

## Supporting Information

### X-ray Absorption Spectroscopic Characterization of the Diferric-peroxo Intermediate of Human Deoxyhypusine Hydroxylase in the Presence of its Substrate eIF5a

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**General EXAFS considerations:** In the fit tables of EXAFS data, N refers to the number of scatterers used for a particular shell, R is the distance of the scattering shell,  $\sigma^2$  is the mean-squared deviation (or Debye-Waller factor),  $E_0$  is the edge shift parameter, and the goodness of fit (GOF) parameters are calculated as  $F = \sqrt{\sum k^6 (\chi_{\text{exp}} - \chi_{\text{calc}})^2}$ ,

$F' = \sqrt{\sum k^6 (\chi_{\text{exp}} - \chi_{\text{calc}})^2 / \sum k^6 \chi_{\text{exp}}^2}$ . For all fits, the amplitude reduction factor ( $S_0^2$ ) was set to 0.9.

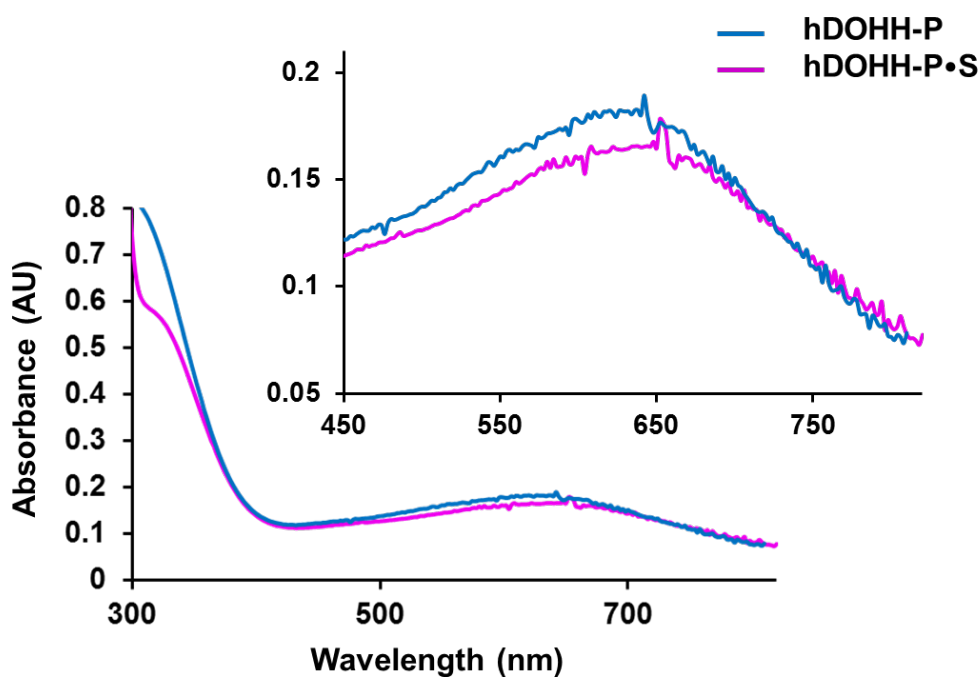


Figure S1. UV-visible absorption spectra of hDOHH-**P** (blue) and hDOHH-**P•S** (purple). Concentration of hDOHH-**P** in both samples is 75  $\mu\text{M}$  with 1.2 eq. of eIF5A(Dhp) added to make the hDOHH- **P•S** sample. Both samples were prepared in 50 mM Tris-HCl, 125 mM NaCl buffer with spectra recorded at 25  $^{\circ}\text{C}$ . Inset: zoom in on the 630 nm LMCT transition.

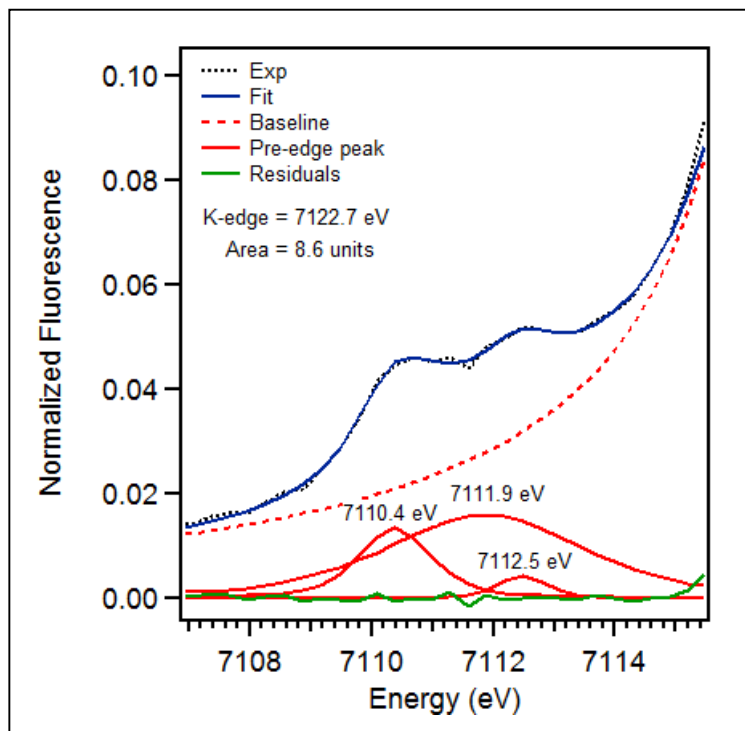


Figure S2. Pre-edge region analysis of hDOHH-R. The experimental data (black dotted), baseline (red dashed), pre-edge peak components (red solid), residuals (green solid) and total fit (blue solid) are shown.

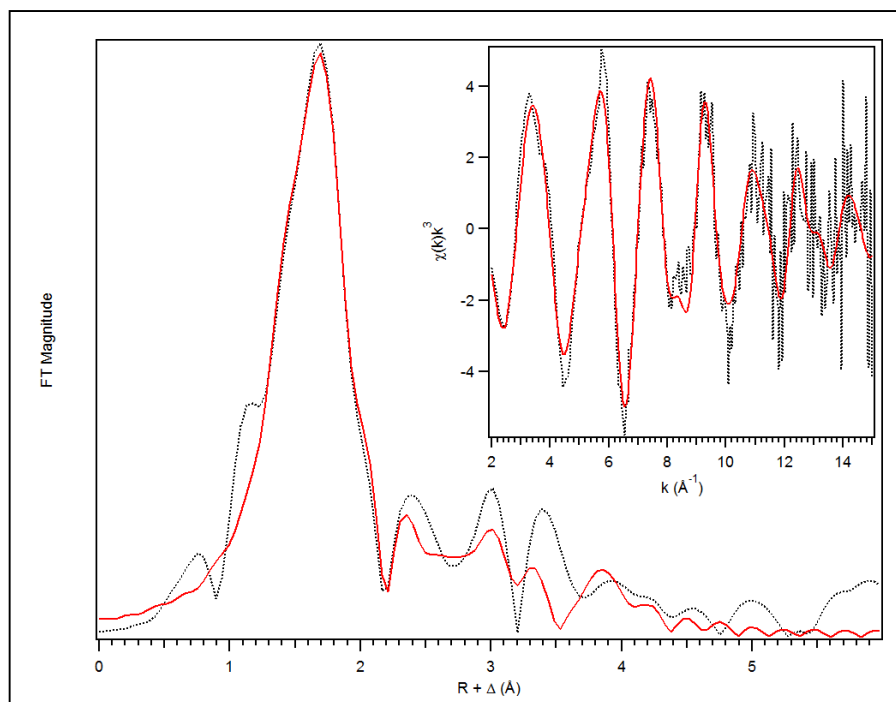


Figure S3. EXAFS spectrum of hDOHH-R. Fit (red solid line) of the unfiltered (black dotted) EXAFS data (inset) and corresponding Fourier transform (Table S1, Fit 12). Data was fit between  $k = 2 - 15 \text{ \AA}^{-1}$ .

