

## **Supporting material**

### **Iron L<sub>2,3</sub>-edge X-ray Absorption and Magnetic Circular Dichroism Studies of Molecular Iron Complexes with Relevance to the FeMoco and FeVco Active Sites of Nitrogenase**

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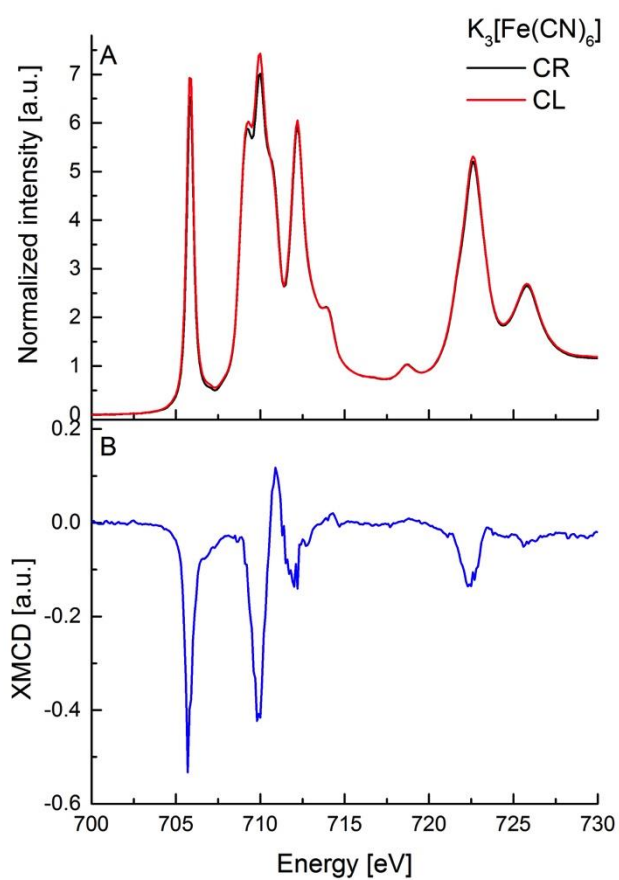


Figure S1. Experimental Fe L<sub>2,3</sub>-edge X-ray Absorption spectra of K<sub>3</sub>[Fe(CN)<sub>6</sub>] complex obtained with right (black) and left (red) polarized photons (A); experimental Fe XMCD spectrum of K<sub>3</sub>[Fe(CN)<sub>6</sub>] (B).

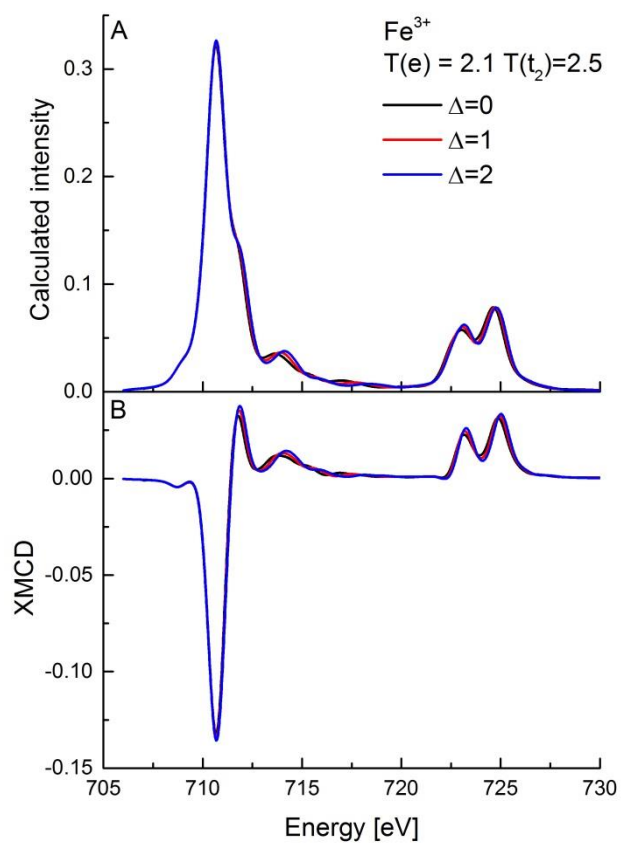


Figure S2. Calculated Fe L<sub>2,3</sub>-edge XAS (A) and XMCD (B) spectra of an Fe<sup>3+</sup> system in T<sub>d</sub> symmetry with different values of Δ.

