Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Spin State Preference and Bond Formation/Cleavage Barriers in Ferrous-Dioxygen Heme Adducts: Remarkable Dependence on Methodology

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Table S1. Computed geometrical parameters for all dioxygen-bound models (first scanning step//last scanning step) using the M06-2X functional.

Complex	Fe-S	Fe-N_{axial}	Fe-O	O-O
S=0 $[Fe(Im)(Por)(OO)]^{0}$	-	2.03//1.98	1.84//3.84	1.21//1.20
S=1 $[Fe(Im)(Por)(OO)]^{0}$	-	2.06//2.20	1.87//4.07	1.29//1.19
S=2 $[Fe(Im)(Por)(OO)]^{0}$	-	2.38//2.16	1.88//3.88	1.29//1.19
S=3 $[Fe(Im)(Por)(OO)]^{0}$	-	2.32//2.24	2.06//3.86	1.29//1.21
S=0 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.37//2.36	-	1.81//3.41	1.24//1.21
S=1 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.33//2.48	-	1.92//3.52	1.30//1.19
S=2 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.36//2.41	-	1.98//3.58	1.28//1.19
S=3 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.47//2.42	-	2.05//3.65	1.30//1.19

Table S2. Computed geometrical parameters for all dioxygen-bound models (first scanning step//last scanning step) using the M06L functional.

Complex	Fe-S	Fe-N_{axial}	Fe-O	O-O
S=0 $[Fe(Im)(Por)(OO)]^{0}$	-	2.07//1.89	1.75//3.55	1.27//1.24
S=1 $[Fe(Im)(Por)(OO)]^{0}$	-	2.01//1.89	1.85//3.65	1.26//1.22
S=2 $[Fe(Im)(Por)(OO)]^{0}$	-	2.34//2.19	1.91//3.71	1.27//1.22
S=3 $[Fe(Im)(Por)(OO)]^{0}$	-	2.22//2.13	2.19//3.79	1.26//1.22
S=0 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.33//2.37	-	1.79//3.59	1.28//1.26
S=1 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.32//.23	-	1.90//3.50	1.28//1.24
S=2 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.42//2.33	-	2.00//3.60	1.28//1.24
S=3 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.37//2.33	-	2.46//3.66	1.25//1.24

Table S3.Computed geometrical parameters for all dioxygen-bound models (first scanning step//last scanning step) using the BP86 functional.

Complex	Fe-S	Fe-N_{axial}	Fe-O	O-O
S=0 $[Fe(Im)(Por)(OO)]^0$	-	2.07//1.86	1.75//3.75	1.28//1.24
S=1 $[Fe(Im)(Por)(OO)]^0$	-	2.02//1.87	1.75//3.75	1.29//1.23
S=2 $[Fe(Im)(Por)(OO)]^0$	-	2.16//2.16	1.91//3.71	1.28//1.24
S=3 $[Fe(Im)(Por)(OO)]^0$	-	2.27//2.11	1.92//3.92	1.28//1.24
S=0 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.32//2.32	-	1.79//3.59	1.30//1.26
S=1 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.31//2.21	-	1.90//3.50	1.30//1.25
S=2 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.31//2.39	-	2.00//3.60	1.30//1.25
S=3 $[Fe(SCH_3)(Por)(OO)]^{1-}$	2.36//2.33	-	2.46//3.66	1.26//1.25

Table S4. Atomic charges and spin densities for the Fe(II)-NO model (BP86).

	Fe spin (charge)	S spin (charge)	NO spin (charge)
S=1/2	0.55(0.95)	0.06(-0.39)	0.37(-0.40)
S=3/2	1.39(0.97)	0.17(-0.50)	1.42(-0.38)
S=5/2	3.19(1.08)	0.19(-0.35)	1.31(-0.47)

Table S5. Atomic charges and spin densities for the Fe(II)-NO model (B3LYP).

	Fe spin (charge)	S spin (charge)	NO spin (charge)
S=1/2	-0.14(0.98)	0.02(-0.30)	1.08(-0.37)
S=3/2	3.87(1.14)	1.24(-0.42)	0.18(-0.28)
S=5/2	3.76(1.08)	0.17(-0.40)	0.89(-0.24)

Table S6. Atomic charges and spin densities for the Fe(II)-NO model (M06L).