Table S1. Fit parameters for the unfiltered EXAFS data of hDOHH-R, between  $k = 2 - 15 \text{ \AA}^{-1}$ .  
Fit 12 gives the most reasonable fit of the experimental data.

Fit	Fe-N				Fe-O			Fe•••Fe			Fe•••C			GOF		
	N	R( $\text{\AA}$ )	$\sigma^2(10^{-3})$		N	R( $\text{\AA}$ )	$\sigma^2(10^{-3})$	N	R( $\text{\AA}$ )	$\sigma^2(10^{-3})$	N	R( $\text{\AA}$ )	$\sigma^2(10^{-3})$	$E_0$	F	F'
1	6	2.15	4.71											-5.97	360	509
2	5	2.15	3.73											-5.59	384	526
3	4	2.15	2.71											-5.16	433	558
4	5	2.17	3.01	1	2.05	1.77								-6.97	350	503
5	4	2.18	2.54	2	2.07	3.25								-7.55	347	500
6	5	2.17	3.30	1	2.05	2.27				3	3.11	5.41	-6.21	317	478	
7	4	2.18	2.85	2	2.08	3.49				3	3.10	5.49	-6.69	313	475	
8	4	2.17	2.64	2	2.07	3.51	1	3.46	7.04	3	3.09	6.58	-7.28	299	464	
9	5	2.17	3.04	1	2.05	1.88	1	3.47	7.17	3	3.10	6.48	-6.72	304	468	
10	5	2.17	3.19	1	2.05	2.02	1	3.47	7.26	3	3.10	6.56	-6.20	287	453	
										4	4.36	3.61				
11	4	2.18	2.99	2	2.08	3.92	1	3.46	7.02	3	3.09	6.54	-6.70	281	450	
										4	4.35	3.24				
<b>12</b>	<b>4</b>	<b>2.18</b>	<b>2.78</b>	<b>2</b>	<b>2.07</b>	<b>3.39</b>	<b>1</b>	<b>3.47</b>	<b>5.18</b>	<b>3</b>	<b>3.10</b>	<b>6.20</b>	<b>-6.80</b>	<b>272</b>	<b>443</b>	
										<b>3</b>	<b>3.68</b>	<b>4.05</b>				
										<b>3</b>	<b>4.35</b>	<b>2.51</b>				
13	5	2.17	3.15	1	2.05	1.85	1	3.47	5.33	3	3.11	6.13	-6.36	277	446	
										3	3.68	3.79				
										3	4.36	2.88				
14	5	2.17	3.42	1	2.06	2.32				3	3.11	5.39	-5.70	280	449	
										3	4.05	2.01				
										4	4.36	1.81				
15	5	2.17	3.05	1	2.05	1.75	1	3.46	5.07	3	3.69	4.64	-7.01	299	464	
										4	4.35	2.57				
16	5	2.16	3.10	1	2.05	2.07	1	3.47	6.10	3	3.10	6.34	-7.05	300	465	
										3	3.70	4.78				
17	4	2.17	2.72				1	3.48	5.86	3	3.12	5.85	-4.80	354	505	
										3	3.70	3.70				
										4	4.37	2.17				
18	6	2.15	4.71				1	3.48	5.79	3	3.12	5.97	-5.70	286	454	
										3	3.69	3.62				
										4	4.37	2.25				

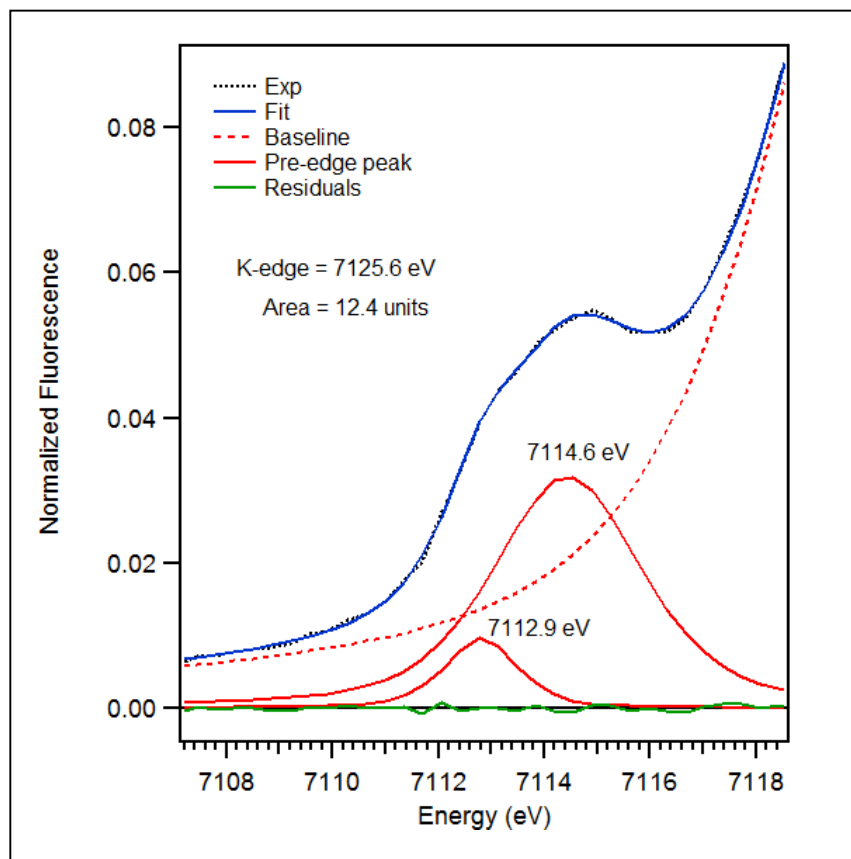


Figure S4. Pre-edge region analysis of hDOHH-P. The experimental data (black dotted), baseline (red dashed), pre-edge peak components (red solid), residuals (green solid) and total fit (blue solid) are shown

