Electronic Supporting Information

Electronic Structures and Spectroscopic Signatures of Diiron Intermediates Generated from Nonheme Iron(II)-Thiolate Complexes and O_2

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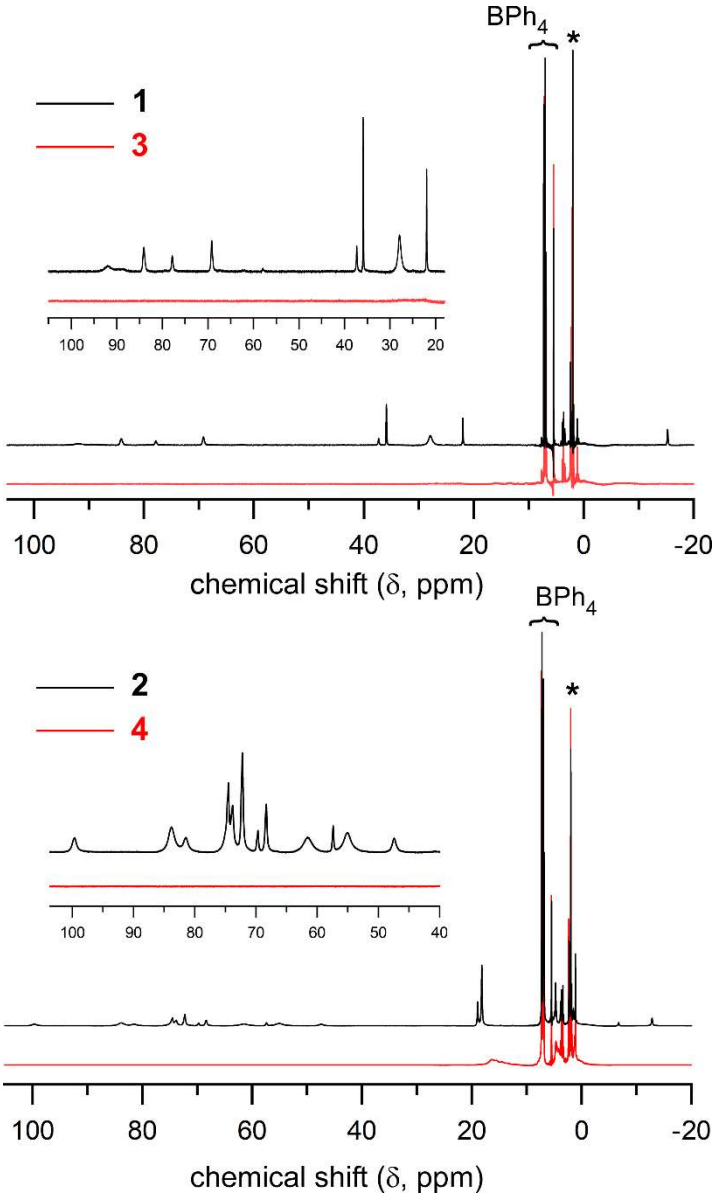


Figure S1. ^{1}H NMR spectra of **1–4** in CD_3CN at –40 °C. The insets highlight the loss of downfield paramagnetically-shifted peaks upon exposure of **1** (top) and **2** (bottom) to O_2. The BPh_4 peaks in the diamagnetic region were used to normalize spectral intensities. Peaks marked with an asterisk (*) arises from residual CH_3CN.

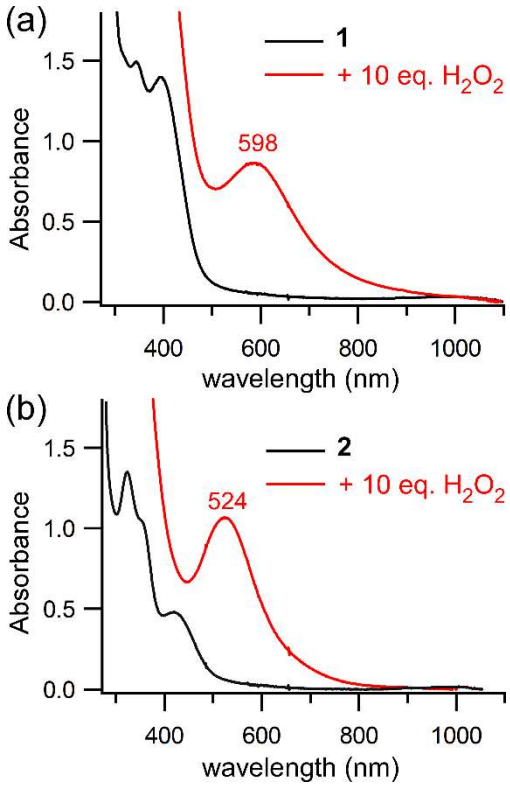


Figure S2. UV-vis absorption spectra of the Fe(II) precursors (**1** and **2**; black lines) and H_2O_2-generated intermediates (**3** and **4**; red lines). Spectra were measured at –40 °C in CH_3CN before and after addition of 10 equiv. of H_2O_2 to **1** (top) and **2** (bottom). The initial concentrations of **1** and **2** were 0.82 and 0.90 mM, respectively.

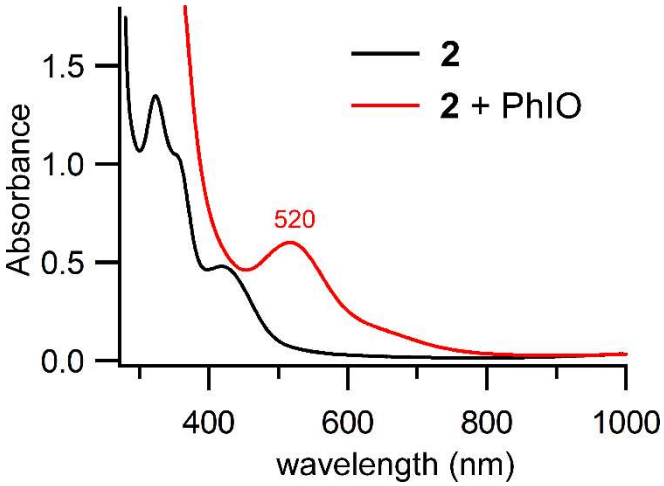


Figure S3. UV-vis absorption spectra of the reaction of **2** (black line) with one equivalent of PhIO to generate intermediate **4** (red line). The reaction was performed in CH_3CN at -40 °C. The initial concentration of **2** was 0.90 mM.

