Supporting Information for

X-ray Absorption Spectroscopy and Reactivity of Thiolate-Ligated Fe^{III}-OOR Complexes

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Table S1. Least-squares Fits of the EXAFS Data for the Iron(II) complexes **1 – 3** as Crystalline Solids in Boron Nitride Matrix

complex	coord no.	R_{as} (Å)[a]	σ^{2b}	coord no.	R_{as} (Å)[a]	σ^{2b}	coord no.	R_{as} (Å)[a]	σ^{2b}	E_0	F^c
1	1S	2.33	2.0	1C	3.51	3.0	2C	4.24	5.0	-7.08	1.19
	4N	2.06	4.0	8C	2.95	10.0	3C	3.27	8.0		
2	1S	2.32	2.0	1C	3.42	3.0	2C	4.14	5.0	-6.90	1.35
	4N	2.12	4.0	8C	3.03	10.0	3C	3.31	8.0		
3	1S	2.35	2.0	1C	3.53	3.0	2C	4.25	5.0	-7.28	1.53
	4N	2.10	4.0	8C	3.02	10.0	3C	3.29	8.0		

[a]Absorber-scatterer distance. [b]Debye-Waller factor (Å^2) × 10^3.

[c] $F = \sum_i k_i^6 \left[\chi_{\exp}(i) - \chi_{calc}(i)\right]^2 / \sum_j k_j^6 \left|\chi_{\exp}(j)\right|$. The accuracy in the determination of the bond lengths is approximately 0.02 Å and the precision is 0.004 Å.

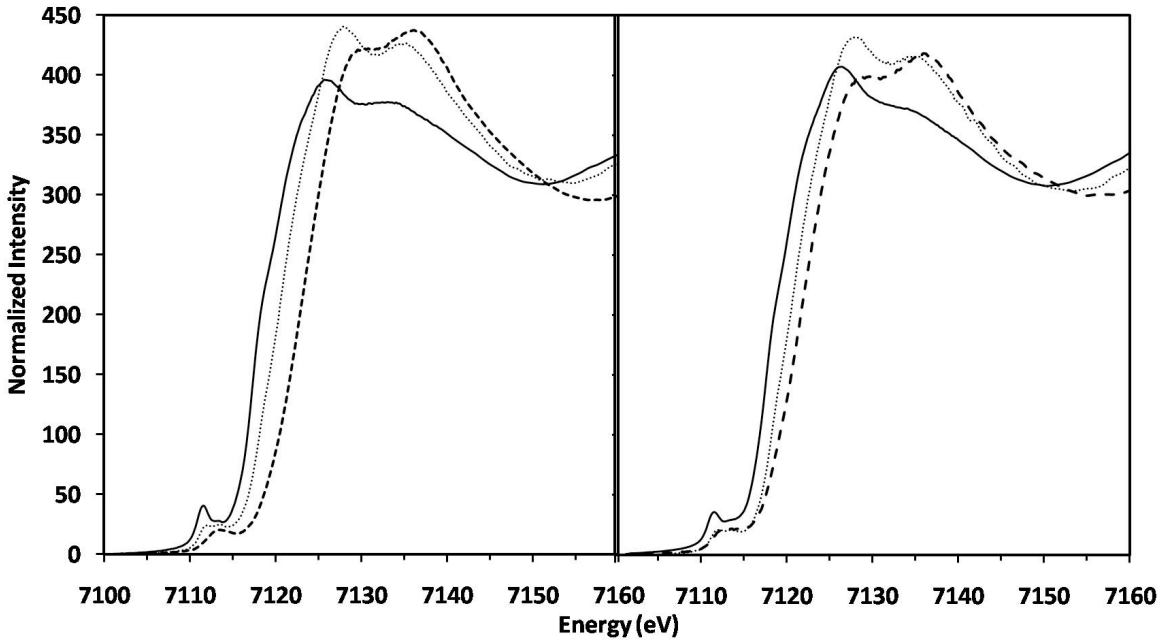

Figure S1. Normalized Fe K-Edge XANES of $[Fe^{II}([15]aneN_4)(SC_6H_4\text{-}p\text{-}Cl)]BF_4$ (**2**) as a crystalline solid dispersed in BN matrix (–) and dissolved in CH_2Cl_2 (···), and $[Fe^{III}([15]aneN_4)(SC_6H_4\text{-}p\text{-}Cl)(OOtBu)]BF_4$ (**2a**) (---) dissolved in CH_2Cl_2 (left panel) and $[Fe^{II}([15]aneN_4)(SC_6H_4\text{-}p\text{-}NO_2)]BF_4$ (**3**) as a crystalline solid dispersed in BN matrix (–) and dissolved in CH_2Cl_2 (···), and $[Fe^{III}([15]aneN_4)(SC_6H_4\text{-}p\text{-}NO_2)(OOtBu)]BF_4$ (**3a**) (---) dissolved in CH_2Cl_2 (right panel).

