Supporting Information for

Hydrogen bonding effects on the reactivity of [X-Fe^{III}–O–Fe^{IV}=O] (X = OH, F) complexes towards C–H bond cleavage

Genqiang Xue,[‡] Caiyun Geng,[&] Shengfa Ye,[&] Adam T. Fiedler,[‡] Frank Neese,[&,*] and Lawrence Que, Jr.[‡,*]

[‡]Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, 207 Pleasant St. SE, Minneapolis, Minnesota 55455, United States

[&]Max-Planck Institut für Chemische Energiekonversion, Stiftstr. 34-36, D-45470 Mülheim an der Ruhr, Germany

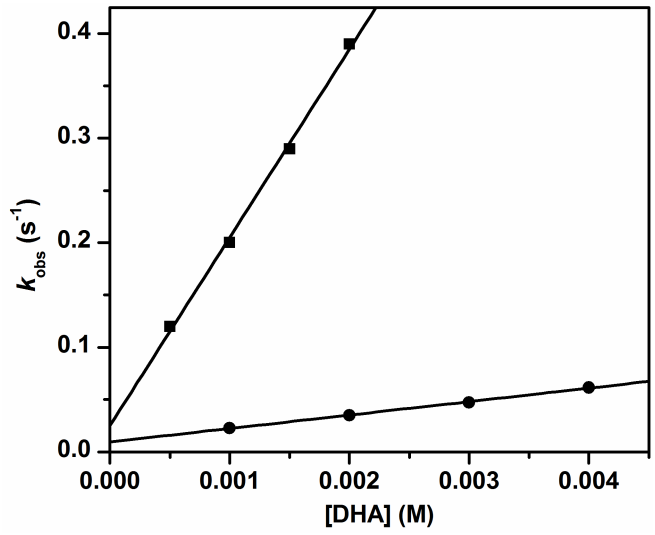

Figure S1. k_{obs} vs [substrate] plots for oxidation of DHA by **1**-F (squares) and **1**-OH (circles), with k_2 of 180(6) M^{-1} s^{-1} and 12.8(4) M^{-1} s^{-1}, respectively. Conditions: in 3:1 CH_2Cl_2-MeCN at -85 ºC. For all experiments except one, **1**-F was generated from 0.2 mM **1**. For the oxidation of 0.5 mM DHA, **1**-F was generated from 0.1 mM **1**.

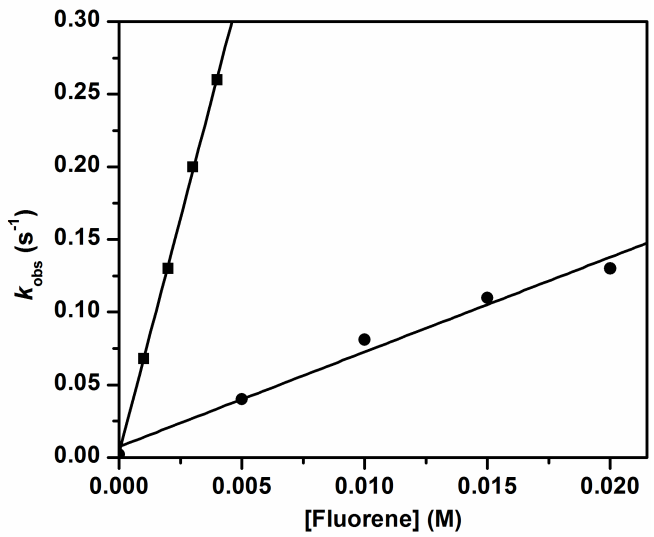

Figure S2. k_{obs} vs [substrate] plots for oxidation of fluorene by **1**-F (squares) and **1**-OH (circles), with k_2 of 65(1) M^{-1} s^{-1} and 6.5(5) M^{-1} s^{-1}, respectively. Conditions: in 3:1 CH_2Cl_2-MeCN at -80 ºC.