	Fe spin (charge)	S spin (charge)	NO spin (charge)
S=1/2	0.43(-0.45)	0.04(1.21)	0.51(-0.36)
S=3/2	4.48(1.33)	0.17(-0.50)	-1.29(-0.32)
S=5/2	3.86(1.29)	0.25(-0.41)	0.70(-0.27)

Table S7. Atomic charges and spin densities for the Fe(II)-NO model (M06)

	Fe spin (charge)	S spin (charge)	NO spin (charge)
S=1/2	-0.04(0.99)	0.03(-0.21)	1.00(-0.40)
S=3/2	3.98(1.14)	0.17(0.42)	1.31(-0.11)
S=5/2	3.97(1.09)	0.19(-0.39)	0.66(-0.29)

Table S8. Atomic charges and spin densities for the Fe(II)-NO model (M06HF).

	Fe spin (charge)	S spin (charge)	NO spin (charge)
S=1/2	-0.91(1.08)	0.04(-0.30)	1.80(-0.55)
S=3/2	1.99(0.99)	0.03(-0.55)	1.04(0.04)
S=5/2	3.93(0.96)	0.02(-0.49)	0.98(0.03)

Table S9. Atomic charges and spin densities for the Fe(II)-NO model (M06-2X).

	Fe spin (charge)	S spin (charge)	NO spin (charge)
S=1/2	0.02(1.12)	0.00(-0.47)	0.96(-0.11)
S=3/2	1.96(0.96)	0.04(-0.46)	0.99(0.03)
S=5/2	3.84(1.04)	0.06(-0.51)	1.01(0.02)

Table S10. Atomic charges and spin densities for the Fe(II)-NO model (MP2).

	Fe spin (charge)	S spin (charge)	NO spin (charge)
S=1/2	0.11(1.30)	-0.01(-0.57)	0.92(-0.06)
S=3/2	2.07(1.35)	-0.03(-0.56)	0.89(-0.01)
S=5/2	3.96(1.32)	0.01(-0.58)	0.99(0.02)

Table S11. Computed geometrical parameters for aqua-bound Hemoglobin (BP86).

Complex	Fe-N_{axial}	Fe-O
S=0 $[Fe(Im)(Por)(H_2O)]^0$	1.91	2.09
S=1 $[Fe(Im)(Por)(H_2O)]^0$	2.22	2.51
S=2 $[Fe(Im)(Por)(H_2O)]^0$	2.16	2.43
S=3 $[Fe(Im)(Por)(H_2O)]^0$	2.17	2.49

Table S12. Computed geometrical parameters for all aqua-bound models (M06-2X).

Complex	Fe-S	Fe-N_{axial}	Fe-O
S=0 $[Fe(Im)(Por)(H_2O)]^0$	-	2.02	2.03
S=1 $[Fe(Im)(Por)(H_2O)]^0$	-	2.20	2.29
S=2 $[Fe(Im)(Por)(H_2O)]^0$	-	2.17	2.26
S=3 $[Fe(Im)(Por)(H_2O)]^0$	-	2.07	2.28
S=0 $[Fe(SCH_3)(Por)(H_2O)]^{1-}$	2.44	-	2.16
S=1 $[Fe(SCH_3)(Por)(H_2O)]^{1-}$	2.47	-	2.51
S=2 $[Fe(SCH_3)(Por)(H_2O)]^{1-}$	2.41	-	2.54
S=3 $[Fe(SCH_3)(Por)(H_2O)]^{1-}$	2.34	-	2.54

Table S13. Computed geometrical parameters for all aqua-bound models (M06L).

Complex	Fe-S	Fe-N_{axial}	Fe-O
S=0 $[Fe(Im)(Por)(H_2O)]^0$	-	1.92	2.02
S=1 $[Fe(Im)(Por)(H_2O)]^0$	-	2.07	2.23
S=2 $[Fe(Im)(Por)(H_2O)]^0$	-	2.13	2.26
S=3 $[Fe(Im)(Por)(H_2O)]^0$	-	2.09	2.26
S=0 $[Fe(SCH_3)(Por)(H_2O)]^{1-}$	2.26	-	2.16
S=1 $[Fe(SCH_3)(Por)(H_2O)]^{1-}$	2.41	-	2.52
S=2 $[Fe(SCH_3)(Por)(H_2O)]^{1-}$	2.33	-	2.54
S=3 $[Fe(SCH_3)(Por)(H_2O)]^{1-}$	2.31	-	2.54