Electronic Supplementary Information – First-principles study of molecular hydrogen binding to heme in competition with O_2, NO and CO

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Table S1. DFT total energy with BSSE correction (E_{tot}), zero-point correction (ZPC), thermal correction (TC) at T = 298.15 K, corrected energy (E_{corr}), and binding energy (E_b) in heme-DM and -H compounds, where heme is modeled by FePIm, model1 and model2, and DM is the diatomic molecule including H_2, O_2, CO and NO.

Compound	E_{tot} (Ha)	ZPC (Ha)	TC (Ha)	E_{corr} (Ha)	E_b (kcal/mol)
H_2	-1.176632	0.010005	0.012365	-1.154262	
H	-0.502156	0.000000	0.001416	-0.500740	
O_2	-150.259125	0.003268	0.005634	-150.250223	
NO	-129.8476059	0.004113	0.006474	-129.837019	
CO	-113.2968119	0.004698	0.007058	-113.285056	
FePIm	-1338.060830	0.352659	0.373323	-1337.334848	
FePIm–H_2	-1339.236939	0.366917	0.388574	-1338.481448	4.81
FePIm–H	-1338.576458	0.352596	0.371451	-1337.852411	-10.56
FePIm–O_2	-1488.366061	0.356994	0.380552	-1487.628515	-27.26
FePIm–NO	-1467.959639	0.357856	0.384960	-1467.216823	-28.21
FePIm–CO	-1451.388226	0.359755	0.381953	-1450.646518	-16.70
Model1	-633.717745	0.210840	0.222177	-633.284728	
Model1–H_2	-634.891674	0.224678	0.237182	-634.429814	5.76
Model1–H	-634.294379	0.212841	0.224541	-633.856997	-44.88
Model1–O_2	-784.030127	0.214435	0.228789	-783.586903	-32.60
Model1–NO	-747.047297	0.211937	0.225905	-746.609455	-24.89
Model1–CO	-763.612595	0.227394	0.231292	-763.153909	-20.18
Model2	-478.839191	0.134294	0.144397	-478.560500	
Model2–H_2	-480.022099	0.155162	0.165269	-479.701668	8.22
Model2–H	-479.426759	0.142606	0.152690	-479.131463	-44.07
Model2–O_2	-629.169228	0.142870	0.154465	-628.871893	-38.38
Model2–NO	-592.182366	0.135053	0.145059	-591.902254	-35.58
Model2–CO	-608.753853	0.147444	0.158951	-608.447458	-31.34

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Table S2. Mulliken charges of ligand (side ligand (porphyrin, vinylogous amidine $C_3H_5N_2^-$, amidine $CH_3N_2^-$) plus Im or NH_3 ligand), Fe, and DM (H_2, O_2, NO, CO) or H in heme-DM or H compounds.

Compound	Ligand	Fe	DM or H
FePIm	-1.046	1.046	
FePIm–H_2	-1.040	0.901	0.139
FePIm–H	-0.829	0.769	0.060
FePIm–O_2	-0.822	1.104	-0.282
FePIm–NO	-0.913	0.983	-0.070
FePIm–CO	-0.969	0.831	0.138
Model1	-0.884	0.884	
Model1–H_2	-0.845	0.709	0.136
Model1–H	-0.688	0.466	0.222
Model1–O_2	-0.578	0.923	-0.345
Model1–NO	-0.766	0.870	-0.104
Model1–CO	-0.722	0.641	0.080
Model2	-0.719	0.719	
Model2–H_2	-0.664	0.480	0.184
Model2–H	-0.510	0.396	0.114
Model2–O_2	-0.334	0.725	-0.391
Model2–NO	-0.451	0.609	-0.157
Model2–CO	-0.521	0.471	0.050