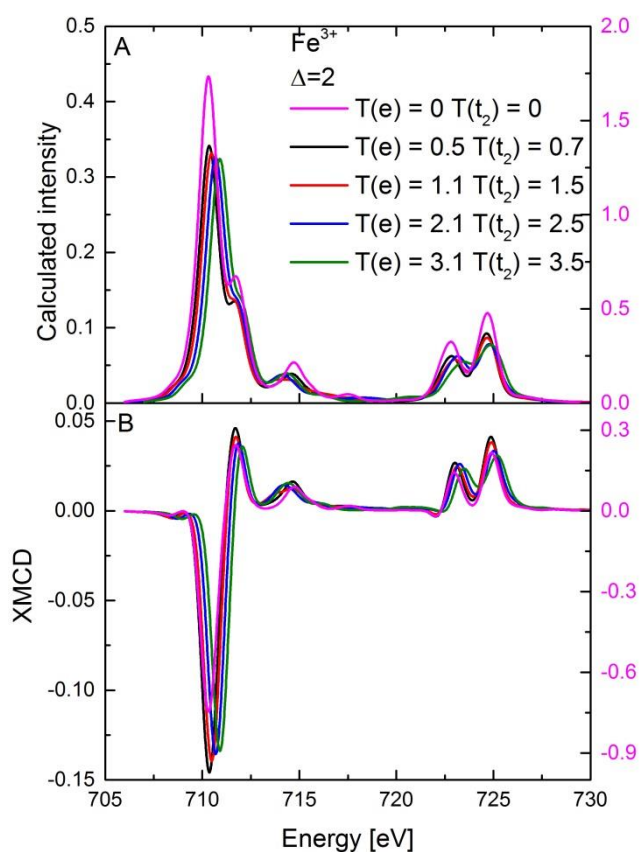


Figure S3. Calculated Fe  $L_{2,3}$ -edge XAS (A) and XMCD (B) spectra of an  $\text{Fe}^{3+}$  system with different charge transfers values. Note: the right (magenta) y-axis corresponds to the spectrum with charge transfer parameters set to 0.

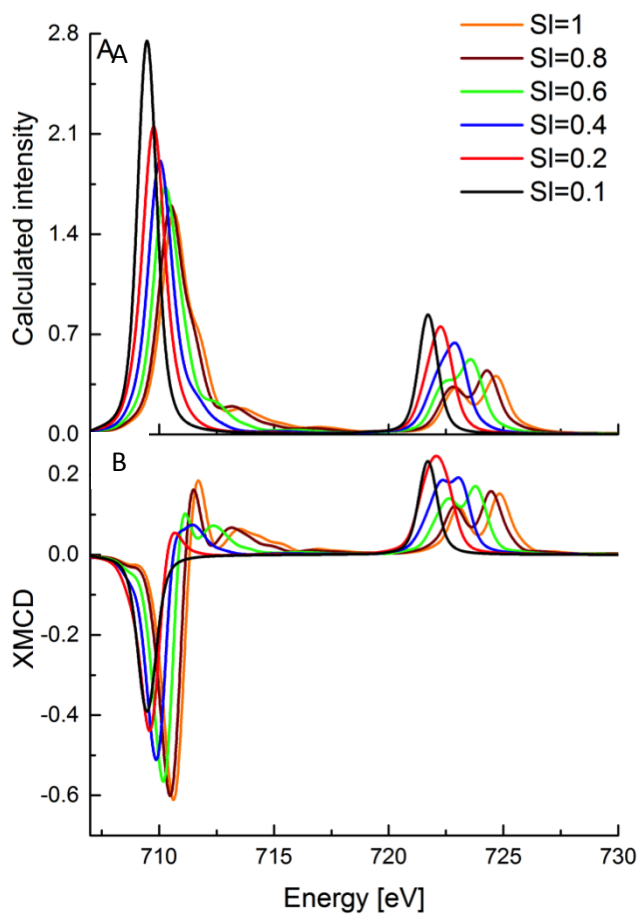


Figure S4. Calculated Fe  $L_{2,3}$ -edge XAS (A) and XMCD (B) spectra of a  $\text{Fe}^{3+}$  complex in  $T_d$  symmetry with  $10Dq=-0.5$ ,  $B=100$  meV and reduced Slater-Condon-Shortley integrals (SI). For clarity, only every second step is shown in the plot.

