

Supplementary Material

Metal coordination properties of a chromophoric Desferrioxamine (DFO) derivative. Insight on the coordination stoichiometry and thermodynamic stability of Zr^{4+} complexes.

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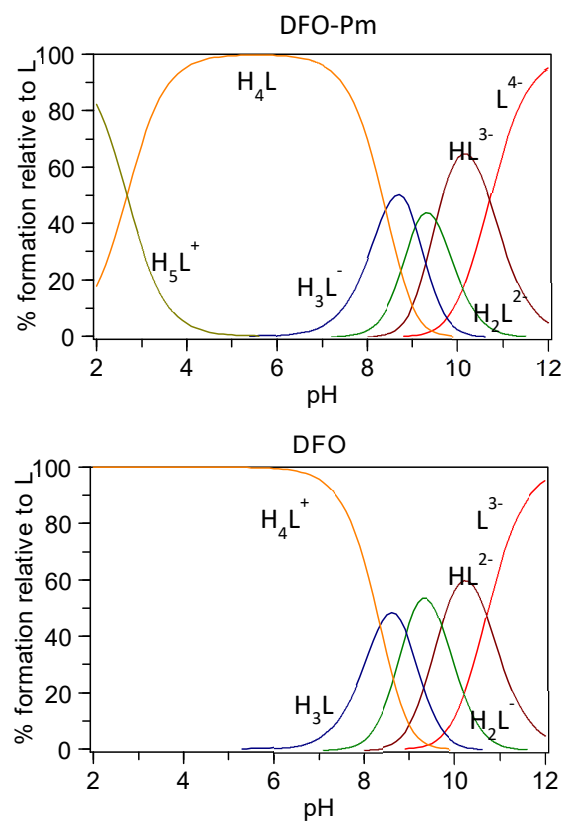


Figure S1. Distribution diagrams of the species formed by DFO-Pm (H_4L) and DFO (H_3L) as a function of pH. $[DFO-Py] = [DFO] = 1 \times 10^{-3}$ M.

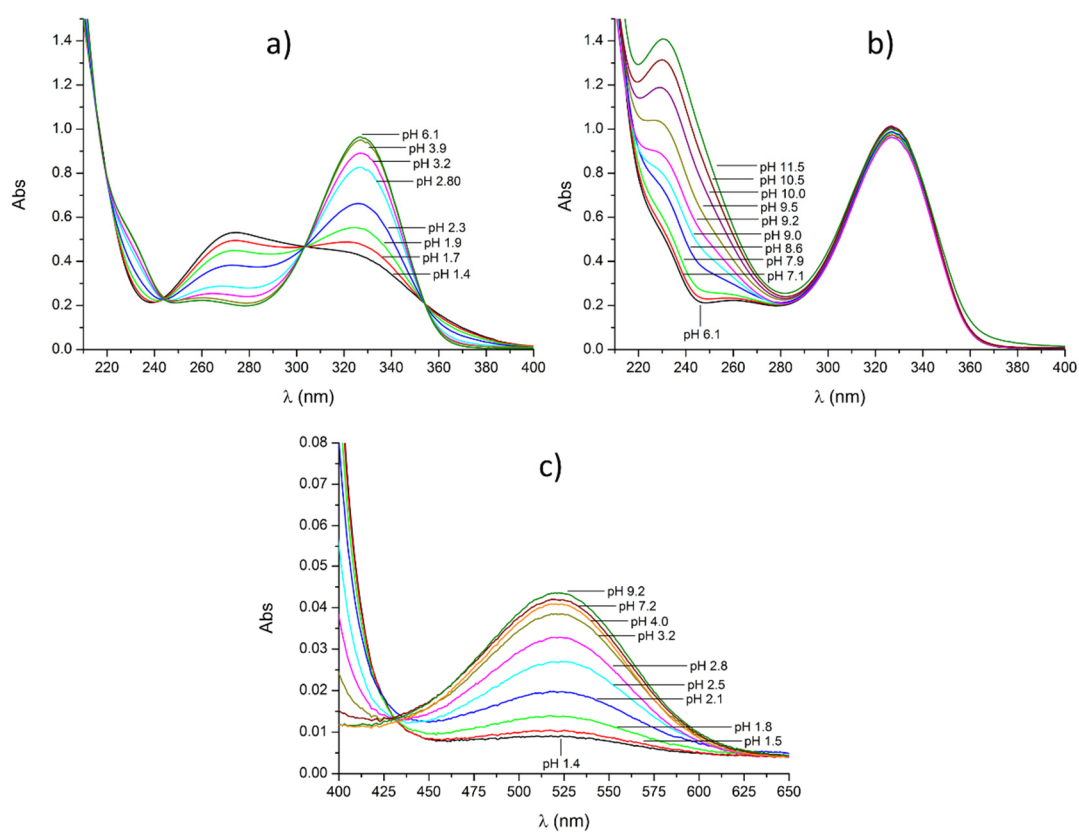


Figure S2. Uv-vis spectra of DFO-Pm in the pH ranges: a) 1.4-6.2, b) 6.1-11.5. c) Spectra in the Vis region, pH 1.5-9.2. $[\text{DFO-Pm}] = 4.25 \times 10^{-5}$ M.