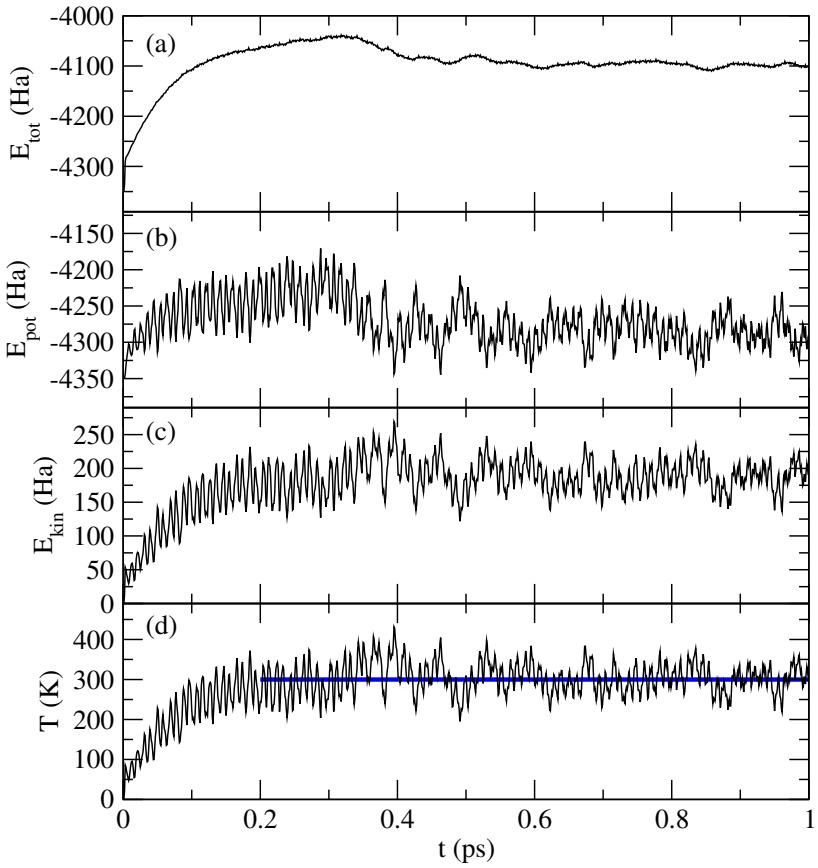

Fig. S1 (a) Total energy (E_{tot}), (b) potential energy (E_{pot}), (c) kinetic energy (E_{kin}), and (d) temperature (T) along the QMD simulation time (t) in FePIm–$H_2 \cdots$NO system.

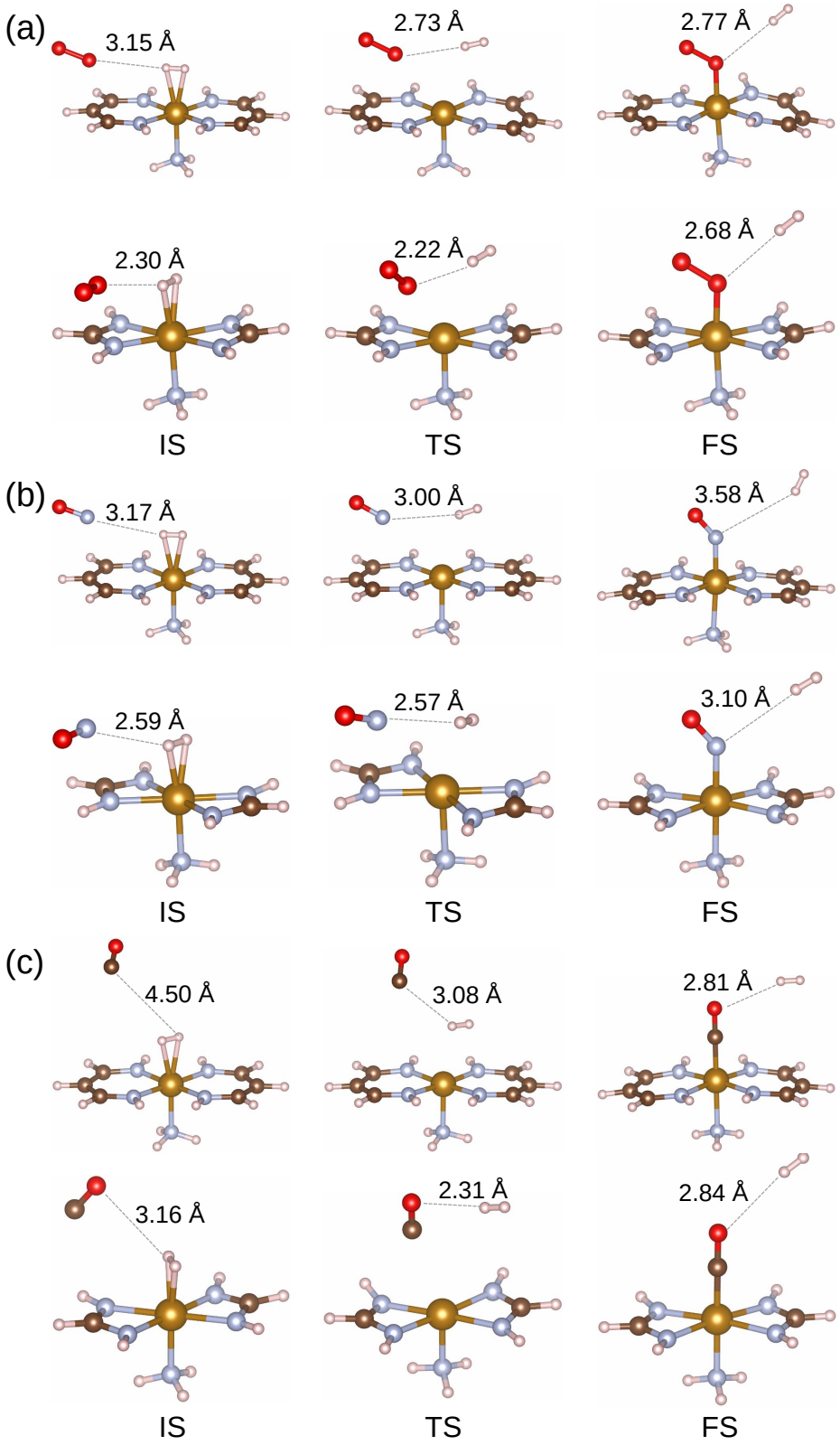

Fig. S2 Optimized geometries of molecular complexes composed of heme with model1 (top) and model2 (bottom), H_2 molecule, and diatomic molecule including (a) O_2, (b) NO, and (c) CO, corresponding to initial state (IS), transition state (TS) and final state (FS).

