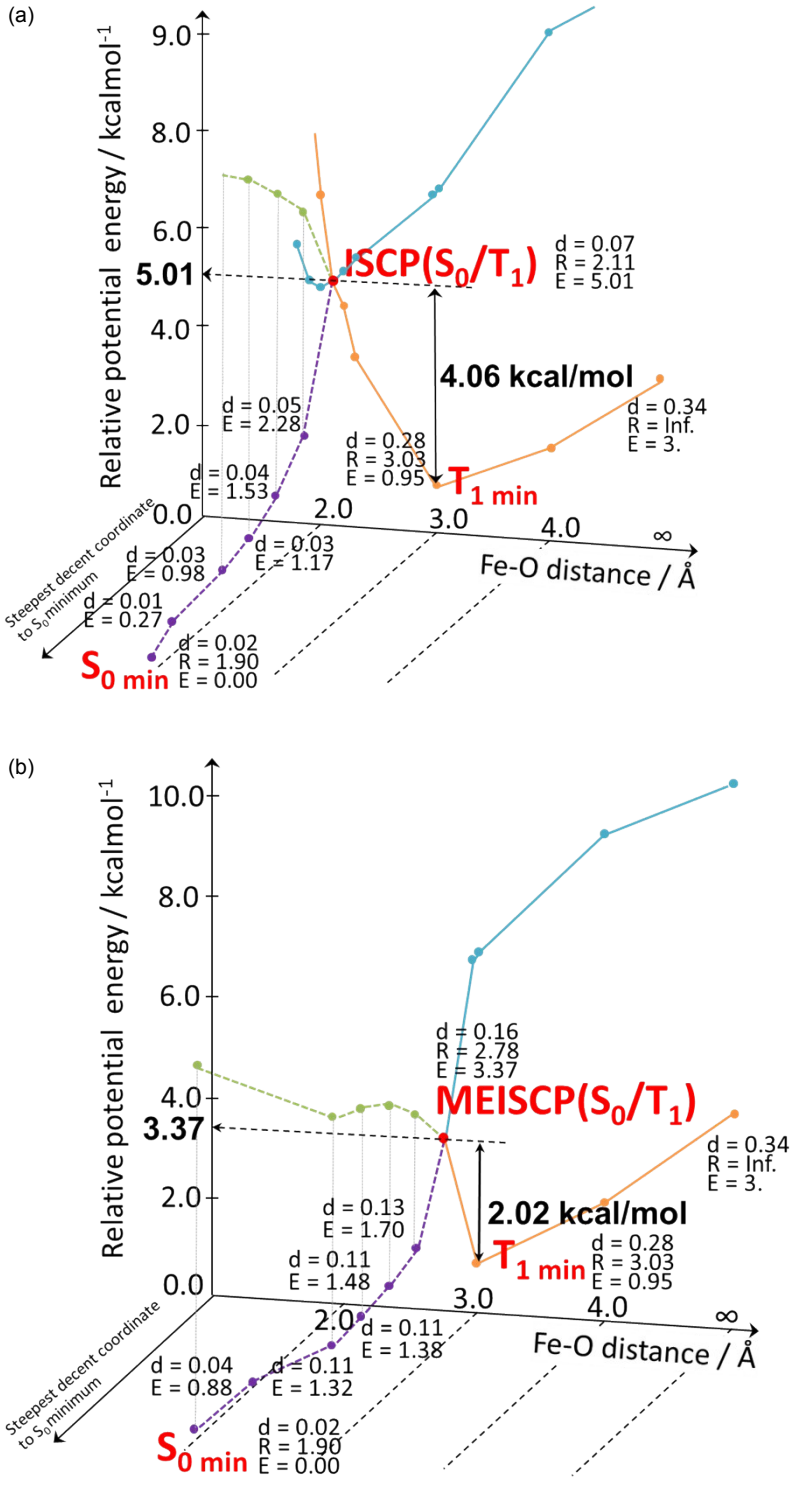


Figure S2. Two dimensional potential energy curves for O_2 binding calculated at the B3LYP/cc-pVDZ level. (a) Intersystem crossing pathway along the Fe-O fixed coordinate and (b) that via the

MEISC point. The orange plots denote potential curve of the T_1 state to which the structures were optimized. Blue plots denote the S_0 state obtained by the single-point calculation at the triplet geometry. Purple plots were S_0 states along the steepest decent pathway. Green plots were T_1 state obtained with the single-point calculation at the S_0 structures.