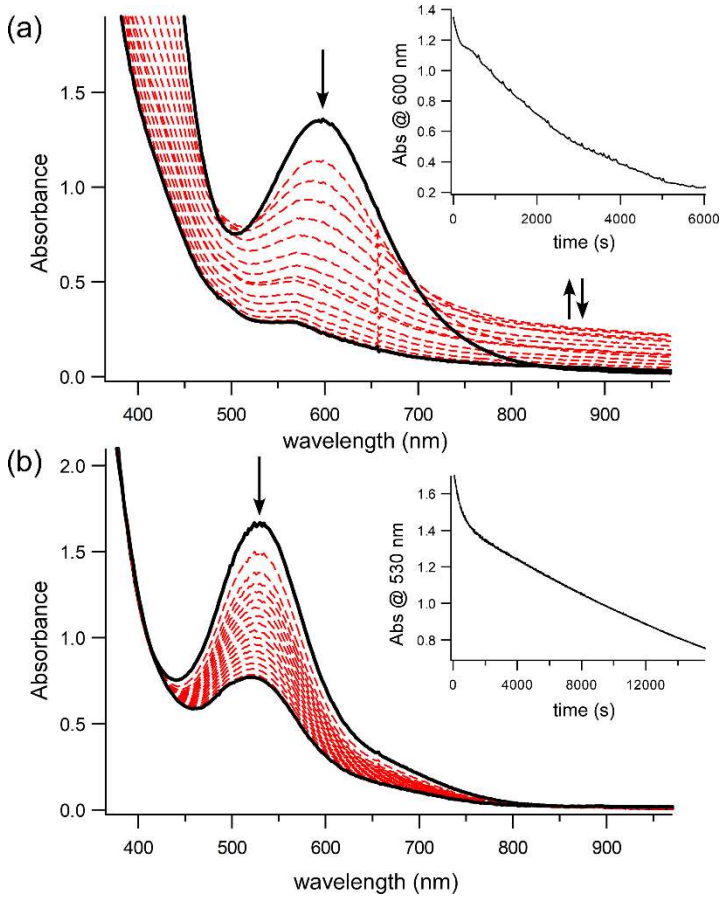


Figure S4. UV-visible absorption spectra showing the decay of **3** (a) and **4** (b) at -40 °C in CH_3CN. Samples were generated by exposing solution of the precursor Fe(II) complexes (0.9 mM) to O_2. The spectra shown here were collected at intervals of 400 and 960 s for **3** and **4**, respectively. The decay of **3** is initially accompanied by an increase in absorption intensity in near-IR region ($\lambda >$ 700), although intensity in this region eventually returns to the baseline. The decay of **4** is not complete even after 4.5 hr. at -40 °C. *Insets:* Plots of absorption *versus* time at the indicated wavelengths.

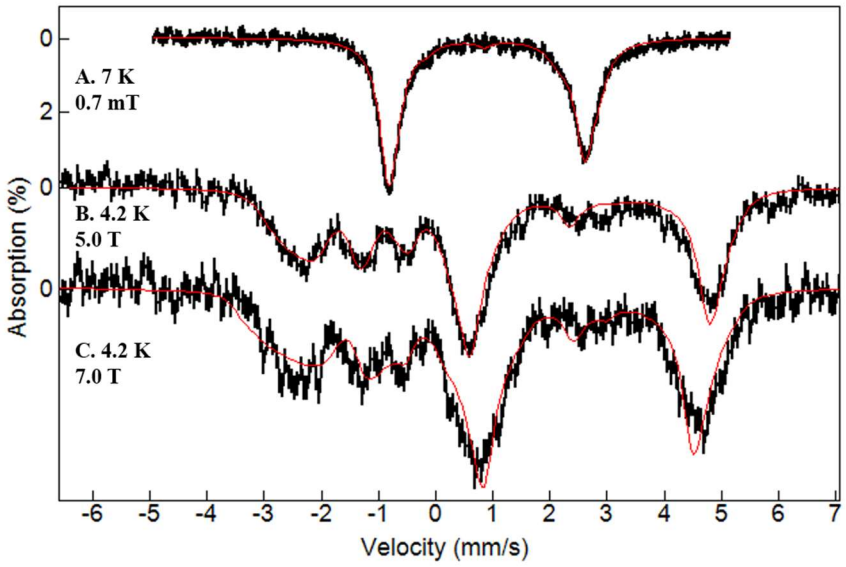


Figure S5. Variable-field, variable-temperature MB spectra of complex **2**, precursor to **4**. The hatch marks are the experimental data, and the colored lines are spectral fits generated with the parameters in Table 2 as described in Experimental Methods.

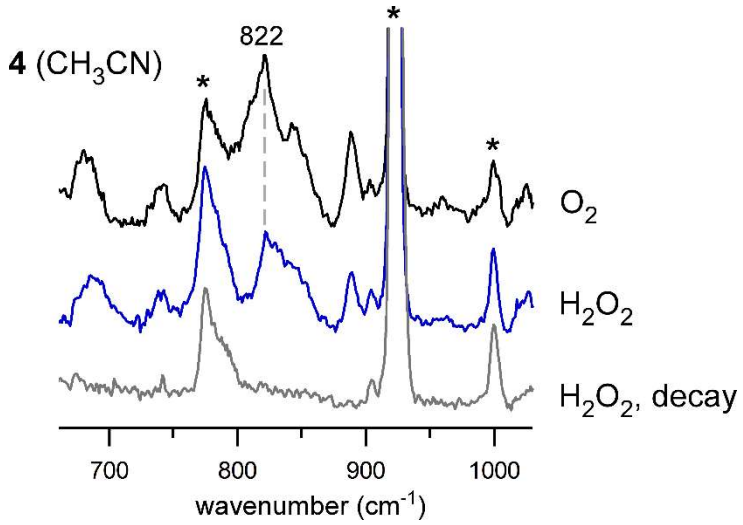


Figure S6. Comparison of resonance Raman spectra of **4** prepared with O_2 (top, black line) and H_2O_2 (middle, blue line) in CH_3CN. Both spectra exhibit an intense peak at 822 cm^{-1}. Warming the H_2O_2-generated sample to room temperature results in the decay of **4**; the spectrum of the decay product (gray line) lacks the feature at 822 cm^{-1}. All spectra were collected using laser excitation of 501.7 nm applied to frozen samples at 77 K. Peaks arising from CH_3CN solvent are marked with an asterisk (*).