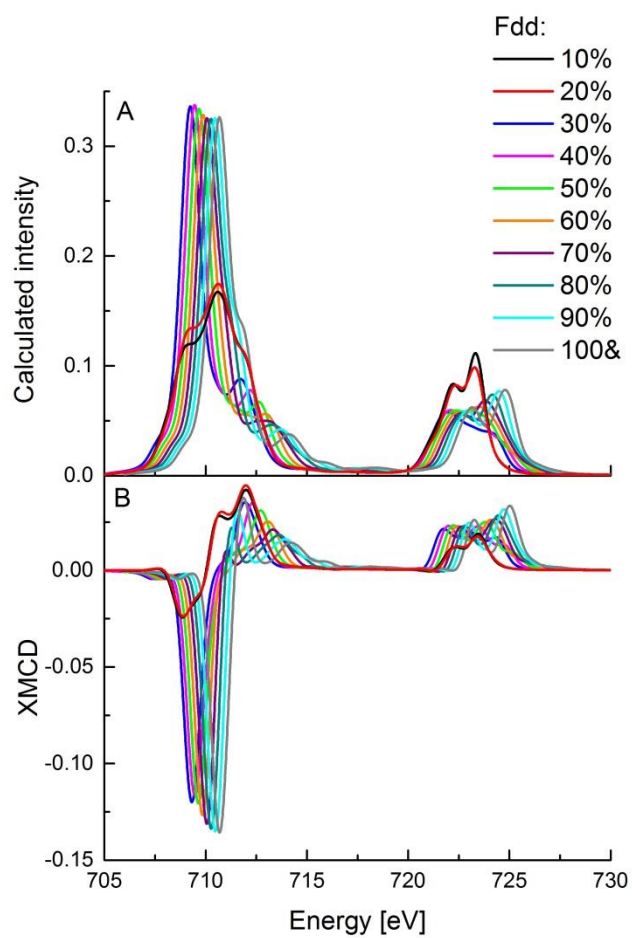


Figure S5. Calculated Fe L<sub>2,3</sub>-edge XAS (A) and XMCD (B) spectra of an Fe<sup>3+</sup> complex for different d-d repulsion parameters (F<sub>dd</sub>)