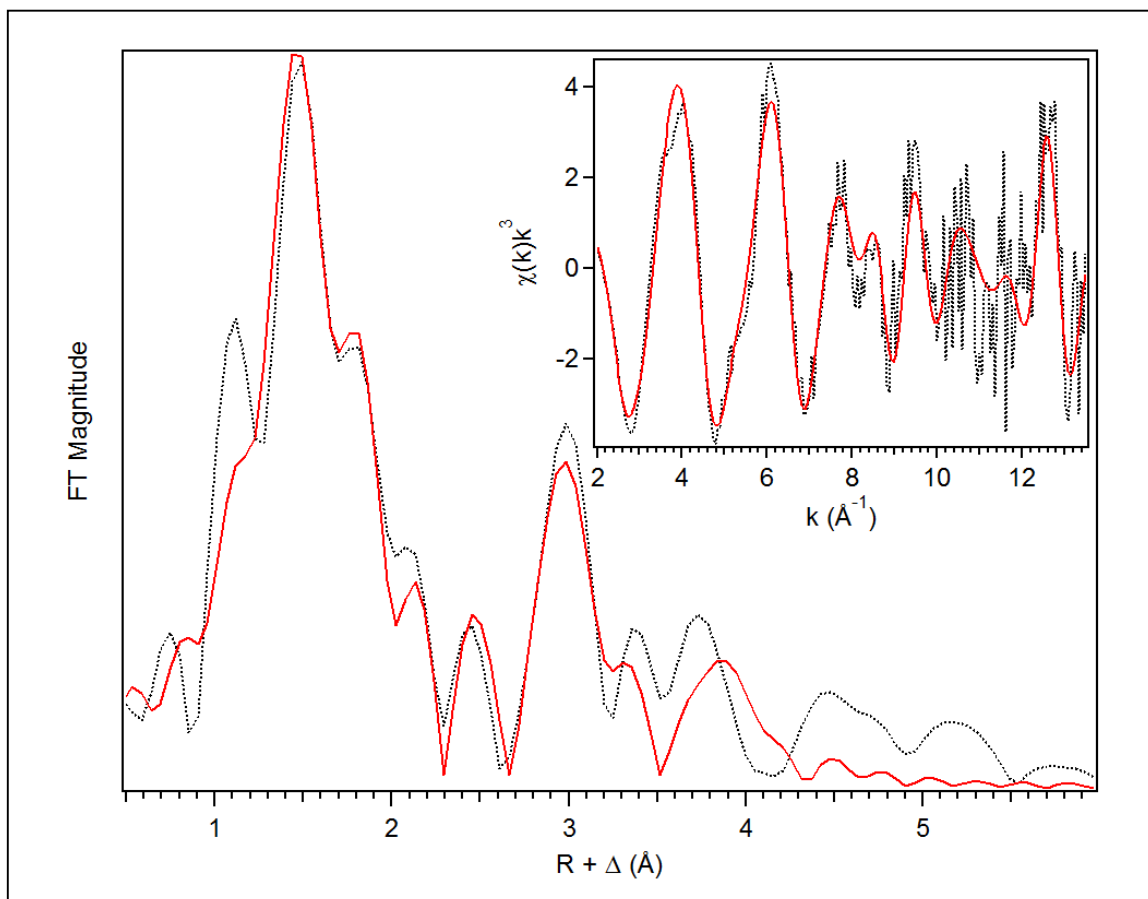


Figure S5. EXAFS spectrum of hDOHH-P. Fit (red solid line) of the unfiltered (black dotted) EXAFS data (inset) and corresponding Fourier transform (Table S2, Fit 14). Data was fit between  $k = 2 - 13.5 \text{\AA}^{-1}$ .

Table S2. Fit parameters for the unfiltered EXAFS data of hDOHH-P, between  $k = 2 - 13.5 \text{ \AA}^{-1}$ .  
Fit 14 gives the most reasonable fit of the experimental data.

Fit	Fe-N			Fe-O			Fe•••Fe			Fe•••C			GOF		
	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	$E_0$	F	F'
1	6	2.08	12.12										0.79	392	637
2	5	2.08	10.51										1.30	410	652
3	4	2.09	8.80										2.31	446	680
4	3	2.11	6.86										3.63	504	723
5	3	2.13	1.44	1	1.97	-1.40							1.19	331	586
6	3	2.15	1.33	2	1.98	1.73							-0.21	305	562
7	4	2.14	3.10	2	1.96	2.04							-0.32	300	558
8	3	2.15	0.56	2	1.99	0.74							-2.27	297	554
				1	1.90	4.49									
9	3	2.14	1.46	2	1.97	1.82	1	3.42	3.05				-0.79	233	491
10	3	2.14	1.36	2	1.97	1.77	1	3.42	3.33	3	4.30	0.08	-0.60	209	465
11	3	2.14	1.37	2	1.97	1.79	1	3.42	3.30	4	4.30	1.51	-0.51	207	464
12	3	2.15	0.99	2	1.99	1.63	1	3.41	3.21	4	2.29	1.61	-2.09	198	453
				1	1.91	6.68									
13	3	2.14	1.53	2	1.97	1.93	1	3.42	2.03	4	4.30	1.44	-0.78	197	452
										3	3.60	3.31			
<b>14</b>	<b>3</b>	<b>2.15</b>	<b>1.95</b>	<b>3</b>	<b>1.98</b>	<b>4.57</b>	<b>1</b>	<b>3.41</b>	<b>1.86</b>	<b>4</b>	<b>4.29</b>	<b>1.55</b>	<b>-1.76</b>	<b>190</b>	<b>444</b>
										<b>3</b>	<b>3.58</b>	<b>2.93</b>			

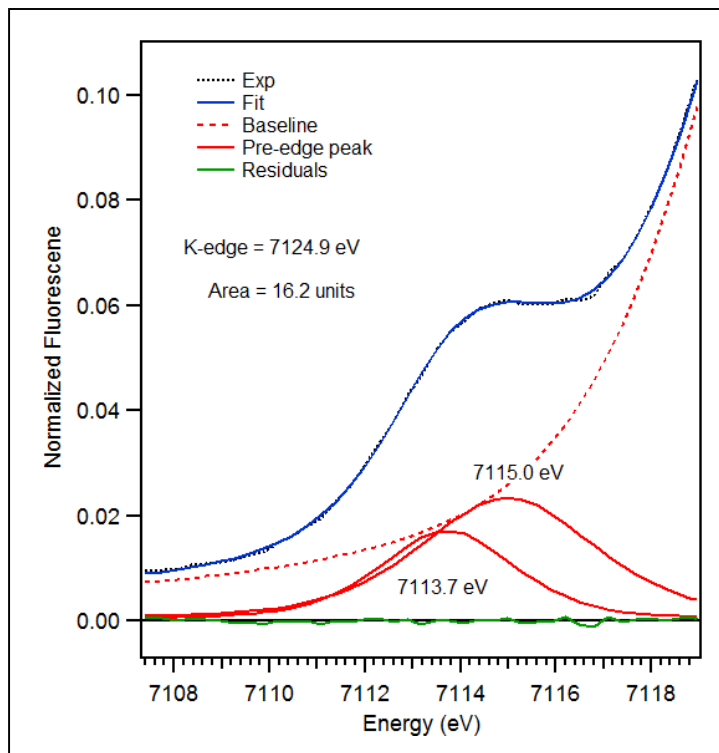


Figure S6. Pre-edge region analysis of hDOHH-P•S. The experimental data (black dotted), baseline (red dashed), pre-edge peak components (red solid), residuals (green solid) and total fit (blue solid) are shown

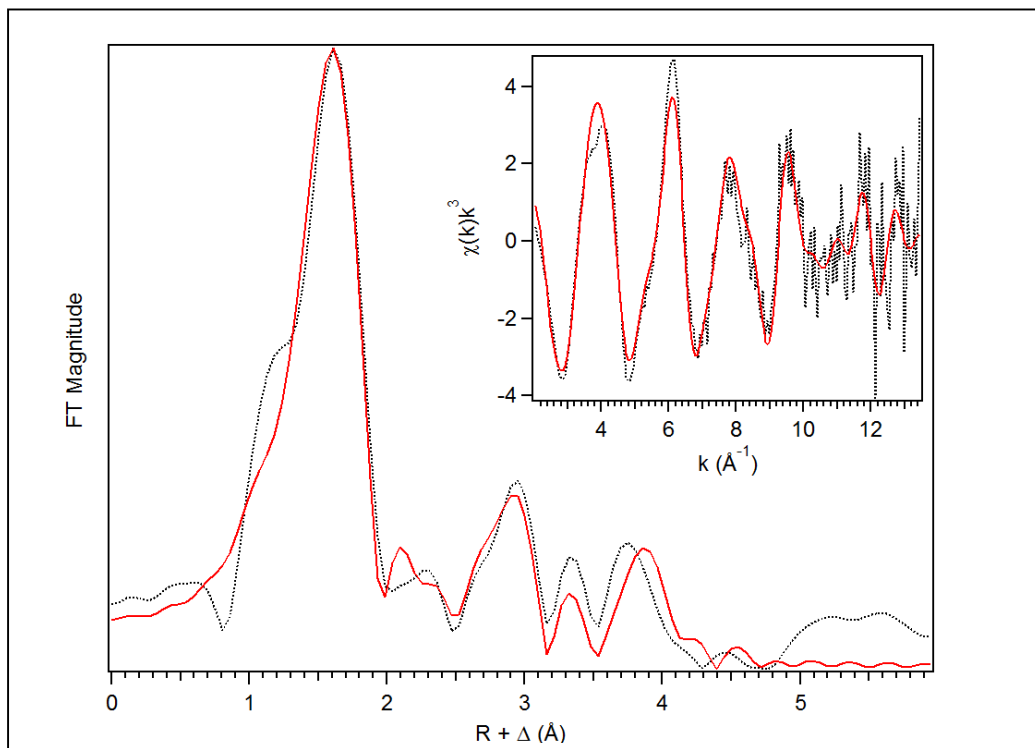


Figure S7. EXAFS spectrum of hDOHH-P•S. Fit (red solid line) of the unfiltered (black dotted) EXAFS data (inset) and corresponding Fourier transform (Table S3, Fit 17). Data was fit between  $k = 2 - 13.5 \text{ \AA}^{-1}$ .