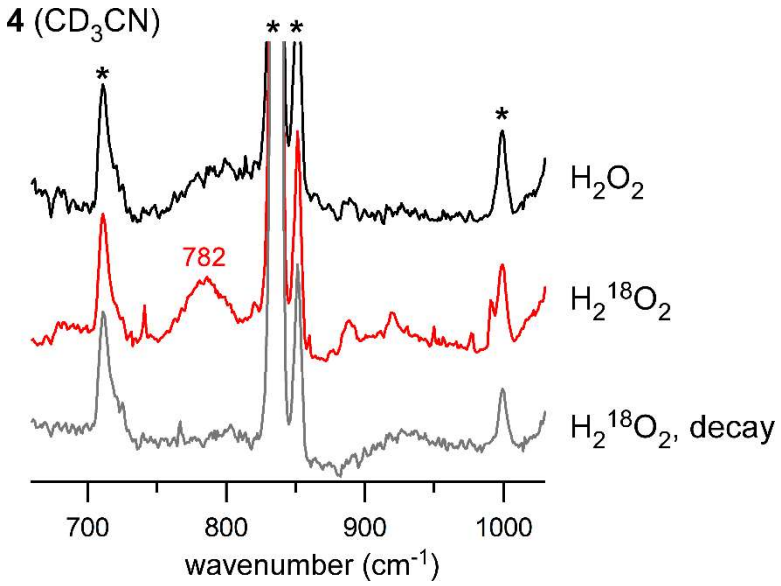


Figure S7. Comparison of resonance Raman spectra of **4** prepared with H_2O_2 (top, black line) and $H_2{}^{18}O_2$ (middle, red line) in CD_3CN. The isotopically-active peak of **4** at ~820 cm^{-1}, which is partially obscured by solvent peaks, shifts to 782 cm^{-1} in the $H_2{}^{18}O_2$ spectrum. Warming the $H_2{}^{18}O_2$-generated sample to room temperature results in the decay of **4**; the spectrum of the decay product (gray line) lacks the feature at 782 cm^{-1}. All spectra were collected using laser excitation of 501.7 nm applied to frozen samples at 77 K. Peaks arising from CD_3CN solvent are marked with an asterisk (*).

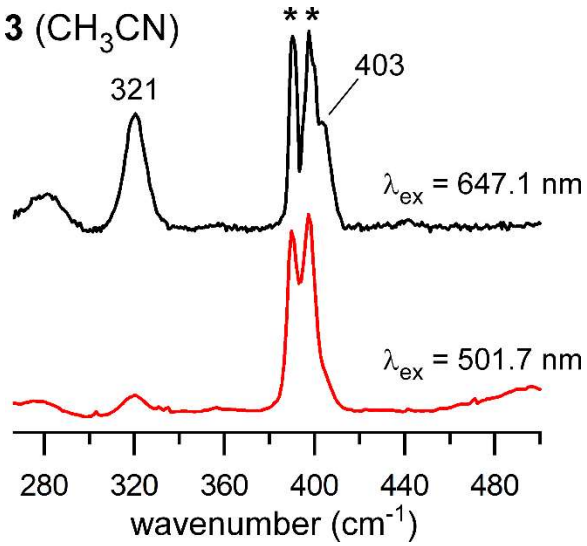


Figure S8. Resonance Raman spectra of **3** obtained with laser excitations of 647.1 nm (top, black line) and 501.7 nm (bottom, red line) applied to the same sample. Spectral intensities are normalized with respect to the CH_3CN solvent peaks (*). The sample was prepared by reaction of **1** (10 mM) with O_2 in CH_3CN.

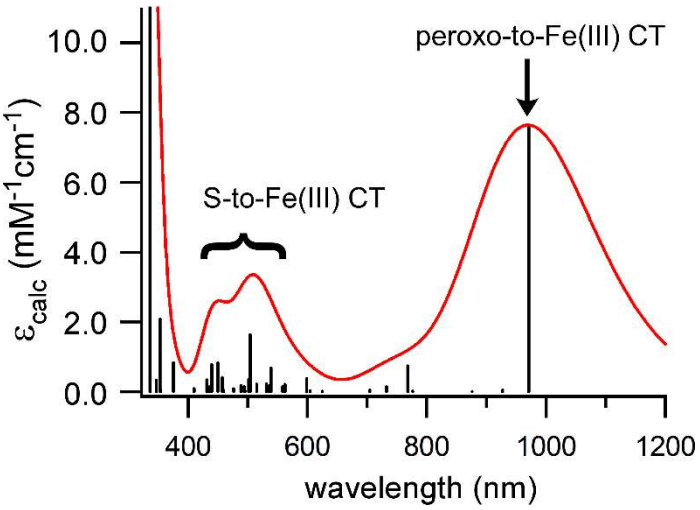


Figure S9. TD-DFT computed absorption spectrum (solid red line) of **P2**. The black sticks correspond to the energies and intensities of computed transitions. The predominant character of the most intense transitions is indicated.