Single-Scattering Analysis

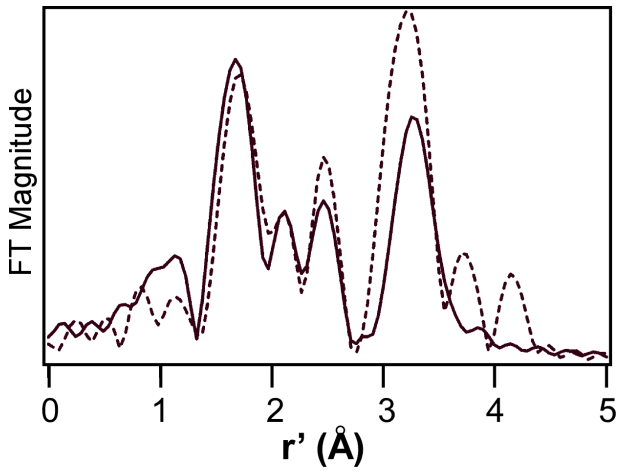

Figure S3. Experimental Fourier-transformed Fe K-edge data (dashed line) obtained at 10 K with a 2.1 mM solution of **1-F** in 3:1 PrCN:MeCN. Fourier-transform range: k = 2.1 – 14.5 $Å^{-1}$. The best fit (solid line) was obtained with the following parameters: 2 N/O at 1.80 Å ($\Delta\sigma^2$, 0.0084), 2 N/O at 2.07 Å (0.0025), 2 N/O at 2.18 Å (0.0005), 6 C at 2.99 Å (0.0074), and 1 Fe at 3.64 Å (0.0005). Only single-scattering mechanisms were included in the fit. *Note the poor fit to the Fe scatterer feature at r = 3.2 Å, indicating the need to include multiple-scattering features.*

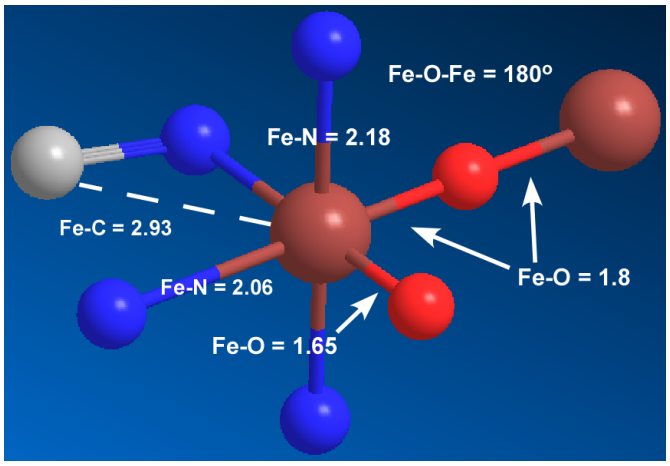

Figure S4. Model of **1-F** employed in *FEFF* calculations of the Fe K-edge EXAFS data. All bond angles around the "primary" Fe center were set to 90° and the O-Fe-O-Fe dihedral angle was set to 0°.

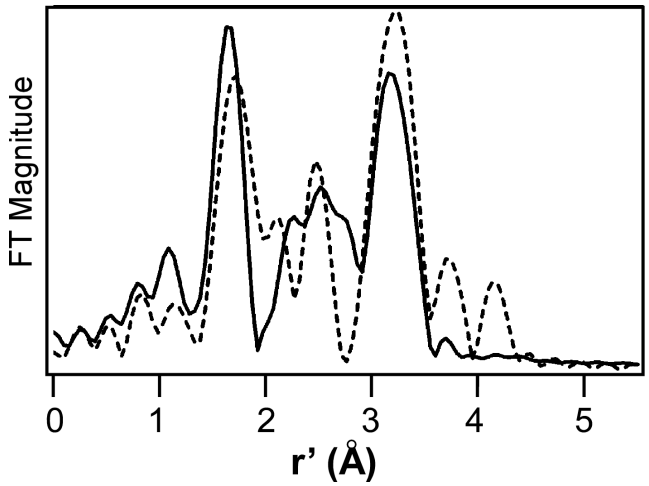

Figure S5. Solid line: Fourier-transform of Fe K-edge EXAFS data ***computed*** for **1-F** using the model shown in Figure S5 and the *FEFF* program. Dashed line: Experimental data obtained for **1-F**; Fourier-transformed range: $k = 2.1 - 14.5$ Å^{-1}.