Table S3. Fit parameters for the unfiltered EXAFS data of hDOHH-P•S, between  $k = 2 - 13.5 \text{ \AA}^{-1}$ . Fit 17 gives the most reasonable fit of the experimental data.

Fit	Fe-N			Fe-O			Fe•••Fe			Fe•••C			GOF		
	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	$E_0$	F	F'
1	6	2.08	9.45										-4.13	228	540
2	5	2.08	7.76										-3.40	223	553
3	4	2.09	6.06										-2.86	233	546
4	3	2.09	4.29										-2.25	268	585
5	3	2.12	4.15	1	2.00	1.90							-2.51	212	521
6	3	2.10	12.28	2	2.05	5.41							-3.18	208	516
7	4	2.11	6.48	1	1.99	4.77							-3.34	210	518
8	4	2.12	5.70	1	1.99	3.17	1	3.07	7.49				-2.67	169	465
9	4	2.12	5.69	1	1.99	3.00				3	3.10	3.26	-2.67	170	465
10	4	2.11	5.48	1	1.98	3.44	1	3.07	7.44	4	4.30	1.31	-2.65	143	427
11	4	2.11	5.86	1	1.99	3.61	1	3.08	8.0	4	4.30	1.42	-3.00	140	423
										2	3.41	4.02			
12	4	2.10	5.94	1	1.97	5.86				4	4.29	1.30	-4.46	172	469
										2	3.43	1.42			
13	4	2.11	5.50	1	1.97	4.24				4	4.30	1.15	-3.62	134	414
										2	3.43	3.15			
										3	3.09	3.71			
14	4	2.11	5.43	1	1.97	4.05				3	3.09	3.28	-3.62	146	432
										4	4.30	1.16			
15	4	2.10	5.67	1	1.97	4.99	1	3.43	7.95	4	4.29	0.98	-4.44	164	458
16	4	2.1	5.24	1	1.97	3.80	1	3.43	10.99	3	3.09	3.97	-3.87	135	414
										4	4.29	3.99			
<b>17</b>	<b>4</b>	<b>2.11</b>	<b>5.61</b>	<b>1</b>	<b>1.98</b>	<b>4.47</b>	<b>1</b>	<b>3.41</b>	<b>5.44</b>	<b>3</b>	<b>3.09</b>	<b>6.50</b>	<b>-3.90</b>	<b>132</b>	<b>411</b>
										<b>3</b>	<b>3.56</b>	<b>3.51</b>			
										<b>4</b>	<b>4.30</b>	<b>1.72</b>			
18	4	2.11	5.75	1	1.98	4.52	1	3.41	5.61	3	3.61	3.20	-4.00	38	421
							1	3.07	11.32	4	4.29	1.92			
19	4	2.10	6.32	2	1.98	10.78	1	3.48	13.37	2	3.38	1.82	-5.34	140	424
							1	3.07	10.03	4	4.28	1.32			
20	5	2.09	7.05	1	1.94	8.36	1	3.07	8.68	3	3.41	5.49	-4.94	148	435
										4	4.28	1.02			
21	4	2.09	5.95	2	1.96	11.61	1	3.40	4.58	3	3.08	7.63	-5.84	134	414
										3	3.59	2.50			
										4	4.28	2.02			
22	4	2.10	5.83	1.5	1.97	8.81	1	3.40	4.99	3	3.08	7.24	-5.14	132	411
										3	3.59	3.17			
										4	4.29	1.66			
23	4.5	2.09	6.41	1.5	1.95	10.26	1	3.41	4.71	3	3.08	7.13	-5.40	135	416
										3	3.60	2.45			
										4	4.29	1.89			
24	4.5	2.10	6.40	1	1.96	7.00	1	3.41	5.18	3	3.09	6.67	-4.56	134	415
										3	3.60	3.12			
										4	4.29	1.87			

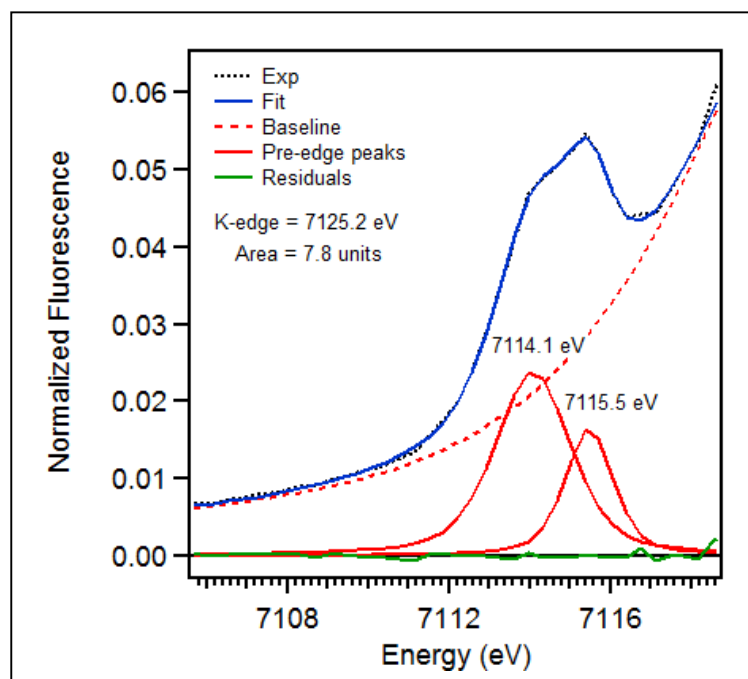


Figure S8. Pre-edge region analysis of hDOHH-D. The experimental data (black dotted), baseline (red dashed), pre-edge peak components (red solid), residuals (green solid) and total fit (blue solid) are shown.