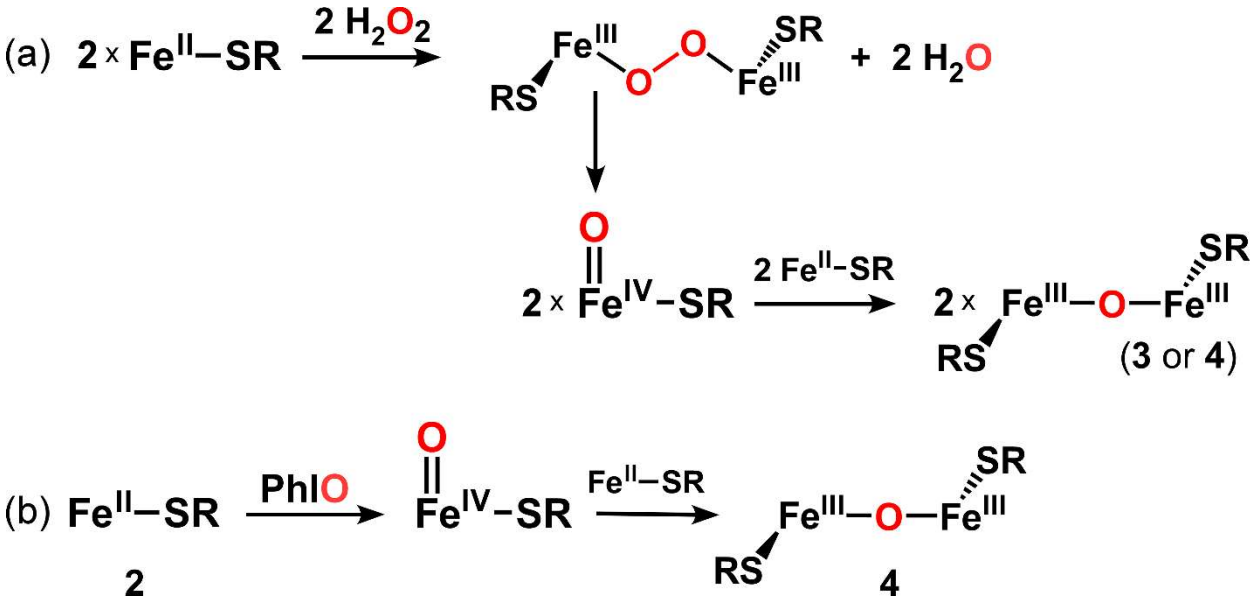
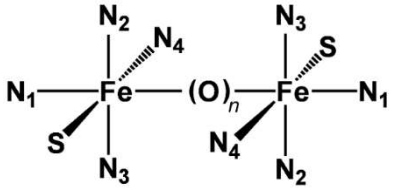


Figure S10. Proposed Mechanisms for Formation of Intermediates **3** and **4** using (a) H_2O_2 and (b) iodosylbeneze (PhIO).

Table S1. Selected Metric Parameters for DFT-Generated Models $\mathbf{3}^{\mathbf{DFT}}$, $\mathbf{4}^{\mathbf{DFT}}$, **P1**, and **P2**.[a]

		$[Fe_2(\mu\text{-}O)(SMes)_2(\mathbf{L}^{\mathbf{A}})_2]^{2+}$ ($\mathbf{3}^{\mathbf{DFT}}$)		$[Fe_2(\mu\text{-}O)(SCy)_2(\mathbf{L}^{\mathbf{B}})_2]^{2+}$ ($\mathbf{4}^{\mathbf{DFT}}$)	
		Fe1	Fe2	Fe1	Fe2
Bond Distances (Å)	Fe–O	1.871	1.870	1.874	1.874
	Fe–S	2.328	2.327	2.310	2.310
	Fe–N1 (pyr)	2.364	2.360	2.357	2.357
	Fe–N2 (pyr/imid)	2.235	2.233	2.188	2.189
	Fe–N3 (imid)	2.187	2.207	2.189	2.188
	Fe–N4 (amime)	2.355	2.354	2.470	2.470
	Fe···Fe	3.741		3.743	
Bond angles (deg)	S–Fe–O	94.9	94.7	95.5	95.5
	Fe–O–Fe	177.6		174.9	
		$[Fe_2(\mu\text{-}O_2)(SMes)_2(\mathbf{L}^{\mathbf{A}})_2]^{2+}$ (**P1**)		$[Fe_2(\mu\text{-}O_2)(SCy)_2(\mathbf{L}^{\mathbf{B}})_2]^{2+}$ (**P2**)	
		Fe1	Fe2	Fe1	Fe2
Bond Distances (Å)	Fe–O	1.932	1.970	1.969	1.971
	Fe–S	2.308	2.304	2.287	2.286
	Fe–N1 (pyr)	2.277	2.292	2.321	2.298
	Fe–N2 (pyr/imid)	2.234	2.200	2.150	2.150
	Fe–N3 (imid)	2.163	2.192	2.162	2.189
	Fe–N4 (amime)	2.361	2.363	2.508	2.500
	Fe···Fe	4.785		4.745	
Bond angles (deg)	S–Fe–O	92.1	93.0	91.0	92.8
	Fe–O–O	130.1	117.2	118.6	116.7

[a] The numbering scheme used for the metric parameters is shown here:



n = 1 ($\mathbf{3}^{\mathbf{DFT}}$, $\mathbf{4}^{\mathbf{DFT}}$) *n* = 2 (**P1**, **P2**)

Table S2. Comparison of Selected Metric Parameters for DFT-Generated Model $\mathbf{4}^{\mathbf{DFT}}$ and X-ray Structures of $[Fe_2(\mu\text{-}O)(6\text{-}H\text{-}DPEN\text{-}N_4S^{Me2})_2]^{2+}$ and $[Fe_2(\mu\text{-}O)(6\text{-}Me\text{-}DPEN\text{-}N_4S^{Me2})_2]^{2+}$.[a,c]

		$[Fe_2(\mu\text{-}O)(SCy)_2(\mathbf{L}^{\mathbf{B}})_2]^{2+}$ ($\mathbf{4}^{\mathbf{DFT}}$)		$[Fe_2(\mu\text{-}O)(6\text{-}H\text{-}DPEN\text{-}N_4S^{Me2})_2]^{2+}$ [b]	$[Fe_2(\mu\text{-}O)(6\text{-}Me\text{-}DPEN\text{-}N_4S^{Me2})_2]^{2+}$ [b]
		Fe1	Fe2		
Bond Distances (Å)	Fe–O1	1.874	1.874	1.799	1.782
	Fe–S1	2.310	2.310	2.271	2.303
	Fe–N1	2.357	2.357	2.155	2.163
	Fe–N2	2.188	2.189	2.160	2.390
	Fe–N3	2.189	2.188	2.168	2.429
	Fe–N4	2.470	2.470	2.222	2.208
	Fe···Fe	3.743		3.566	3.563
Bond angles (deg)	S–Fe–O	95.5	95.5	104.6	101.8
	Fe–O–Fe	174.9		175.9	180.0

[a] The X-ray crystal structures were reported in S. Toledo, P. C. Y. Poon, M. Gleaves, J. Rees, D. M. Rogers, W. Kaminsky and J. A. Kovacs, *Inorg. Chim. Acta*, 2021, **524**, 120422.

[b] Because the metric parameters for the two Fe(III) site are very similar, values are only provided for a single Fe center.