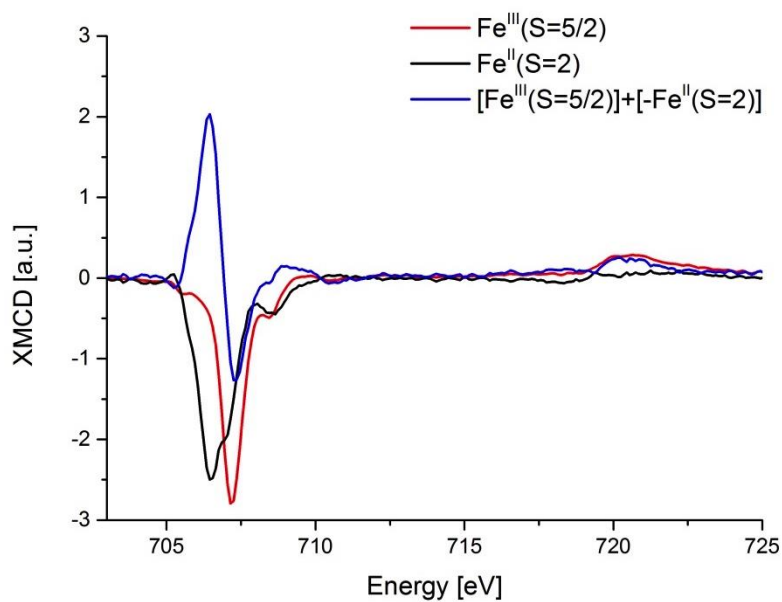
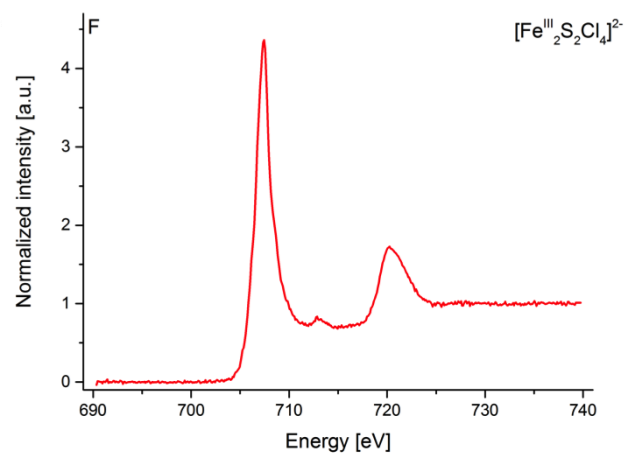
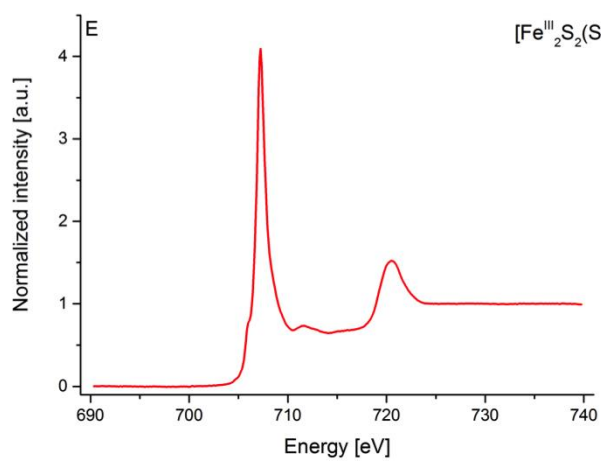
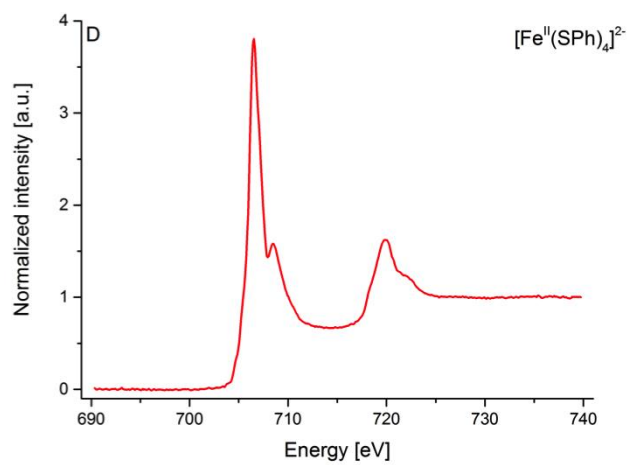
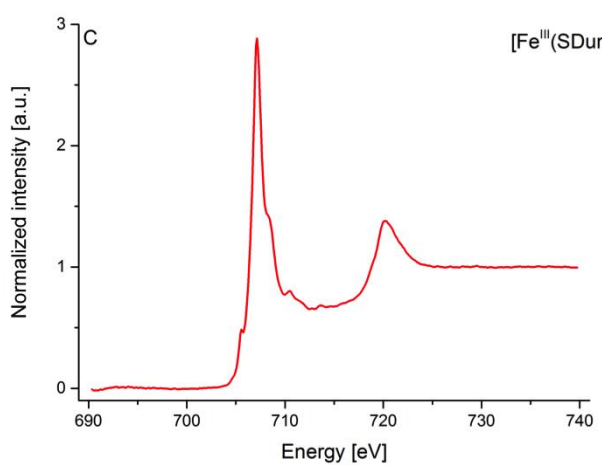
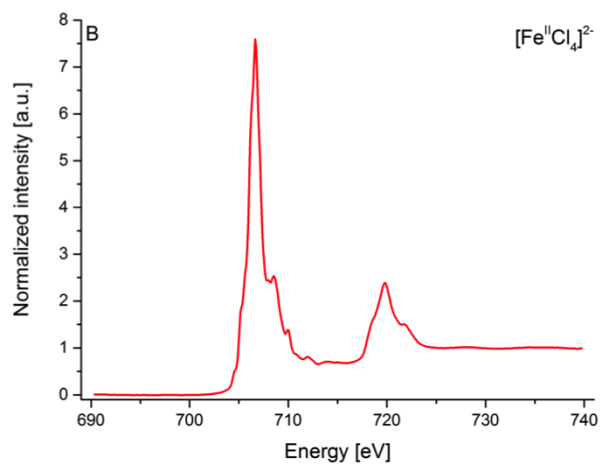
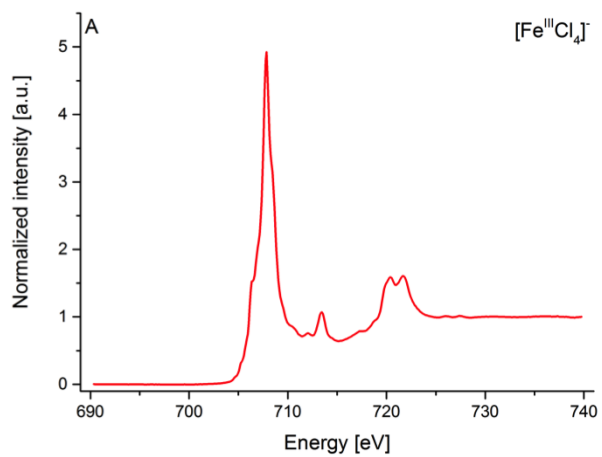


Figure S6. Experimental Fe  $L_{2,3}$ -edge XMCD spectra of  $[\text{Fe}^{\text{III}}(\text{SDur})_4]^-$  (red) and  $[\text{Fe}^{\text{II}}(\text{SPh})_4]^{2-}$  (black) complexes. The blue spectrum represents an empirical “prediction” for an  $\text{Fe}^{\text{II,III}}\text{S}_2$  system generated by adding the inverse signal of the XMCD spectrum of  $[\text{Fe}^{\text{II}}(\text{SPh})_4]^{2-}$  to the XMCD spectrum of  $[\text{Fe}^{\text{III}}(\text{SDur})_4]^-$ . This assumes that the  $S=5/2$  Fe(III) site is the majority spin (with a negative sign at the  $L_3$ -edge) and the  $S=2$  Fe(II) site is the minority spin (with a positive sign at the  $L_3$ -edge).