S3. Atomic coordinates of optimized structures

S0 minimum structure

C	0	-0.558808	0.011924	-4.139397
C	0	-1.011389	0.023697	-2.842252
C	0	1.162372	-0.031835	-2.727349
N	0	0.068190	-0.003727	-1.983968
C	0	0.146292	3.413108	0.027170
C	0	-3.416455	0.118184	0.064225
C	0	1.361209	2.734530	0.070699
C	0	2.655191	3.379574	0.083397
C	0	3.591906	2.384716	0.135654
C	0	2.865990	1.134161	0.150682
C	0	2.779423	-1.335092	0.149906
C	0	3.415991	-2.633320	0.133990
C	0	2.411960	-3.560179	0.081357
C	0	1.166312	-2.826155	0.069444
C	0	-1.307034	-2.736011	0.028780
C	0	-2.600486	-3.381396	0.009858
C	0	-3.539145	-2.387629	0.033636
C	0	-2.816029	-1.137086	0.061092
C	0	-2.729617	1.328358	0.060587
C	0	-3.363364	2.626380	0.032498
C	0	-2.357456	3.552042	0.008820
C	0	-1.112374	2.817745	0.028398
N	0	1.509364	1.367178	0.111385
N	0	1.409754	-1.472649	0.110895
N	0	-1.457559	-1.368209	0.058155
N	0	-1.358241	1.463937	0.058087
Fe	0	0.013501	-0.001995	0.121034
O	0	0.055121	-0.002927	2.027391
O	0	-1.020226	0.032153	2.700093
H	0	-2.021985	0.049528	-2.460447
H	0	2.174785	-0.057688	-2.349119
H	0	0.182819	4.499714	0.002816
H	0	-4.503023	0.156263	0.066018
H	0	4.488111	-2.794053	0.162914
H	0	-2.750635	-4.455366	-0.008725
H	0	4.672637	2.470027	0.164981
H	0	2.807225	4.453272	0.062710
H	0	-4.620073	-2.473670	0.034827
H	0	2.488484	-4.641870	0.059929
H	0	-4.435619	2.787857	0.033244
H	0	-2.432086	4.633883	-0.010103
H	0	-1.069946	0.024806	-5.091123
C	0	-0.093183	-3.418013	0.026626
C	0	3.465257	-0.122995	0.172395
H	0	-0.132840	-4.504505	0.002070
H	0	4.551546	-0.161084	0.204815
N	0	0.826443	-0.023415	-4.047309
H	0	1.474640	-0.040122	-4.822121

T1 minimum structure

C	0	-0.332232	0.421596	-4.451242
C	0	-0.685412	0.734520	-3.160639
C	0	0.894565	-0.755535	-3.013520

N	0	0.084440	-0.003720	-2.284150
C	0	-0.103826	3.468122	0.078971
C	0	-3.422700	-0.091284	0.040407
C	0	1.176903	2.886922	0.116153
C	0	2.426315	3.611752	0.148663
C	0	3.432137	2.674073	0.164354
C	0	2.796882	1.376556	0.141907
C	0	2.889046	-1.135040	0.108902
C	0	3.616420	-2.392996	0.151719
C	0	2.683056	-3.394184	0.139928
C	0	1.377871	-2.755993	0.089659
C	0	-1.134088	-2.839148	0.092936
C	0	-2.384118	-3.563532	0.097574
C	0	-3.389507	-2.625467	0.082787
C	0	-2.753407	-1.328465	0.068500
C	0	-2.844525	1.182426	0.023233
C	0	-3.572897	2.440590	0.053228
C	0	-2.639916	3.440998	0.064235
C	0	-1.333686	2.802488	0.041355
N	0	1.430703	1.535293	0.121190
N	0	1.536136	-1.388132	0.055298
N	0	-1.387468	-1.487245	0.082589
N	0	-1.491078	1.435050	-0.001398
Fe	0	0.023989	0.025353	-0.136601
O	0	-0.085381	0.081645	2.777452
O	0	-0.896081	-0.640338	3.335059
H	0	-1.428379	1.428524	-2.792545
H	0	1.624652	-1.448707	-2.618809
H	0	-0.140844	4.555793	0.097239
H	0	-4.510380	-0.130818	0.048598
H	0	4.696354	-2.484125	0.203536
H	0	-2.477844	-4.644279	0.112809
H	0	4.503500	2.842970	0.190984
H	0	2.519360	4.692599	0.159412
H	0	-4.461273	-2.793610	0.083117
H	0	2.849027	-4.465670	0.180012
H	0	-4.653713	2.531224	0.079373
H	0	-2.806110	4.512482	0.101250
H	0	-0.686232	0.769605	-5.410939
C	0	0.146595	-3.421141	0.093266
C	0	3.466588	0.139447	0.134212
H	0	0.182398	-4.508832	0.115240
H	0	4.553882	0.179073	0.167360
N	0	0.674443	-0.528176	-4.338324
H	0	1.160492	-0.974075	-5.103880