[c] The atomic numbering scheme is shown here:

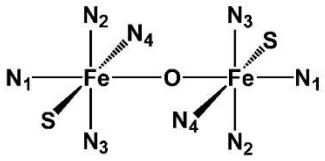


Table S3. Cartesian Coordinates (Å) of the DFT-Optimized Model of $\mathbf{3^{DFT}}$.

Fe	-1.866915000000	-0.162920000000	-0.152771000000
Fe	1.861777000000	-0.195108000000	0.151136000000
O	-0.001590000000	-0.140425000000	0.001043000000
S	1.864073000000	-0.294082000000	2.476279000000
S	-1.875954000000	-0.133028000000	-2.480480000000
N	-2.349270000000	-0.072463000000	2.150756000000
N	-4.158646000000	-0.691992000000	0.083712000000
C	-2.190116000000	3.621039000000	1.830463000000
N	-2.165241000000	1.950440000000	0.324085000000
C	-3.808982000000	0.019018000000	2.385286000000
H	-4.078932000000	1.087101000000	2.355834000000
H	-4.067002000000	-0.345491000000	3.395222000000
C	-4.639740000000	-0.690676000000	1.343452000000
C	-5.875915000000	-1.255891000000	1.668135000000
H	-6.228276000000	-1.239755000000	2.700448000000
C	-6.645424000000	-1.834395000000	0.658907000000
H	-7.614483000000	-2.279050000000	0.888183000000
C	-6.145415000000	-1.842282000000	-0.643326000000
H	-6.705486000000	-2.287802000000	-1.464888000000
C	-4.897797000000	-1.269639000000	-0.882827000000
H	-4.461983000000	-1.266881000000	-1.882044000000
C	-1.666340000000	1.164860000000	2.613331000000
H	-0.582072000000	0.967458000000	2.585790000000
H	-1.936768000000	1.427889000000	3.651465000000
C	-2.011312000000	2.267762000000	1.664384000000
N	-2.438340000000	4.117965000000	0.564518000000
H	-2.632773000000	5.088506000000	0.335679000000
C	-2.418868000000	3.085417000000	-0.315946000000
H	-2.596078000000	3.192641000000	-1.380992000000
C	-1.748599000000	-1.297672000000	2.718626000000
H	-2.142796000000	-1.509244000000	3.728832000000
H	-0.664680000000	-1.115306000000	2.823529000000
N	2.342519000000	0.069737000000	-2.138362000000
N	4.167658000000	-0.621130000000	-0.115821000000
C	2.278833000000	-3.666800000000	-2.327952000000
N	1.932317000000	-2.269418000000	-0.600750000000
C	3.797860000000	0.233741000000	-2.364126000000
H	4.029753000000	1.307063000000	-2.272487000000
H	4.070004000000	-0.058863000000	-3.393406000000
C	4.656723000000	-0.504718000000	-1.366348000000
C	5.922426000000	-0.982055000000	-1.718669000000
H	6.280711000000	-0.871473000000	-2.743098000000
C	6.712072000000	-1.595400000000	-0.746987000000
H	7.705140000000	-1.970626000000	-0.996889000000
C	6.201043000000	-1.729268000000	0.544578000000
H	6.775791000000	-2.208255000000	1.336708000000
C	4.925139000000	-1.237751000000	0.811961000000

H	4.480885000000	-1.334778000000	1.802564000000
C	1.616217000000	1.303629000000	-2.503242000000
H	0.535896000000	1.075826000000	-2.478436000000
H	1.861830000000	1.645545000000	-3.524949000000
C	1.783368000000	-1.135990000000	-2.804695000000
H	2.191144000000	-1.260048000000	-3.823419000000
H	0.697312000000	-0.974544000000	-2.901021000000
C	2.025963000000	-2.360277000000	-1.978348000000
N	2.330365000000	-4.364506000000	-1.136310000000
H	2.515621000000	-5.358322000000	-1.038086000000
C	2.124370000000	-3.488766000000	-0.117970000000
H	2.137682000000	-3.765893000000	0.930699000000
H	2.418064000000	-4.151105000000	-3.287520000000
H	-2.163038000000	4.258256000000	2.706759000000
C	3.188931000000	0.162850000000	3.561288000000
C	4.267759000000	0.980011000000	3.168120000000
C	3.125460000000	-0.284239000000	4.897676000000
C	5.250219000000	1.342128000000	4.091130000000
C	4.114381000000	0.078559000000	5.810786000000
C	5.179293000000	0.894772000000	5.414075000000
H	4.340212000000	1.324713000000	2.136535000000
H	2.293935000000	-0.916619000000	5.211438000000
H	6.077727000000	1.978605000000	3.773728000000
H	4.051760000000	-0.276652000000	6.840310000000
H	5.948827000000	1.180292000000	6.131656000000
C	-3.216191000000	0.475027000000	-3.466741000000
C	-4.264098000000	1.259540000000	-2.945084000000
C	-3.203095000000	0.188049000000	-4.847453000000
C	-5.266079000000	1.746417000000	-3.786042000000
C	-4.210083000000	0.676712000000	-5.679066000000
C	-5.244154000000	1.459520000000	-5.154741000000
H	-4.297732000000	1.473743000000	-1.876616000000
H	-2.397133000000	-0.419956000000	-5.260380000000
H	-6.071909000000	2.352610000000	-3.368800000000
H	-4.186360000000	0.444949000000	-6.744773000000
H	-6.028705000000	1.841738000000	-5.808187000000
C	1.903404000000	2.393974000000	-1.500121000000
C	1.938656000000	3.743773000000	-1.859213000000
N	2.085700000000	1.995356000000	-0.220918000000
C	2.152491000000	4.706901000000	-0.872653000000
C	2.278444000000	2.927979000000	0.730905000000
C	2.319509000000	4.291892000000	0.449310000000
H	1.809858000000	4.030285000000	-2.903828000000
H	2.197806000000	5.764771000000	-1.134657000000
H	2.402396000000	2.552374000000	1.747457000000
H	2.494081000000	5.007261000000	1.252497000000
C	-1.922528000000	-2.509758000000	1.830582000000
C	-2.037396000000	-3.796899000000	2.364529000000
N	-1.888749000000	-2.301392000000	0.498194000000

C	-2.108374000000	-4.890133000000	1.501134000000
C	-1.957529000000	-3.355331000000	-0.334445000000
C	-2.062906000000	-4.666931000000	0.123741000000
H	-2.077032000000	-3.935052000000	3.445791000000
H	-2.209250000000	-5.900825000000	1.898623000000
H	-1.937755000000	-3.120858000000	-1.400563000000
H	-2.126779000000	-5.489818000000	-0.587776000000

Table S4. Cartesian Coordinates (Å) of the DFT-Optimized Model of $\mathbf{4}^{\mathbf{DFT}}$.