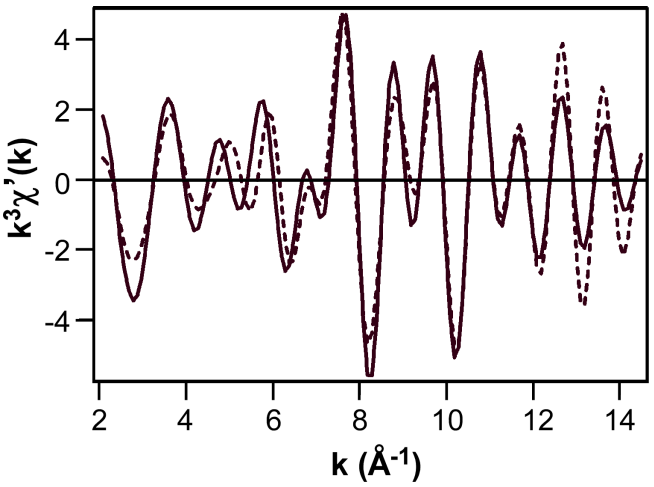

Figure S6. Experimental Fe K-edge data (dashed line) obtained at 10 K with a 2.1 mM solution of **1-F** in 3:1 PrCN:MeCN. Back-transformation range: r' = 0.13 – 4.30 Å. The best fit (solid line) was obtained with the following parameters: 0.5 O/N at 1.66 Å ($\Delta\sigma^2$, 0.0084), 1.5 O/N at 1.83 Å (0.0049), 1 N/O at 2.04 Å (0.0012), 3 N/O at 2.17 (0.0021), 6.5 C at 3.04 Å (0.0085), and 1 Fe at 3.56 Å (0.0037). The fit also included a multiple-scattering feature arising from the nearly linear Fe–O–Fe unit.

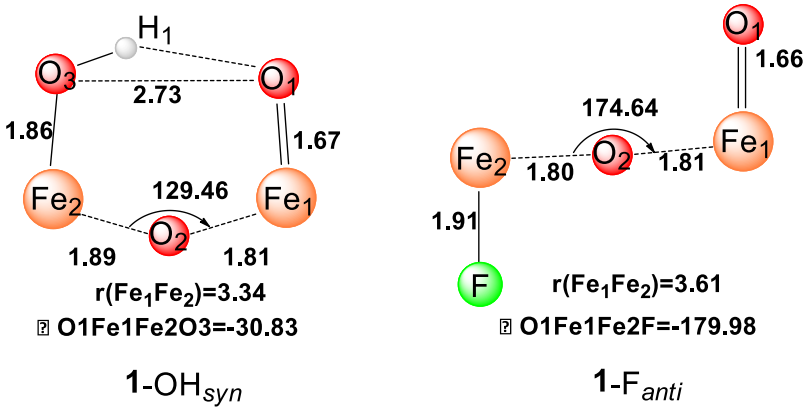

Figure S7. Geometric data from theoretical results for **1**-OH_{syn} and **1**-F_{anti} published in De Hont, R. F.; Xue, G.; Hendrich, M. P.; Que, L., Jr.; Bominaar, E. L.; Münck, E. *Inorg. Chem.* **2010**, *49*, 8310-8322.