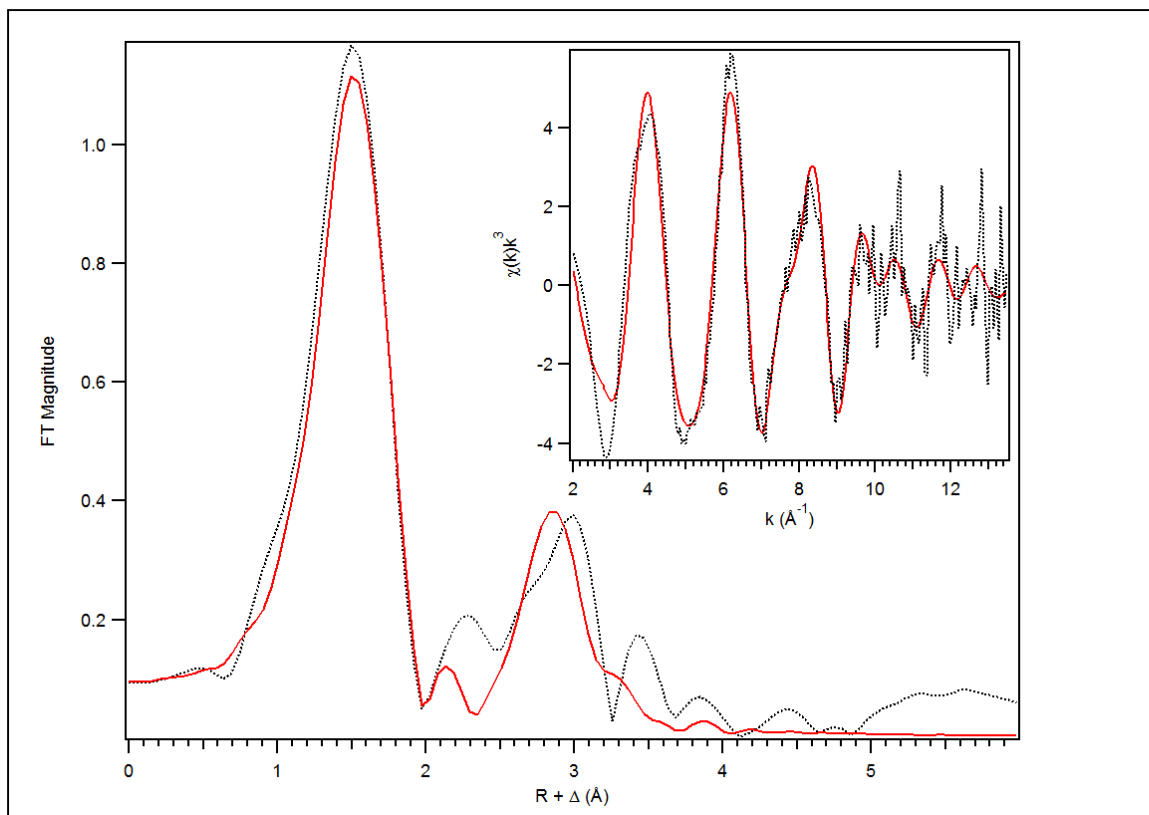


Figure S9. EXAFS spectrum of hDOHH-D. Fit A (red solid line) of the unfiltered (black dotted) EXAFS data (inset) and corresponding Fourier transform (Table S4, Fit 11). Fit A includes an Fe•••Fe distance at 3.07 Å. Data was fit between  $k = 2 - 13.5 \text{ \AA}^{-1}$

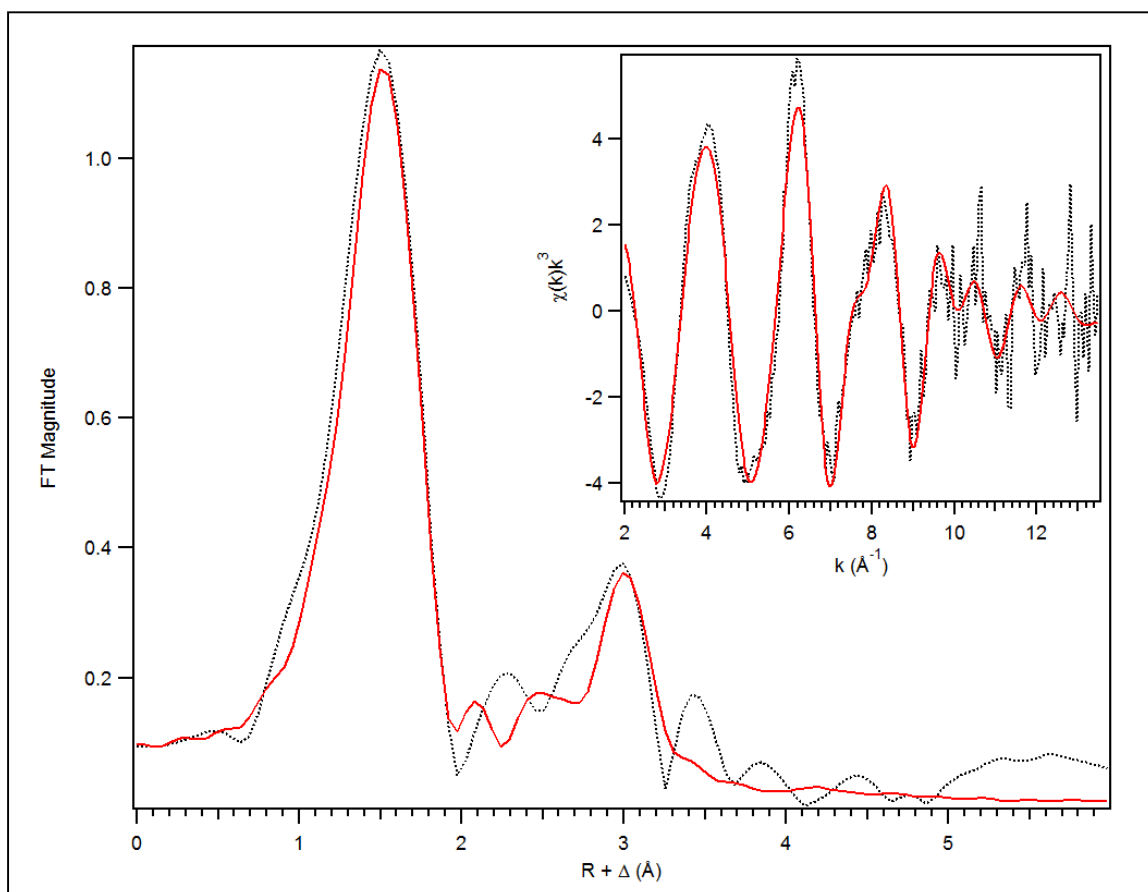


Figure S10. EXAFS spectrum of hDOHH-D. Fit B (red solid line) of the unfiltered (black dotted) EXAFS data (inset) and corresponding Fourier transform (Table S5, Fit 8). Fit B includes an Fe•••Fe distance at 3.42 Å and is the preferred fit for hDOHH-D. Data was fit between  $k = 2 - 13.5 \text{ \AA}^{-1}$ .

Table S4. Fit parameters for the unfiltered EXAFS data of hDOHH-D Fit A, between  $k = 2 - 13.5 \text{ \AA}^{-1}$ . Fit 11 gives the most reasonable fit of the experimental data.

Fit	Fe-N			Fe-O			Fe•••Fe			Fe•••C			GOF		
	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	$E_0$	F	F'
1	6	2.03	8.25										-0.93	233	431
2	5	2.03	6.92										-0.73	273	466
3	4	2.03	5.57										-0.41	340	521
4	5	2.07	5.50	1	1.93	0.87							-0.77	209	409
5	5	2.08	6.35	2	1.94	3.93							-1.52	197	396
6	4	2.09	4.43	2	1.96	2.78							-1.18	207	406
7	3	2.10	2.32	2	1.95	1.74							-0.96	233	431
8	4	2.09	4.58	2	1.95	2.88	1	3.07	6.22				-0.44	151	348
9	4	2.10	4.56	2	1.96	2.68				4	3.09	4.46	0.42	178	377
10	4	2.09	4.36	2	1.95	2.72				4	3.07	7.03	-0.39	127	319
										4	3.43	2.27			
<b>11</b>	<b>4</b>	<b>2.07</b>	<b>4.05</b>	<b>2</b>	<b>1.93</b>	<b>2.81</b>	<b>1</b>	<b>3.07</b>	<b>9.87</b>	<b>5</b>	<b>3.41</b>	<b>3.51</b>	<b>-2.90</b>	<b>133</b>	<b>326</b>

Table S5. Fit parameters for the unfiltered EXAFS data of hDOHH-D Fit B, between  $k = 2 - 13.5 \text{ \AA}^{-1}$ . Fit 8 gives the most reasonable fit of the experimental data.