Fe	-1.868415000000	-0.019569000000	-0.106276000000
Fe	1.868824000000	-0.018329000000	0.106733000000
O	0.000185000000	-0.102841000000	0.000995000000
S	2.216916000000	0.075715000000	-2.175183000000
S	-2.217474000000	0.074813000000	2.175580000000
N	-1.872827000000	-0.217193000000	-2.568723000000
N	-4.059493000000	0.381421000000	-0.875870000000
N	-1.611036000000	-3.817051000000	-1.971401000000
N	-2.060239000000	-2.138881000000	-0.617649000000
N	-1.597356000000	3.474534000000	-2.506397000000
N	-1.780585000000	2.035102000000	-0.853355000000
C	-3.259641000000	-0.370214000000	-3.055675000000
H	-3.495445000000	-1.446575000000	-3.050148000000
H	-3.349240000000	-0.034368000000	-4.104383000000
C	-4.297586000000	0.318799000000	-2.200952000000
C	-5.481465000000	0.799395000000	-2.768066000000
H	-5.634306000000	0.733652000000	-3.846351000000
C	-6.458327000000	1.353988000000	-1.941717000000
H	-7.391411000000	1.730422000000	-2.362252000000
C	-6.209316000000	1.427666000000	-0.571475000000
H	-6.934941000000	1.862110000000	0.115534000000
C	-4.996276000000	0.940629000000	-0.089250000000
H	-4.740525000000	1.006366000000	0.967765000000
C	-1.087159000000	-1.448718000000	-2.791785000000
H	-0.026624000000	-1.214725000000	-2.585682000000
H	-1.158898000000	-1.820015000000	-3.832179000000
C	-1.584080000000	-2.467362000000	-1.818080000000
C	-2.118037000000	-4.376493000000	-0.811282000000
H	-2.252038000000	-5.445545000000	-0.696248000000
C	-2.392624000000	-3.318162000000	0.018330000000
H	-2.814810000000	-3.327556000000	1.015828000000
C	-1.206418000000	1.009509000000	-3.050873000000
H	-1.467713000000	1.234848000000	-4.102019000000
H	-0.114720000000	0.838856000000	-3.007469000000
C	-1.547159000000	2.160886000000	-2.156351000000
C	-1.875248000000	4.216947000000	-1.372190000000
H	-1.974207000000	5.295608000000	-1.398240000000
C	-1.990534000000	3.303826000000	-0.353474000000

H	-2.217766000000	3.473003000000	0.692728000000
C	-3.645088000000	-0.308150000000	3.326264000000
H	-3.112953000000	-0.730556000000	4.193011000000
C	-4.606886000000	-1.365252000000	2.791482000000
C	-4.343111000000	0.973592000000	3.784046000000
H	-4.902045000000	1.455644000000	2.969647000000
H	-3.625491000000	1.703219000000	4.180906000000
H	-4.087989000000	-2.308284000000	2.576469000000
H	-5.117550000000	-1.038880000000	1.875991000000
N	1.873093000000	-0.215279000000	2.569141000000
N	4.059683000000	0.383422000000	0.876265000000
N	1.614328000000	-3.815437000000	1.972902000000
N	2.062306000000	-2.137370000000	0.618632000000
N	1.595859000000	3.476258000000	2.505776000000
N	1.780320000000	2.036528000000	0.853134000000
C	3.259876000000	-0.367244000000	3.056478000000
H	3.496216000000	-1.443488000000	3.051941000000
H	3.349126000000	-0.030452000000	4.104910000000
C	4.297688000000	0.321558000000	2.201396000000
C	5.481421000000	0.802719000000	2.768342000000
H	5.634186000000	0.737600000000	3.846676000000
C	6.458228000000	1.357083000000	1.941784000000
H	7.391200000000	1.733933000000	2.362195000000
C	6.209307000000	1.429976000000	0.571482000000
H	6.934881000000	1.864228000000	-0.115703000000
C	4.996413000000	0.942421000000	0.089434000000
H	4.740746000000	1.007523000000	-0.967613000000
C	1.088124000000	-1.447241000000	2.792263000000
H	0.027532000000	-1.213970000000	2.585660000000
H	1.159706000000	-1.818194000000	3.832789000000
C	1.586119000000	-2.465827000000	1.819049000000
C	2.122275000000	-4.374835000000	0.813172000000
H	2.257374000000	-5.443799000000	0.698604000000
C	2.396074000000	-3.316559000000	-0.016778000000
H	2.818629000000	-3.325911000000	-1.014121000000
C	1.205764000000	1.011161000000	3.050662000000
H	1.466421000000	1.236914000000	4.101880000000
H	0.114190000000	0.839847000000	3.006795000000
C	1.546332000000	2.162508000000	2.156016000000
C	1.873900000000	4.218522000000	1.371509000000
H	1.972409000000	5.297229000000	1.397349000000
C	1.989915000000	3.305219000000	0.353035000000
H	2.217417000000	3.474255000000	-0.693131000000
C	3.643631000000	-0.308231000000	-3.326688000000
H	3.110742000000	-0.731497000000	-4.192546000000
C	4.605760000000	-1.364954000000	-2.791733000000
C	4.341280000000	0.973035000000	-3.786354000000
H	4.901135000000	1.455776000000	-2.973019000000
H	3.623312000000	1.702366000000	-4.183121000000

H	4.086904000000	-2.307747000000	-2.575577000000
H	5.117087000000	-1.037878000000	-1.876861000000
H	-1.455151000000	3.851514000000	-3.438671000000
H	1.453154000000	3.853391000000	3.437912000000
H	-1.316945000000	-4.331027000000	-2.796661000000
H	1.320505000000	-4.329374000000	2.798283000000
H	-5.062970000000	0.734924000000	4.582424000000
H	-5.378239000000	-1.576572000000	3.548476000000
H	5.060262000000	0.733551000000	-4.585282000000
H	5.376566000000	-1.576970000000	-3.549088000000

Table S5. Cartesian Coordinates (Å) of the DFT-Optimized Model of **P1**.