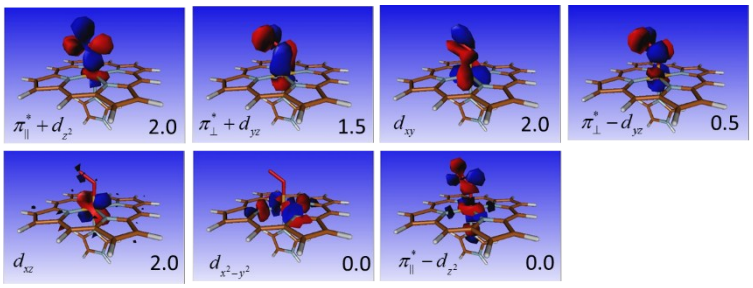
(s0/t1)_MEISCP

C	0	-0.358887	0.452405	-4.245722
C	0	-0.689833	0.757076	-2.947203
C	0	0.865133	-0.760908	-2.836630
N	0	0.078173	-0.003450	-2.088816
C	0	0.077369	3.442753	0.104039
C	0	-3.416271	0.053522	0.024745
C	0	1.322411	2.799351	0.128692
C	0	2.607111	3.462600	0.137275
C	0	3.563364	2.477895	0.144643
C	0	2.860521	1.214102	0.141981
C	0	2.815419	-1.286137	0.127307
C	0	3.479230	-2.576334	0.121892
C	0	2.496212	-3.528597	0.110518
C	0	1.226739	-2.826535	0.107554
C	0	-1.274666	-2.795913	0.074428
C	0	-2.559521	-3.458953	0.047202
C	0	-3.515067	-2.473832	0.027495
C	0	-2.811680	-1.210633	0.042974

C	0	−2.763794	1.288612	0.041387
C	0	−3.428661	2.578506	0.031801
C	0	−2.447216	3.530691	0.054801
C	0	−1.177492	2.828467	0.078447
N	0	1.505107	1.438748	0.136375
N	0	1.449967	−1.467982	0.113532
N	0	−1.457038	−1.435174	0.074790
N	0	−1.398573	1.470149	0.066267
Fe	0	0.023936	0.001937	0.062807
O	0	0.052165	−0.030108	2.229171
O	0	−0.999736	0.092835	2.878537
H	0	−1.415465	1.460549	−2.564537
H	0	1.587719	−1.472384	−2.462890
H	0	0.088894	4.530720	0.107045
H	0	−4.503856	0.075657	0.004332
H	0	4.554532	−2.718099	0.136559
H	0	−2.703380	−4.534187	0.047354
H	0	4.642363	2.588472	0.154464
H	0	2.750069	4.537931	0.138095
H	0	−4.593964	−2.583681	0.007906
H	0	2.604685	−4.607988	0.112972
H	0	−4.504071	2.718825	0.017765
H	0	−2.555894	4.609938	0.064746
H	0	−0.719426	0.817997	−5.196419
C	0	−0.029533	−3.439624	0.088522
C	0	3.466869	−0.049465	0.136538
H	0	−0.041708	−4.527668	0.088098
H	0	4.554714	−0.070182	0.146725
N	0	0.631349	−0.515996	−4.156500
H	0	1.098631	−0.963864	−4.932400

S4. B97D natural orbital and occupation number at S_0 and T_1 minimum structures

(a) S_0 minimum structure



(b) T_1 minimum structure