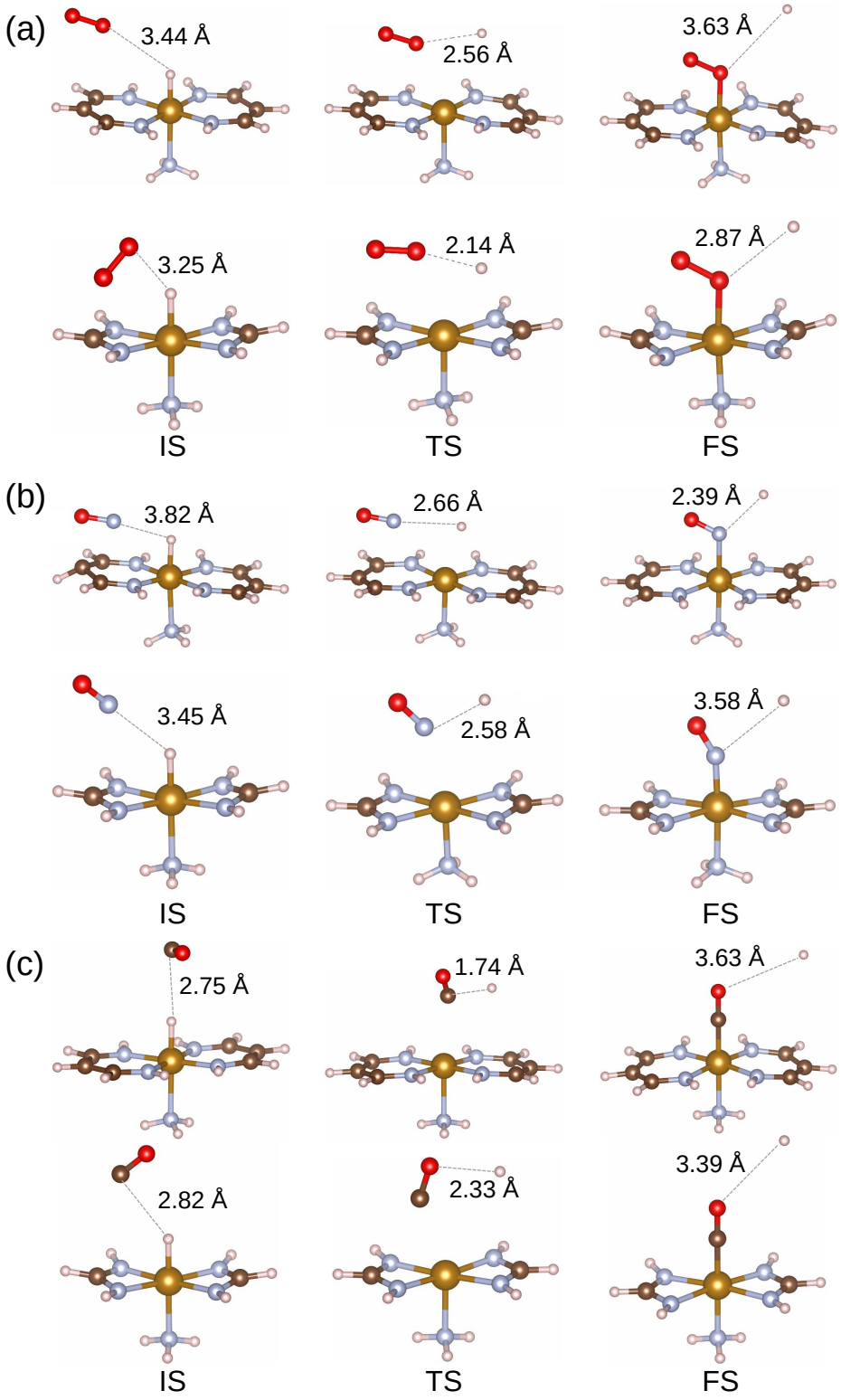

Fig. S3 Optimized geometries of molecular complexes composed of heme with model1 (top) and model2 (bottom), H atom, and diatomic molecule including (a) O_2, (b) NO, and (c) CO, corresponding to initial state (IS), transition state (TS) and final state (FS).