Fit	Fe-N			Fe-O			Fe•••Fe			Fe•••C			GOF		
	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	$E_0$	F	F'
1	6	2.03	8.23										-0.95	233	431
2	5	2.03	6.91										-0.75	273	466
3	4	2.03	5.56										-0.44	340	521
4	4	2.07	3.60	1	1.93	-0.20							-0.41	237	435
5	4	2.09	4.44	2	1.94	2.82							-1.22	206	405
6	5	2.08	6.39	2	1.94	3.97							-1.49	197	396
7	4	2.08	4.20	2	1.94	2.89	1	3.41	3.97				-1.97	141	336
<b>8</b>	<b>4</b>	<b>2.09</b>	<b>4.45</b>	<b>2</b>	<b>1.95</b>	<b>2.88</b>	<b>1</b>	<b>3.42</b>	<b>5.09</b>	<b>3</b>	<b>3.08</b>	<b>4.90</b>	<b>-0.69</b>	<b>127</b>	<b>317</b>
9	4	2.09	4.25	2	1.94	2.73				5	3.43	3.62	-1.28	125	316
										3	3.09	4.73			
10	4	2.09	4.58	2	1.95	2.74				3	3.10	2.65	0.01	166	364

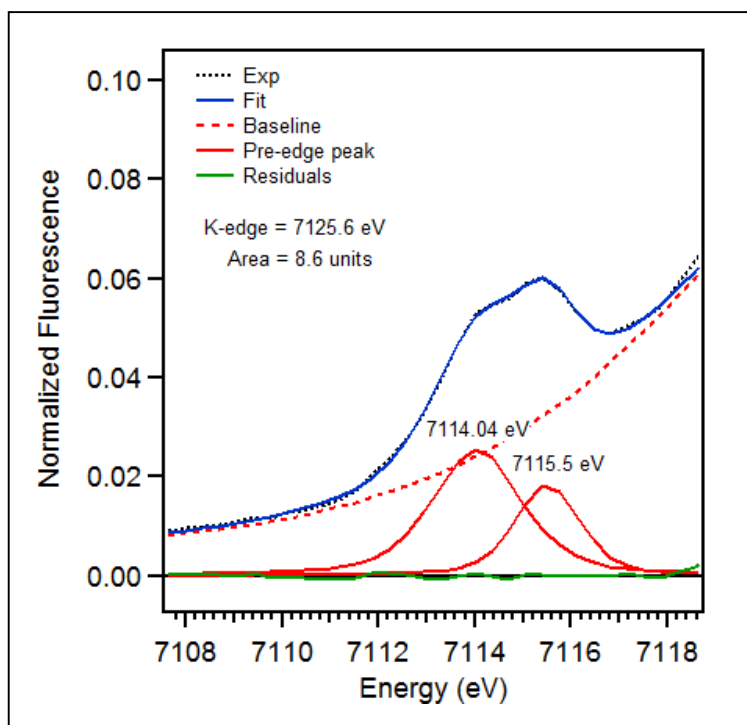


Figure S11. Pre-edge region analysis of hDOHH-D•S. The experimental data (black dotted), baseline (red dashed), pre-edge peak components (red solid), residuals (green solid) and total fit (blue solid) are shown.

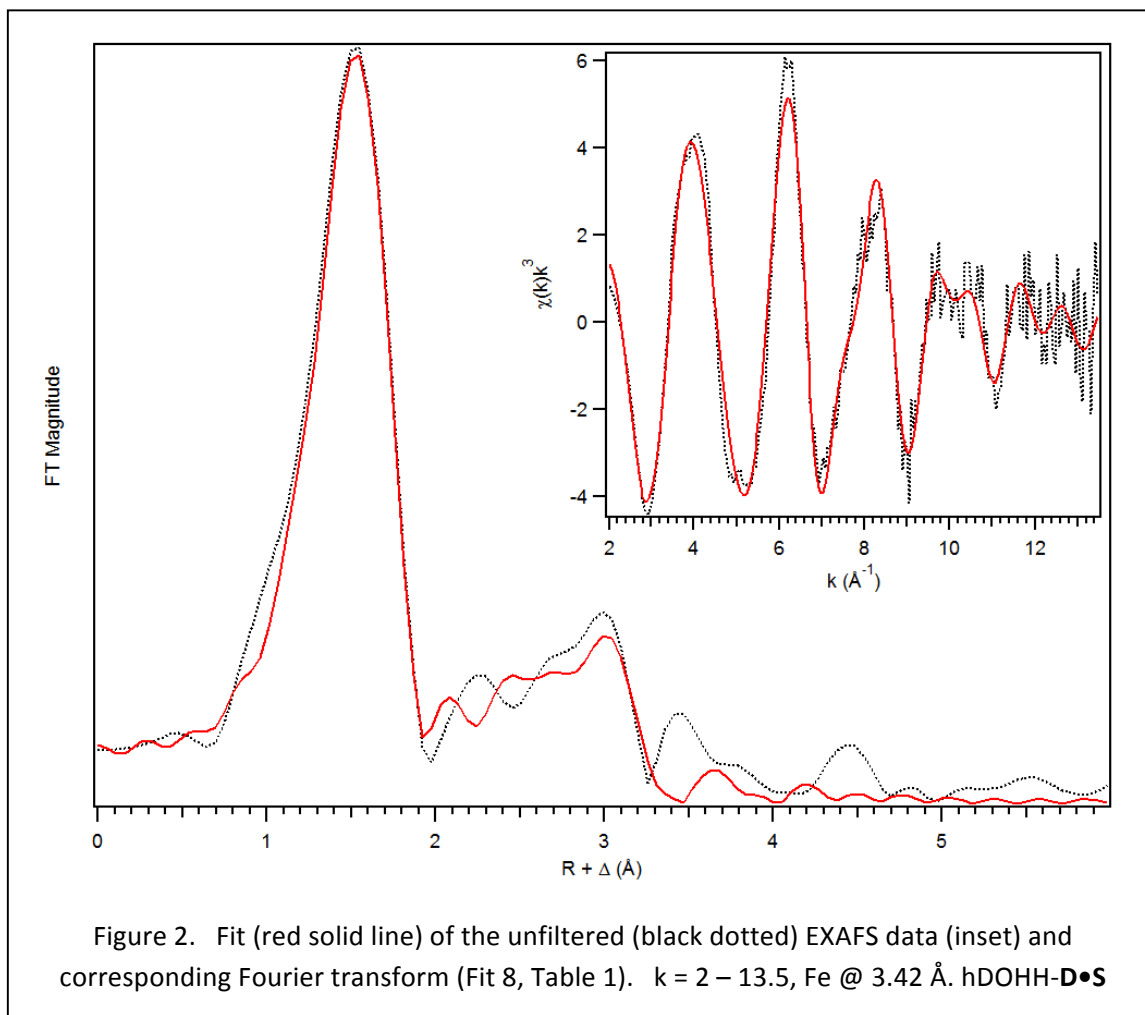


Figure S12. EXAFS spectrum of hDOHH-**D•S**. Fit (red solid line) of the unfiltered (black dotted) EXAFS data (inset) and corresponding Fourier transform (Table S6, Fit 10). Data was fit between  $k = 2 - 13.5 \text{ \AA}^{-1}$ .

Table S6. Fit parameters for the unfiltered EXAFS data of hDOHH-D•S, between  $k = 2 - 13.5 \text{ \AA}^{-1}$   
<sup>1</sup>. Fit 10 gives the most reasonable fit of the experimental data.