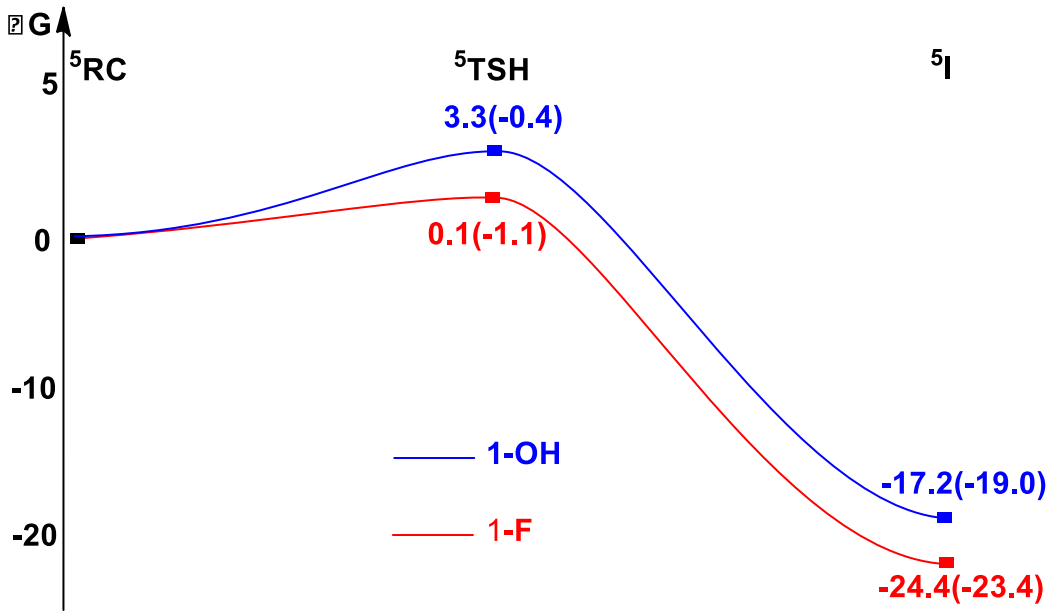

Figure S8. BP86 Calculated Schematic Gibbs free energy (Δ G) surfaces for DHA C-H bond activation by **1**-OH_{syn} and **1**-F_{anti}. In parentheses energies with inclusion of VDW effects are given.

Table S1. Rate constants measured for the Eyring plot for DHA oxidation by **1**-OH (Figure 4).

T (ºC)	-85	-80	-70	-60	-50	-40
$k_2/(M^{-1}\ s^{-1})$	13	28	42	79	1.4×10^2	2.7×10^2

Table S2. Results derived from Gaussian fitting of the **1**-F pre-edge features. Peak height is normalized to the Fe-edge height, area is in units of 10^{-2} eV, and peak position ($E_{1s\rightarrow 3d}$) was calculated after curve fitting by SSExafs. The best fit to the data is #3.

fit	peak #	height	width	area	$E_{1s\rightarrow 3d}$ (eV)
1	1	0.061	3.60	23.3	7114.8
2	1	0.051	2.0	10.8	7113.8
	2	0.047	2.0	10.0	7115.5
	3	0.016	2.0	3.4	7117.1
3	***1***	***0.056***	***2.2***	***13.4***	***7113.8***
	2	***0.039***	***1.8***	***7.5***	***7115.5***
	3	***0.017***	***2.1***	***3.9***	***7117.1***

Table S3, BP86 Calculated Geometry Parameters for the Key Points along the Reaction Pathways. Normal, with VDW effect. In parentheses, without VDW effect.

	$r(Fe_1\text{-}O_1)$	$r(Fe_1\text{-}Fe_2)$	$\angle Fe_1O_2Fe_2(°)$	$\angle O_1Fe_1Fe_2O_3(F)$ (°)	$r(O_1\text{-}O_3)$	$r(O_1\text{-}H_1)$	$r(O_1\text{-}H_2)$	$r(C\text{-}H_2)$
RC(**1**-OH_{syn})	1.68(1.69)	3.23(3.32)	126.94(131.71)	-31.41(-5.62)	2.67(2.60)	1.69(1.61)	~	1.11(1.11)
TSH(**1**-OH_{syn})	1.76(1.77)	3.24(3.33)	127.62(132.98)	-25.39(-19.00)	2.68(2.74)	1.71(1.76)	1.20(1.23)	1.34(1.35)
IN(**1**-OH_{syn})	1.89(1.91)	3.21(3.34)	127.34(134.09)	-36.21(-21.97)	2.85(2.88)	1.94(1.93)	0.98(0.98)	3.33(2.48)
RC(**1**-F_{anti})	1.67(1.67)	3.55(3.53)	173.68(146.45)	-177.18(132.97)	~	~	~	1.11(1.11)
TSH(**1**-F_{anti})	1.74(1.75)	3.54(3.60)	165.60(168.28)	177.79(165.55)	~	~	1.21(1.21)	1.33(1.35)
IN(**1**-F_{anti})	1.87(1.87)	3.55(3.57)	163.54(162.23)	173.25(168.34)	~	~	0.98(0.97)	2.30(5.50)