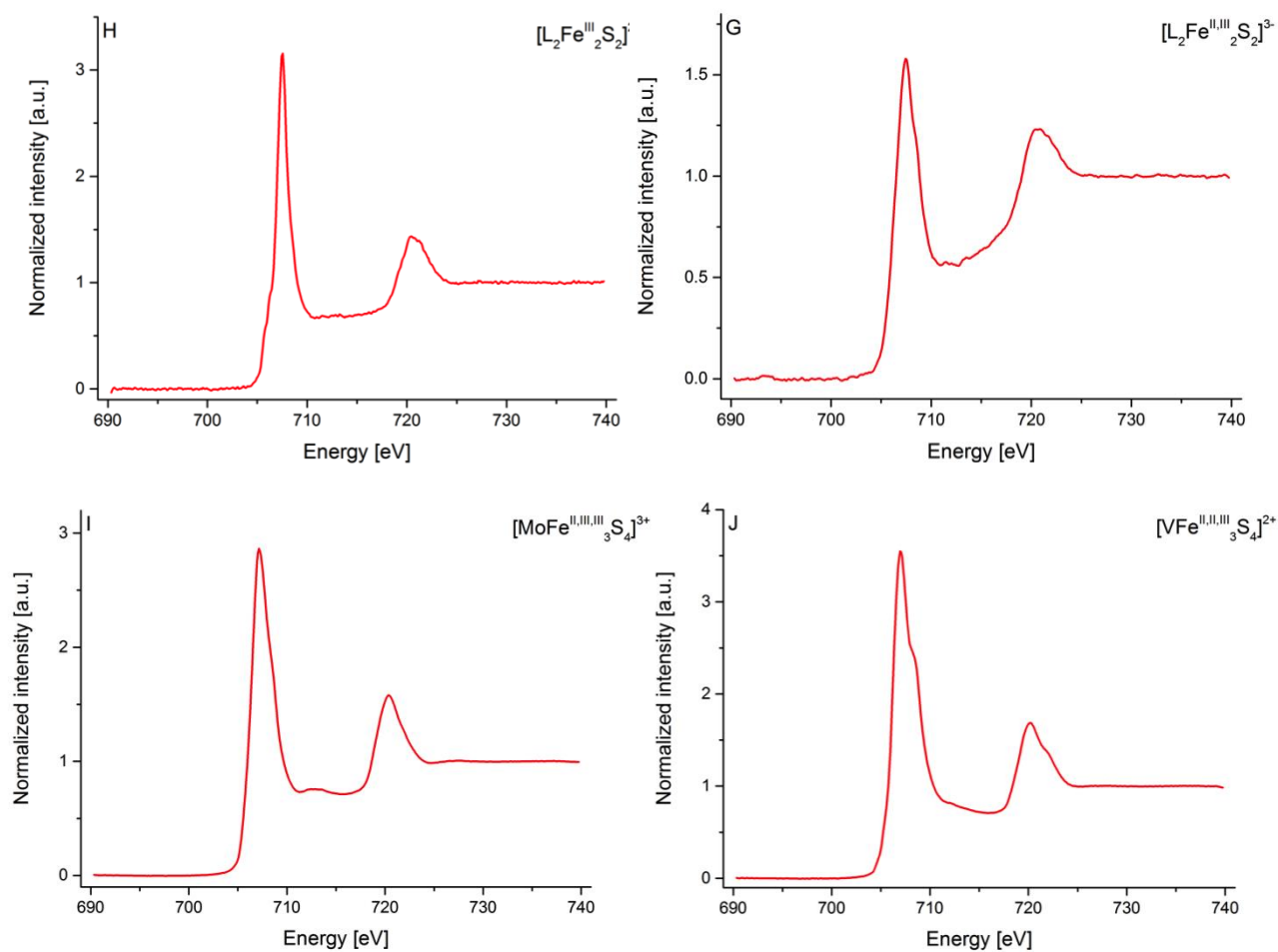


Figure S7. Experimental Fe L<sub>2,3</sub>-edge XAS spectra of  $[Fe^{III}Cl_4]^-$  (A),  $[Fe^{II}Cl_4]^{2-}$  (B),  $[Fe^{III}(SDur)_4]^-$  (C),  $[Fe^{II}(SPh)_4]^{2-}$  (D),  $[Fe^{III}_2S_2(SPh)_4]^{2-}$  (E),  $[Fe^{III}_2S_2Cl_4]^{2-}$  (F),  $[L_2Fe^{II,III}_2S_2]^{3-}$  (G),  $[L_2Fe^{III}_2S_2]^{2-}$  (H),  $[MoFe_3^{II,III,III}S_4]^{3+}$  (I),  $[VFe_3^{II,II,III}S_4]^{2+}$  (J) complexes presented in the extended energy range showing the coalesce of the spectra in the normalization range to 1.

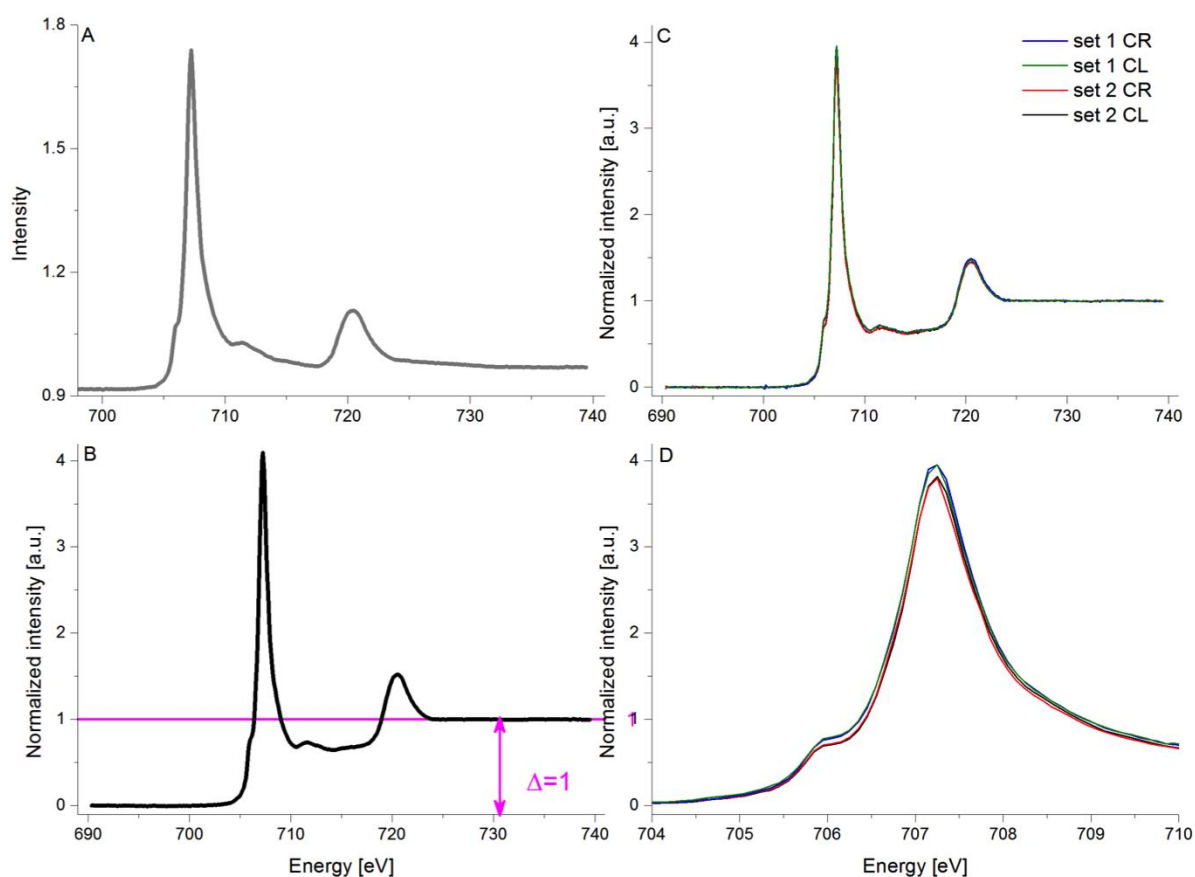
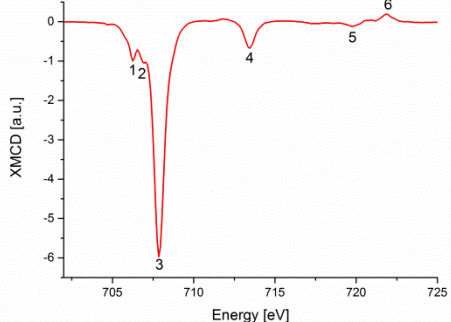
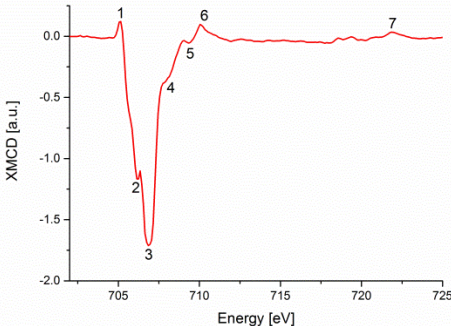
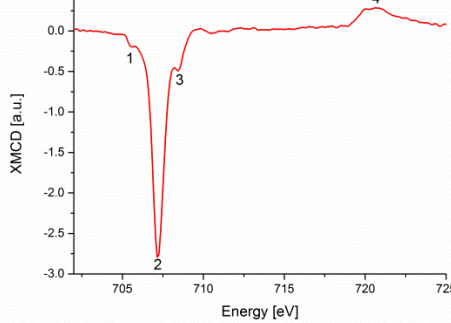
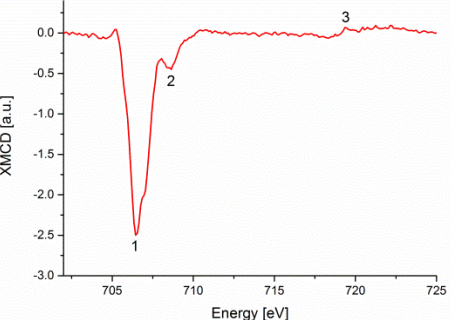
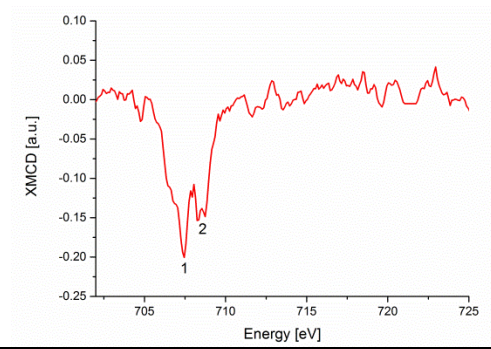
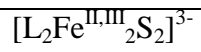