Fit	Fe-N			Fe-O			Fe•••Fe			Fe•••C			GOF		
	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	N	R(Å)	$\sigma^2(10^{-3})$	$E_0$	F	F'
1	6	2.03	7.49										-0.91	181	376
2	5	2.03	6.21										-0.70	218	412
3	4	2.03	4.89										-0.41	284	471
4	3	2.03	3.46										-0.19	391	552
5	5	2.06	5.29	1	1.93	0.95							-0.60	163	356
6	5	2.07	6.59	2	1.94	4.34							-1.39	157	350
7	4	2.08	4.44	2	1.95	2.78							-0.96	161	354
8	4	2.07	4.20	2	1.94	2.79	1	3.42	4.96				-1.54	113	297
9	4	2.08	4.20	2	1.95	2.56	1	3.44	6.17	3	3.08	5.33	-0.45	97	274
<b>10</b>	<b>4</b>	<b>2.08</b>	<b>4.40</b>	<b>2</b>	<b>1.95</b>	<b>2.88</b>	<b>1</b>	<b>3.42</b>	<b>3.51</b>	<b>3</b>	<b>3.08</b>	<b>6.29</b>	<b>-0.71</b>	<b>85</b>	<b>258</b>
										<b>3</b>	<b>3.59</b>	<b>3.30</b>			
11	4	2.08	4.23	2	1.90	2.56	1	3.44	6.14	3	3.08	5.49	-0.37	94	271
										3	4.27	6.60			
12	4	2.08	4.51	2	1.95	2.96	1	3.42	3.30	3	3.08	6.43	-0.55	77	245
										3	3.59	2.68			
										3	4.27	5.46			

Table S7. Component analysis of pre-edge peak fitting for hDOHH species. Pre-edge peaks were fit between 7108 – 7118 eV using PseudoVoigt functions with a 50:50 Gaussian/Lorentzian peak shape.

Species	Component Position (eV)	Component Area (units)	Total Area (units)
hDOHH-R	7110.4	1.93	8.6
	7111.9	6.20	
	7112.5	0.43	
hDOHH-P	7112.9	1.67	12.4
	7114.5	10.7	
hDOHH-P•S	7113.7	5.82	16.2
	7115.0	10.4	
hDOHH-D	7114.1	5.40	7.8
	7114.6	2.40	
hDOHH-D•S	7114.0	5.64	8.6
	7115.5	2.93	

Table S8. Selected distances from crystal structures of ferrous (Fe<sup>II</sup>) synthetic model complexes.

Complex	Fe / Fe <sub>2</sub>	Core OH <sub>x</sub>	Fe-O (Å)	Term. OH <sub>x</sub>	Fe-O (Å)	Fe...Fe (Å)	<Fe-O-Fe	References
[Fe <sub>2</sub> (μ-OH)(μ-OH <sub>2</sub> )(TPA) <sub>2</sub> ](OTf) <sub>2</sub>	Fe <sub>2</sub>	OH	2.098 2.034	-	-	3.216	95.5 °	1
		OH <sub>2</sub>	2.132 2.210	-	-	-	102.2 °	
[Fe <sub>2</sub> (μ-OH) <sub>2</sub> (6-Me <sub>3</sub> -TPA) <sub>2</sub> ](OTf) <sub>2</sub>	Fe <sub>2</sub>	OH	2.033 2.208	-	-	3.221	98.8 °	2
[Fe <sub>2</sub> (μ-OH <sub>2</sub> ) <sub>2</sub> (μ-O <sub>2</sub> CAr <sup>4F-Ph</sup> )(O <sub>2</sub> CAr <sup>4F-Ph</sup> ) <sub>3</sub> (THF) <sub>2</sub> (OH <sub>2</sub> )]	Fe <sub>2</sub>	OH <sub>2</sub>	2.229 2.293 2.232 2.152	OH <sub>2</sub>	2.115	3.288	93.3 ° 97.1 °	3
[Fe <sub>2</sub> (μ-OH <sub>2</sub> ) <sub>2</sub> (μ-O <sub>2</sub> CAr <sup>Tol</sup> ) <sub>2</sub> (O <sub>2</sub> CAr <sup>Tol</sup> ) <sub>2</sub> (THF) <sub>2</sub> ]	Fe <sub>2</sub>	OH <sub>2</sub>	2.326 2.398	-	-	3.043	80.2 °	4
[Fe <sub>2</sub> (μ-OH)(μ-OAc) <sub>2</sub> (TACN) <sub>2</sub> ](ClO <sub>4</sub> )	Fe <sub>2</sub>	OH	1.987	-	-	3.317	113.1 °	5
[Fe(H <sub>2</sub> O) <sub>2</sub> ( <sup>Me2,BzIm</sup> TACN)](OTf) <sub>2</sub>	Fe	-	-	OH <sub>2</sub>	2.113 2.148	-	-	6
[Fe(LN <sub>3</sub> SMe)(H <sub>2</sub> O) <sub>3</sub> ](OTf) <sub>2</sub>	Fe	-	-	OH <sub>2</sub>	2.116 2.086 2.098	-	-	7
[Fe(indH)(CH <sub>3</sub> CN)(H <sub>2</sub> O) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Fe	-	-	OH <sub>2</sub>	2.145 2.163	-	-	8
[Fe(H <sub>2</sub> O) <sub>6</sub> ](C <sub>17</sub> H <sub>13</sub> O <sub>7</sub> S) <sub>2</sub> •8H <sub>2</sub> O	Fe	-	-	OH <sub>2</sub>	2.138 2.155 2.043	-	-	9
[Fe(κN-nicH)(H <sub>2</sub> O) <sub>4</sub> ]	Fe	-	-	OH <sub>2</sub>	2.135	-	-	10
[Fe(bpe) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ](TCNQ) <sub>2</sub>	Fe	-	-	OH <sub>2</sub>	2.107 2.109	-	-	11

TPA = tri-(2-pyridylmethyl)amine, 6-Me<sub>3</sub>-TPA = tri-(6-methyl-2-pyridylmethyl)amine, O<sub>2</sub>CAr<sup>4F-Ph</sup> = 2,6-di-(p-tolyl)benzoate, TACN = N,N',N''-trimethyl-1,4,7-triazacyclononane, <sup>Me2,BzIm</sup>TACN = 1-(2-methyl-1-benzimidazolyl)methyl-4,7-dimethyl-1,4,7-triazacyclononane, indH = 1,3-bis(2'-pyridylimino)isoindoline, C<sub>17</sub>H<sub>13</sub>O<sub>7</sub>S = bis(4',7-dimethoxyisoflavone-3'-sulfonate), nicH = pyridine-3-carboxylic acid, bpe = trans-1,2-bis(4-pyridyl)ethane, TCNQ = tetracyanoquinodimethane

Table S9. Selected distances from crystal structures of ferric (Fe<sup>III</sup>) synthetic model complexes.

Complex	Fe / Fe <sub>2</sub>	Core OH <sub>x</sub>	Fe-O (Å)	Term. OH <sub>x</sub>	Fe-O (Å)	Fe•••Fe (Å)	<Fe-O-Fe	References
[Fe <sub>2</sub> (μ-OH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ((CH <sub>3</sub> ) <sub>2</sub> NC <sub>7</sub> H <sub>2</sub> NO <sub>4</sub> ) <sub>2</sub> ]	Fe <sub>2</sub>	OH	1.937 1.986	OH <sub>2</sub>	2.033	3.118	105.3 °	12
[Fe <sub>2</sub> (μ-OH)(μ-OAc) <sub>2</sub> (HBpz <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub>	Fe <sub>2</sub>	OH	1.960 1.953	-	-	3.438	123.0 °	13
[Fe <sub>2</sub> (μ-OH) <sub>2</sub> (μ-O <sub>2</sub> CAr <sup>Tol</sup> ) <sub>2</sub> (O <sub>2</sub> CAr <sup>Tol</sup> ) <sub>2</sub> (4-CNPy) <sub>2</sub> ]	Fe <sub>2</sub>	OH	1.978 1.945 1.997 1.945	-	-	2.831	92.4 °	14
[Fe <sub>2</sub> (L <sup>amine</sup> ) <sub>2</sub> (μ-OH)]BPh <sub>4</sub>	Fe <sub>2</sub>	OH	2.003 2.017	-	-	3.762	138.6 °	15
[Fe <sub>2</sub> (L <sup>NO<sub>2</sub></sup> ) <sub>2</sub> (μ-OH)]ClO <sub>4</sub>	Fe <sub>2</sub>	OH	1.969 2.003	-	-	3.733	140.1 °	16
[Fe <sub>2</sub> (μ-O)(OH)(OH <sub>2</sub> )(TPA) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Fe <sub>2</sub>	O	1.830 1.780	OH OH <sub>2</sub>	1.914 2.041	3.389	138.9 °	17
[Fe <sub>2</sub> (μ-O)(OH)(OH <sub>2</sub> )(5-Et-TPA) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Fe <sub>2</sub>	O	1.826 1.779	OH OH <sub>2</sub>	1.907 2.049	3.346	136.3 °	18
[Fe(tnpa)(OH)(PhCOO)]ClO <sub>4</sub>	Fe	-	-	OH	1.876	-	-	19
K[FeH <sub>3</sub> 1(OH)]	Fe	-	-	OH	1.932 1.921	-	-	20
[Fe <sub>2</sub> (L <sup>Ph<sup>4</sup></sup> -O)(Ph <sub>3</sub> CCO <sub>2</sub> )(OH)](ClO <sub>4</sub> ) <sub>2</sub>	Fe <sub>2</sub>	OR	2.051 2.008	OH	1.862	3.508	119.6 °	21
[Fe(OH)(L <sup>1</sup> )] [K(DMF) <sub>3</sub> ]	Fe	-	-	OH	1.857	-	-	22
K[Fe <sup>0iPr</sup> (OH)]	Fe	-	-	OH	1.876	-	-	23
[Fe <sub>2</sub> (N-Et-HPTB)(NO)(OH)(DMF) <sub>2</sub> ](BF <sub>4</sub> ) <sub>3</sub>	Fe <sub>2</sub>	OR	1.952 2.044	OH	1.817 1.823	3.621	130.0 °	24