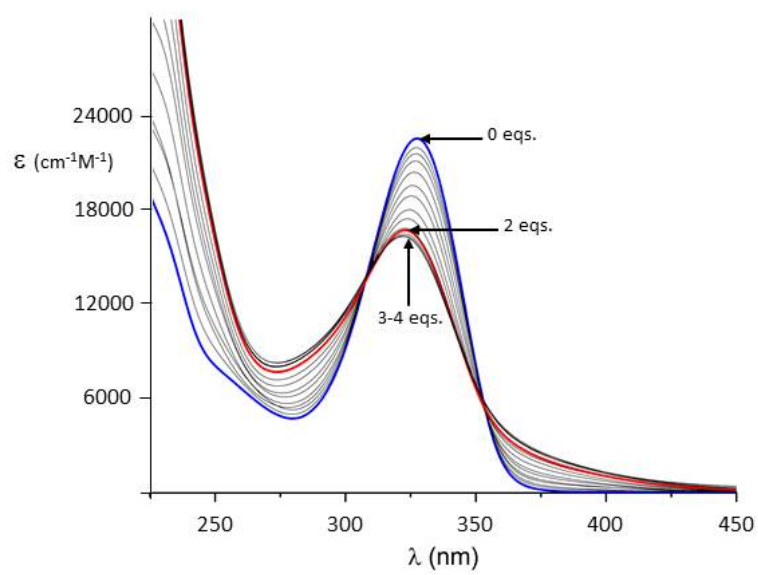


Figure S3. Uv-vis spectral variations upon addition of Cu^{2+} to a DFO-Pm solution ($4.25 \times 10^{-5}\text{M}$, pH 6).

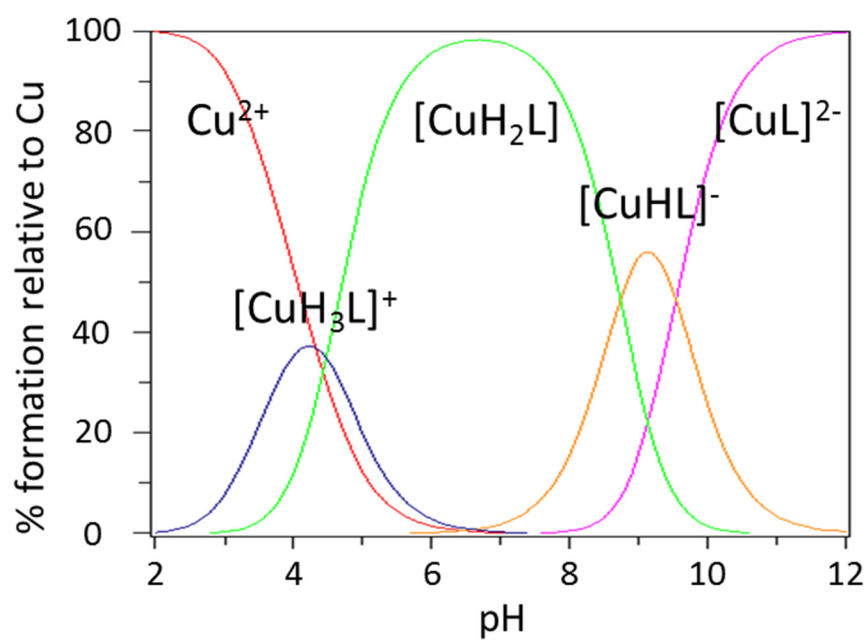


Figure S4. Distribution diagram of the complexes formed by DFO-Pm with Cu^{2+} . $[\text{DFO-Pm}] = [\text{Cu}^{2+}] = 4.25 \times 10^{-5}$ M.