Figure S8. Experimental Fe  $L_{2,3}$ -edge XAS spectra of  $[\text{Fe}_2^{\text{III}}\text{S}_2(\text{SPh})_4]^{2-}$ : averaged of 12 single scans (A); processed averaged data (B); 2 sets (first and last one) of single spectra collected with different polarization (CR, CL) at 0T magnetic field (C); zoom into the L3-edge of the spectra in panel C in order to show the less than 1% deviation in the intensity (based on integrated area) (D). Pink line in panel B indicates the normalization edge jump (equal to 1).

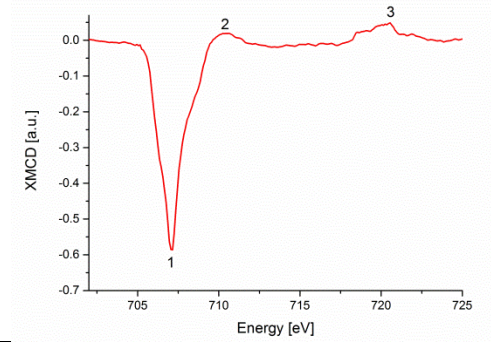
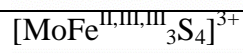
Table S1. Energy values of the main features in the XMCD spectra of the measured compounds. All energies provided within  $\pm 0.02$  eV error. Blue color indicates positive features.

<p><math>[\text{Fe}^{\text{III}}\text{Cl}_4]^-</math></p> 	<ol style="list-style-type: none"> <li>1. 706.3 eV</li> <li>2. 707.0 eV</li> <li>3. 707.9 eV</li> <li>4. 713.5 eV</li> <li>5. 719.8 eV</li> <li>6. 721.9 eV</li> </ol>
<p><math>[\text{Fe}^{\text{II}}\text{Cl}_4]^{2-}</math></p> 	<ol style="list-style-type: none"> <li>1. 705.2 eV</li> <li>2. 706.2 eV</li> <li>3. 706.7 eV</li> <li>4. 708.3 eV</li> <li>5. 709.4 eV</li> <li>6. 710.1 eV</li> <li>7. 721.9 eV</li> </ol>
<p><math>[\text{Fe}^{\text{III}}(\text{SDur})_4]^-</math></p> 	<ol style="list-style-type: none"> <li>1. 705.6 eV</li> <li>2. 707.2 eV</li> <li>3. 708.5 eV</li> <li>4. 720.7 eV</li> </ol>
<p><math>[\text{Fe}^{\text{II}}(\text{SPh})_4]^{2-}</math></p> 	<ol style="list-style-type: none"> <li>1. 706.5 eV</li> <li>2. 708.6 eV</li> <li>3. 719.4 eV</li> </ol>