(CH<sub>3</sub>)<sub>2</sub>NC<sub>7</sub>H<sub>2</sub>NO<sub>4</sub> = bis[4-dimethylamino-2,6-pyridinedicarboxylate], HBpz<sub>3</sub> = hydrotris(1-pyrazolyl)borate, O<sub>2</sub>CAr<sup>Tol</sup> = 2,6-di-(p-tolyl)benzoate, 4-CNPy = 4-cyanopyridine, L<sup>amine</sup> = 2,2'-(2-nethyl-2-(pyridin-2-yl)propane-1,3-diyl)bis(azanediyl)bis(methylene)diphenol, L<sup>NO<sub>2</sub></sup> = 2,2'-(2-Methyl-2(pyridine-2-yl)propane-1,3diyl)bis(azanediyl)-bis(methylene)bis(4-nitrophenol), TPA = tri-(2-pyridylmethyl)amine, 5-Et-TPA = 5-ethyl-tri-(2-pyridylmethyl)amine, tnpa = tris(6-neopentylamino-2-pyridylmethyl)amine, H<sub>3</sub>1 = tris[(N'-tert-butylureaylato)-N-ethyl]amine, L<sup>Ph<sup>4</sup></sup>-O = N,N,N',N'-tetrakis[(1-methyl-2-phenyl-4-imidazolyl)methyl]-1,3-diamino-2-propanolate, L<sup>1</sup> = tris(1-phenyl-2(4-tert-butylalanine))amine, 0<sup>iPr</sup> = Tris(N-isopropylcarbamoylmethyl)amine, N-Et-HPTB = N,N,N',N'-tetrakis[2-(1-ethylbenzimidazolyl)]-2-hydroxy-1,3-diaminopropane



Table S9 (continued). Selected distances from crystal structures of ferric (Fe<sup>III</sup>) synthetic model complexes.

Complex	Fe / Fe <sub>2</sub>	Core OH <sub>x</sub>	Fe-O (Å)	Term. OH <sub>x</sub>	Fe-O (Å)	Fe•••Fe (Å)	<Fe-O-Fe	References
[Fe <sub>2</sub> (N-Et-HPTB)(OH) <sub>2</sub> (DMF) <sub>2</sub> ](BF <sub>4</sub> ) <sub>3</sub>	Fe <sub>2</sub>	OR	1.979 2.044	OH	1.817 1.823	3.954	129.1 °	25
[Fe <sub>2</sub> (μ-OH) <sub>2</sub> (μ-O <sub>2</sub> CAr <sup>4F-Ph</sup> )(O <sub>2</sub> CAr <sup>4F-Ph</sup> ) <sub>3</sub> (OH <sub>2</sub> )(2-Ph <sub>2</sub> P(O)-py)]	Fe <sub>2</sub>	OH	1.981 1.955 1.977 1.981	OH <sub>2</sub>	2.099	2.973	98.2 ° 97.4 °	26
[Fe <sub>2</sub> (μ-OH)(OH <sub>2</sub> ) <sub>2</sub> (4-Ph-hxta)]	Fe <sub>2</sub>	OR OH	2.028 1.989 1.956	OH <sub>2</sub>	1.994	3.090	104.4 ° 100.6 °	27
[Fe <sub>2</sub> (μ-OH) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (Dipic) <sub>2</sub> ]	Fe <sub>2</sub>	OH	1.937 1.993	OH <sub>2</sub>	2.021	3.089	103.6 °	28
[Fe <sub>2</sub> (μ-OH) <sub>2</sub> (μ-O <sub>2</sub> CAr <sup>Tol</sup> )(O <sub>2</sub> CAr <sup>Tol</sup> ) <sub>3</sub> (OH <sub>2</sub> )(Hdmpz) <sub>2</sub> ]	Fe <sub>2</sub>	OH	1.945 1.958 2.013 1.953	OH <sub>2</sub>	2.013	2.996	100.3 °	29
[Fe <sub>2</sub> (μ-O <sub>2</sub> )(Ph <sub>3</sub> PO) <sub>2</sub> (N-Et-HPTB)](BF <sub>4</sub> ) <sub>3</sub>	Fe <sub>2</sub>	OR OO	1.991 1.881	-	-	3.463	120.8 °	30
[Fe <sub>2</sub> (μ-O <sub>2</sub> )(μ-O <sub>2</sub> CPh)(Ph-bimp)](BF <sub>4</sub> ) <sub>2</sub>	Fe <sub>2</sub>	OR OO	2.018 2.001 1.944 1.864	-	-	3.327	111.7 °	31
[Fe <sub>2</sub> (μ-O <sub>2</sub> )(μ-O <sub>2</sub> CCH <sub>2</sub> Ph) <sub>2</sub> {HB(pz') <sub>3</sub> }]	Fe <sub>2</sub>	OO	1.881 1.877	-	-	4.007	-	32
[Fe <sub>2</sub> (6Me <sub>2</sub> -BPP) <sub>2</sub> (μ-OH)(μ-O <sub>2</sub> )](OTf)	Fe <sub>2</sub>	OH OO	1.943 2.006 1.887 1.867	-	-	3.395	118.6 °	33

N-Et-HPTB = N,N,N',N'- tetrakis[2-(1-ethylbenzimidazolyl)]-2-hydroxy-1,3-diaminopropane, O<sub>2</sub>CAr<sup>4F-Ph</sup> = 2,6-di-(p-tolyl)benzoate, 2-Ph<sub>2</sub>P(O)-py = 2-Pyridyldiphenylphosphine oxide, 4-Ph-hxta = 2- hydroxy-5-phenyl-1,3-xylylenedimethanamine-N,N,N',N'-tetraacetate, Dipic = 2,6-pyridinedicarboxylate, O<sub>2</sub>CAr<sup>Tol</sup> = 2,6-di-(p-tolyl)benzoate, Hdmpz = 3,5-dimethylpyrazole, Ph-bimp = 2,6-bis[bis{2-(1-methyl- 4,5-diphenylimidazolyl)methyl} aminomethyl]-4-methylphenolate, pz' = 3,5-bis(isopropyl)- pyrazole, 6Me<sub>2</sub>-BPP = N,N-bis(6-methyl-2-pyridylmethyl-3-amino-propionic acid

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