Fe	-0.006284000000	0.003008000000	0.017172000000
Fe	0.629060000000	-0.202696000000	4.755445000000
O	0.004297000000	0.026202000000	1.949164000000
O	1.067234000000	0.002179000000	2.846175000000
S	0.434413000000	-2.493033000000	4.590176000000
S	-0.673746000000	2.210216000000	-0.090434000000
N	0.593714000000	-2.279623000000	-0.056295000000
N	0.604297000000	-0.387340000000	-2.141230000000
C	-3.049021000000	-2.988875000000	0.199544000000
N	-1.875567000000	-1.084427000000	-0.032521000000
C	0.615481000000	-2.734310000000	-1.463800000000
H	-0.397443000000	-3.094011000000	-1.708543000000
H	1.295032000000	-3.595800000000	-1.591375000000
C	0.961248000000	-1.649154000000	-2.458482000000
C	1.560253000000	-1.961363000000	-3.681794000000
H	1.840934000000	-2.992161000000	-3.902620000000
C	1.789837000000	-0.944254000000	-4.607885000000
H	2.253903000000	-1.166970000000	-5.569344000000
C	1.424830000000	0.360842000000	-4.276235000000
H	1.589457000000	1.189988000000	-4.963515000000
C	0.844465000000	0.595398000000	-3.032103000000
H	0.555311000000	1.600025000000	-2.723008000000
C	-0.469506000000	-2.979252000000	0.711571000000
H	-0.300517000000	-2.765062000000	1.779424000000
H	-0.428979000000	-4.075148000000	0.579306000000
C	-1.796198000000	-2.430042000000	0.291772000000
N	-3.888129000000	-1.954421000000	-0.171119000000
H	-4.886954000000	-2.032192000000	-0.340040000000
C	-3.149212000000	-0.824760000000	-0.303864000000
H	-3.556555000000	0.138692000000	-0.592028000000
C	1.912990000000	-2.354247000000	0.603775000000
H	2.424589000000	-3.308496000000	0.382522000000
H	1.736505000000	-2.317412000000	1.691142000000
N	0.751356000000	2.140272000000	5.040919000000
N	0.761653000000	0.135710000000	7.018152000000

C	4.435583000000	1.605556000000	5.468883000000
N	2.778220000000	0.165714000000	4.986163000000
C	0.432932000000	2.485780000000	6.444692000000
H	-0.657976000000	2.625978000000	6.514495000000
H	0.890754000000	3.449386000000	6.729492000000
C	0.816379000000	1.415369000000	7.441643000000
C	1.144137000000	1.744533000000	8.759708000000
H	1.182878000000	2.790798000000	9.066103000000
C	1.416905000000	0.723188000000	9.669080000000
H	1.670333000000	0.957733000000	10.703587000000
C	1.369942000000	-0.599891000000	9.227675000000
H	1.582118000000	-1.431446000000	9.898937000000
C	1.047774000000	-0.847021000000	7.895474000000
H	1.011588000000	-1.863408000000	7.502309000000
C	-0.280684000000	2.651963000000	4.115098000000
H	0.082819000000	2.504161000000	3.085838000000
H	-0.471974000000	3.731295000000	4.252440000000
C	2.125775000000	2.534788000000	4.639012000000
H	2.394419000000	3.531746000000	5.030313000000
H	2.129002000000	2.596734000000	3.540641000000
C	3.125453000000	1.503090000000	5.062829000000
N	4.874515000000	0.304882000000	5.630363000000
H	5.802823000000	0.025127000000	5.933751000000
C	3.848473000000	-0.534443000000	5.336983000000
H	3.910153000000	-1.615760000000	5.399754000000
H	5.080759000000	2.458454000000	5.645100000000
H	-3.412071000000	-3.996526000000	0.365231000000
C	-0.345922000000	-3.507010000000	5.816685000000
C	-1.262239000000	-3.016494000000	6.768601000000
C	-0.057487000000	-4.887918000000	5.803263000000
C	-1.872423000000	-3.884656000000	7.675813000000
C	-0.666641000000	-5.746838000000	6.716935000000
C	-1.578296000000	-5.251455000000	7.655627000000
H	-1.494374000000	-1.951476000000	6.801719000000
H	0.649573000000	-5.278025000000	5.069824000000
H	-2.583352000000	-3.489926000000	8.403496000000
H	-0.429140000000	-6.811374000000	6.694621000000
H	-2.056271000000	-5.926158000000	8.366239000000
C	-1.478471000000	2.865481000000	-1.525194000000
C	-2.114716000000	2.061523000000	-2.492644000000
C	-1.521915000000	4.267274000000	-1.675262000000
C	-2.776013000000	2.645629000000	-3.574211000000
C	-2.180995000000	4.842312000000	-2.761235000000
C	-2.813109000000	4.036649000000	-3.714323000000
H	-2.081766000000	0.975375000000	-2.398601000000
H	-1.035536000000	4.899047000000	-0.930816000000
H	-3.266165000000	2.009999000000	-4.313662000000
H	-2.203500000000	5.928322000000	-2.862256000000
H	-3.331426000000	4.489507000000	-4.559842000000

C	-1.561763000000	1.866813000000	4.265701000000
C	-2.815413000000	2.453422000000	4.083817000000
N	-1.426975000000	0.549091000000	4.537124000000
C	-3.958671000000	1.659565000000	4.174260000000
C	-2.531262000000	-0.218103000000	4.606885000000
C	-3.813898000000	0.296688000000	4.436571000000
H	-2.889238000000	3.521328000000	3.876070000000
H	-4.947798000000	2.100960000000	4.046398000000
H	-2.364148000000	-1.278024000000	4.802184000000
H	-4.678176000000	-0.361693000000	4.518815000000
C	2.815598000000	-1.188982000000	0.259052000000
C	4.202402000000	-1.337056000000	0.171501000000
N	2.225485000000	0.014649000000	0.112601000000
C	4.995608000000	-0.211607000000	-0.054303000000
C	2.989570000000	1.099405000000	-0.103484000000
C	4.379085000000	1.033185000000	-0.187418000000
H	4.651267000000	-2.325957000000	0.274382000000
H	6.079095000000	-0.307500000000	-0.135118000000
H	2.451859000000	2.042542000000	-0.220562000000
H	4.958365000000	1.938017000000	-0.369350000000

Table S6. Cartesian Coordinates (Å) of the DFT-Optimized Model of **P2**.