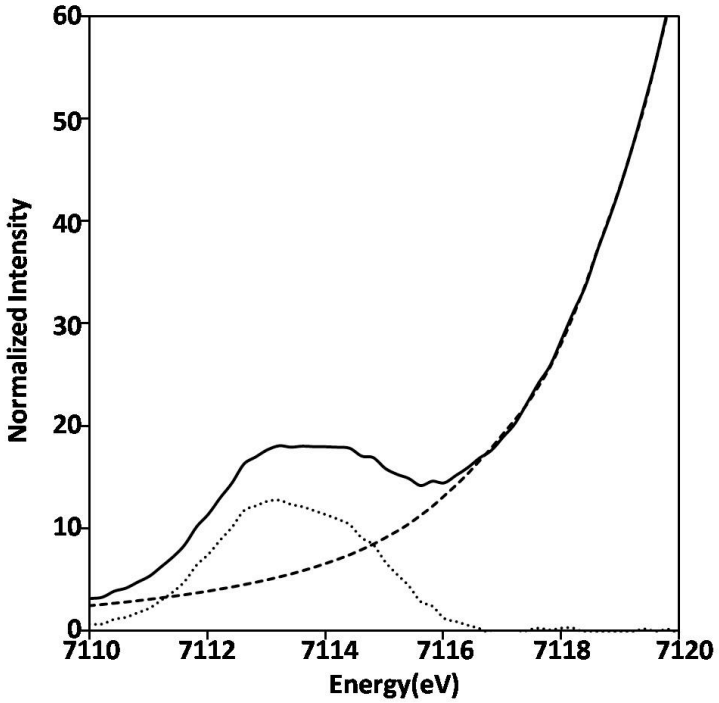

Figure S2. Pre-edge region of the normalized Fe K-Edge XANES of **1a** showing the raw data (—), the least-squares fit used to simulate the edge and XANES peak (---), and the raw data after subtraction of the least-squares fit to give the isolated pre-edge feature (···).

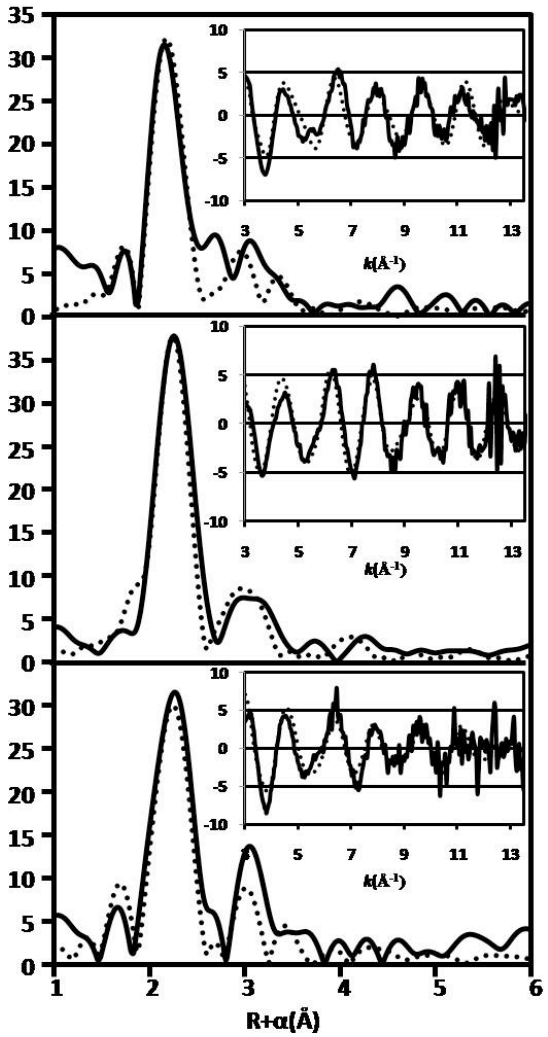

Figure S3. Fourier transforms of Fe K-edge EXAFS data and EXAFS spectra (insets), experimental data (—) and theoretical fits (···) for solid state samples of (bottom) $[Fe^{II}([15]aneN_4)(SC_6H_5)]BF_4$ (**1**), (middle) $[Fe^{II}([15]aneN_4)(SC_6H_4\text{-}p\text{-}Cl)]BF_4$ (**2**), and (top) $[Fe^{II}([15]aneN_4)(SC_6H_4\text{-}p\text{-}NO_2)]BF_4$ (**3**).