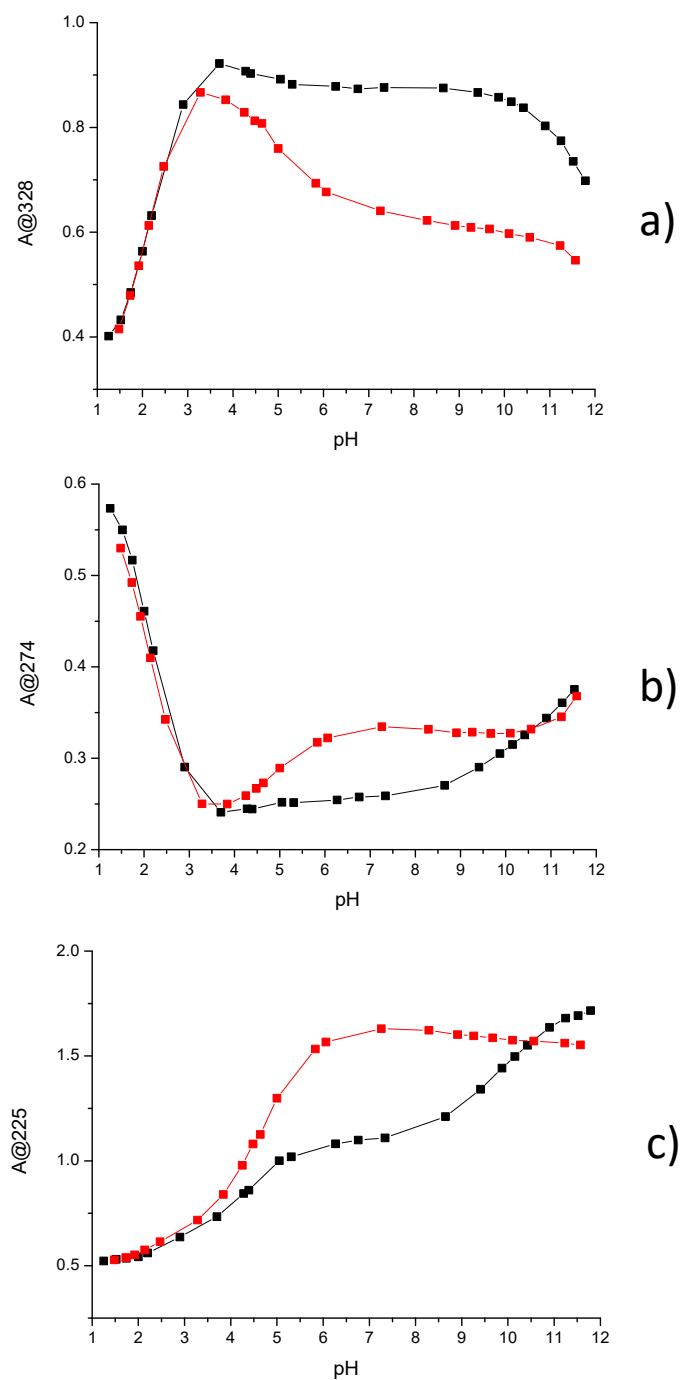


Figure S5. Comparison between the pH dependence of the absorbances at 328 nm (a), 274 nm (b) and 225 nm (c) of solutions containing DFO-Pm 4.25×10^{-5} M and Cu^{2+} 4.25×10^{-5} M (black squares) or 8.5×10^{-5} M (red squares).