Fe	-2.342314000000	-0.313754000000	-0.101536000000
Fe	2.365689000000	0.226555000000	0.145562000000
O	-0.388482000000	-0.552501000000	-0.140357000000
O	0.417558000000	0.500833000000	0.272534000000
S	-2.351065000000	-0.443828000000	2.181598000000
S	2.338757000000	0.280656000000	-2.139461000000
N	-2.097010000000	-0.243248000000	-2.596323000000
N	-4.455087000000	0.028333000000	-0.999833000000
N	-1.882047000000	-3.889233000000	-2.310008000000
N	-2.396013000000	-2.350974000000	-0.823700000000
N	-1.787595000000	3.399717000000	-2.033520000000
N	-2.173847000000	1.767921000000	-0.611937000000
C	-3.436597000000	-0.306176000000	-3.209181000000
H	-3.649819000000	-1.363983000000	-3.435027000000
H	-3.456494000000	0.225834000000	-4.177353000000
C	-4.571508000000	0.185835000000	-2.334306000000
C	-5.736277000000	0.689850000000	-2.920919000000
H	-5.789740000000	0.811789000000	-4.003843000000
C	-6.823495000000	1.020544000000	-2.113083000000
H	-7.741715000000	1.411340000000	-2.552801000000
C	-6.709639000000	0.842290000000	-0.734583000000
H	-7.530409000000	1.081518000000	-0.059208000000
C	-5.507912000000	0.354871000000	-0.226972000000
H	-5.367973000000	0.218815000000	0.844804000000
C	-1.304693000000	-1.458038000000	-2.872964000000
H	-0.263701000000	-1.255597000000	-2.571339000000

H	-1.306161000000	-1.738479000000	-3.943894000000
C	-1.861414000000	-2.560907000000	-2.026977000000
C	-2.446888000000	-4.556342000000	-1.236094000000
H	-2.583174000000	-5.631281000000	-1.231189000000
C	-2.760746000000	-3.583788000000	-0.320648000000
H	-3.226050000000	-3.686193000000	0.652576000000
C	-1.375859000000	1.016481000000	-2.851898000000
H	-1.527153000000	1.380744000000	-3.886076000000
H	-0.294428000000	0.826181000000	-2.725394000000
C	-1.798796000000	2.052539000000	-1.856705000000
C	-2.170029000000	3.999383000000	-0.846026000000
H	-2.247321000000	5.074942000000	-0.741142000000
C	-2.409095000000	2.968412000000	0.027069000000
H	-2.736104000000	3.007889000000	1.059461000000
C	-3.770275000000	-0.440329000000	3.390032000000
H	-3.252263000000	-0.668195000000	4.334920000000
C	-4.773776000000	-1.560286000000	3.119030000000
C	-4.410495000000	0.941142000000	3.526437000000
H	-4.911011000000	1.258090000000	2.600606000000
H	-3.662755000000	1.703094000000	3.783788000000
H	-4.280393000000	-2.541167000000	3.106420000000
H	-5.291664000000	-1.429149000000	2.158518000000
N	2.226232000000	0.132633000000	2.635686000000
N	4.504007000000	0.474516000000	0.950987000000
N	1.692358000000	-3.453239000000	2.090407000000
N	2.291150000000	-1.846780000000	0.710309000000
N	2.148112000000	3.827879000000	2.400657000000
N	2.332564000000	2.308828000000	0.821070000000
C	3.589312000000	-0.068858000000	3.162659000000
H	3.751769000000	-1.155381000000	3.251529000000
H	3.687947000000	0.344149000000	4.182896000000
C	4.700848000000	0.469965000000	2.285320000000
C	5.915682000000	0.864323000000	2.853699000000
H	6.037057000000	0.854220000000	3.937930000000
C	6.964334000000	1.259634000000	2.023874000000
H	7.920712000000	1.566478000000	2.448620000000
C	6.761115000000	1.261807000000	0.643993000000
H	7.546413000000	1.567048000000	-0.046771000000
C	5.515828000000	0.872778000000	0.157069000000
H	5.301188000000	0.884882000000	-0.911465000000
C	1.363406000000	-1.041960000000	2.871353000000
H	0.316901000000	-0.757093000000	2.661988000000
H	1.407165000000	-1.404014000000	3.916553000000
C	1.784635000000	-2.110579000000	1.915277000000
C	2.151728000000	-4.075875000000	0.942651000000
H	2.188709000000	-5.154347000000	0.846008000000
C	2.520743000000	-3.062145000000	0.095895000000
H	2.941697000000	-3.125289000000	-0.900068000000
C	1.608594000000	1.411215000000	3.032262000000

H	1.830259000000	1.673354000000	4.084560000000
H	0.516892000000	1.294887000000	2.939047000000
C	2.051206000000	2.503678000000	2.106033000000
C	2.505142000000	4.505241000000	1.247856000000
H	2.653397000000	5.578490000000	1.231542000000
C	2.618493000000	3.543212000000	0.275034000000
H	2.889568000000	3.654134000000	-0.768606000000
C	3.689362000000	-0.155939000000	-3.351433000000
H	3.107792000000	-0.481145000000	-4.228419000000
C	4.568210000000	-1.319358000000	-2.900067000000
C	4.487485000000	1.086514000000	-3.750453000000
H	5.079502000000	1.481400000000	-2.912349000000
H	3.828402000000	1.889809000000	-4.104525000000
H	3.971917000000	-2.223997000000	-2.721586000000
H	5.121819000000	-1.086008000000	-1.979913000000
H	1.336716000000	-3.923100000000	2.917634000000
H	1.985565000000	4.253313000000	3.308516000000
H	-1.535171000000	3.887479000000	-2.887711000000
H	-1.544076000000	-4.323551000000	-3.163793000000
H	-5.537528000000	-1.578089000000	3.912229000000
H	-5.166580000000	0.925320000000	4.326979000000
H	5.186299000000	0.835509000000	-4.563705000000
H	5.305113000000	-1.556459000000	-3.683290000000