1. 707.5 eV

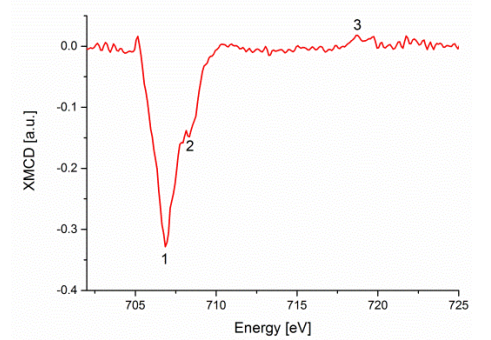
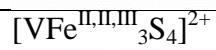
2. 708.3 eV



1. 707.5 eV

2. 710.4 eV

3. 720.5 eV



1. 706.9 eV

2. 708.4 eV

3. 718.8 eV

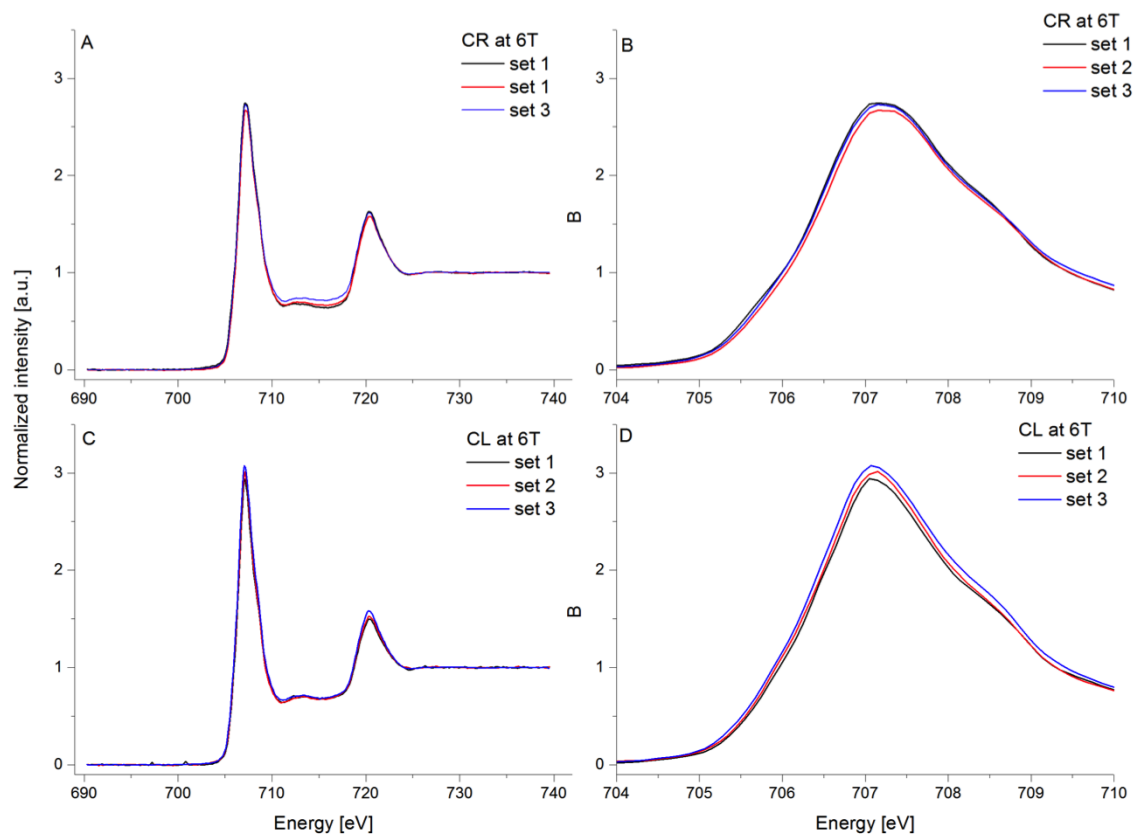


Figure S9. Experimental Fe L<sub>2,3</sub>-edge XAS spectra of [MoFe<sup>II,III,III</sup><sub>3</sub>S<sub>4</sub>]<sup>3+</sup> at 6T magnetic obtained with circular right (A) and circular left (C) polarized light of three successive sets. Zoom into the L<sub>3</sub>-edge of the spectra in panel A and C are shown in B and D, respectively.