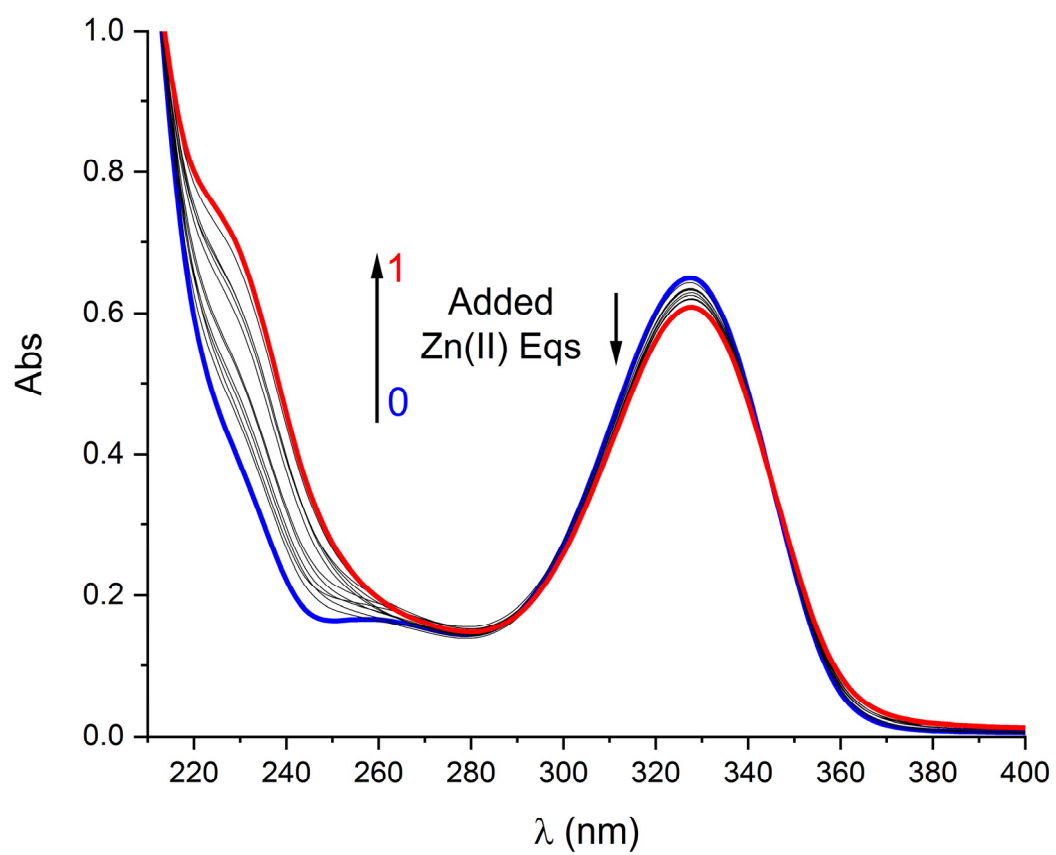


Figure S6. UV-vis absorption spectra of a DFO-Pm solution (3×10^{-5} M, pH 8) upon addition of increasing amounts of Zn^{2+} .

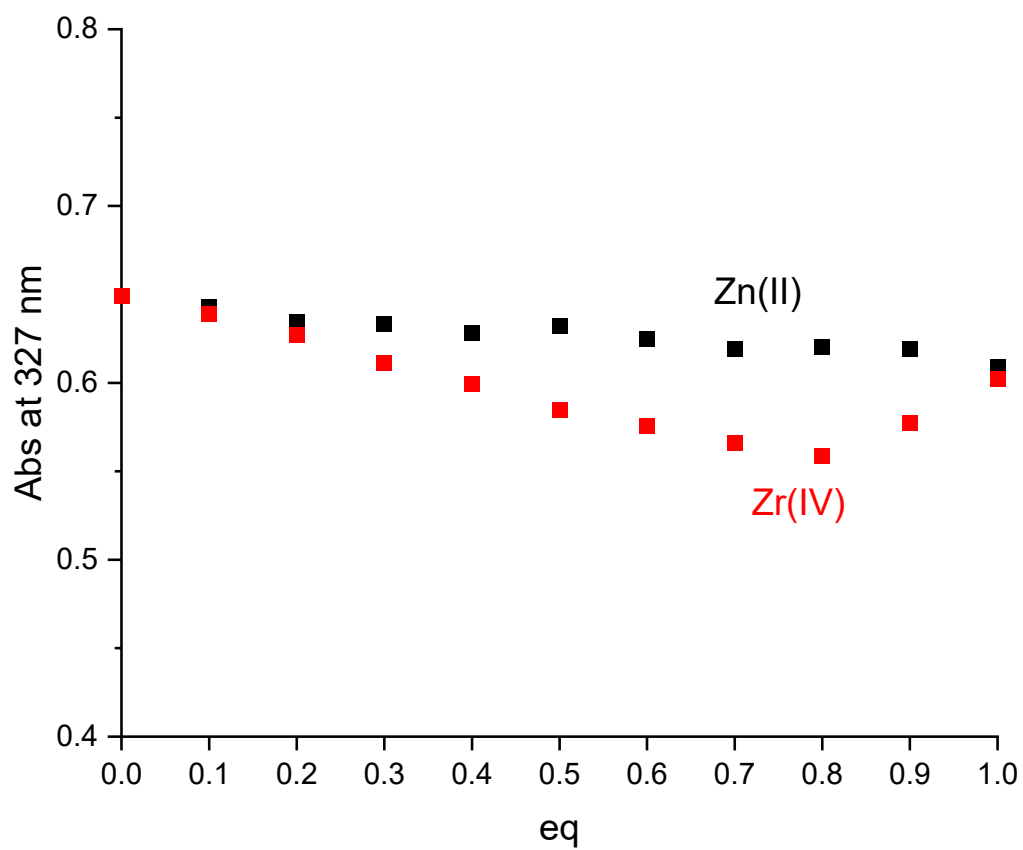


Figure S7. Variation with equivalents of added Zn^{2+} (pH 8.0) or Zr^{4+} (pH 6.0) of the absorptions at 327 nm. $[\text{DFO-Pm}] = 3 \times 10^{-5} \text{ M}$.

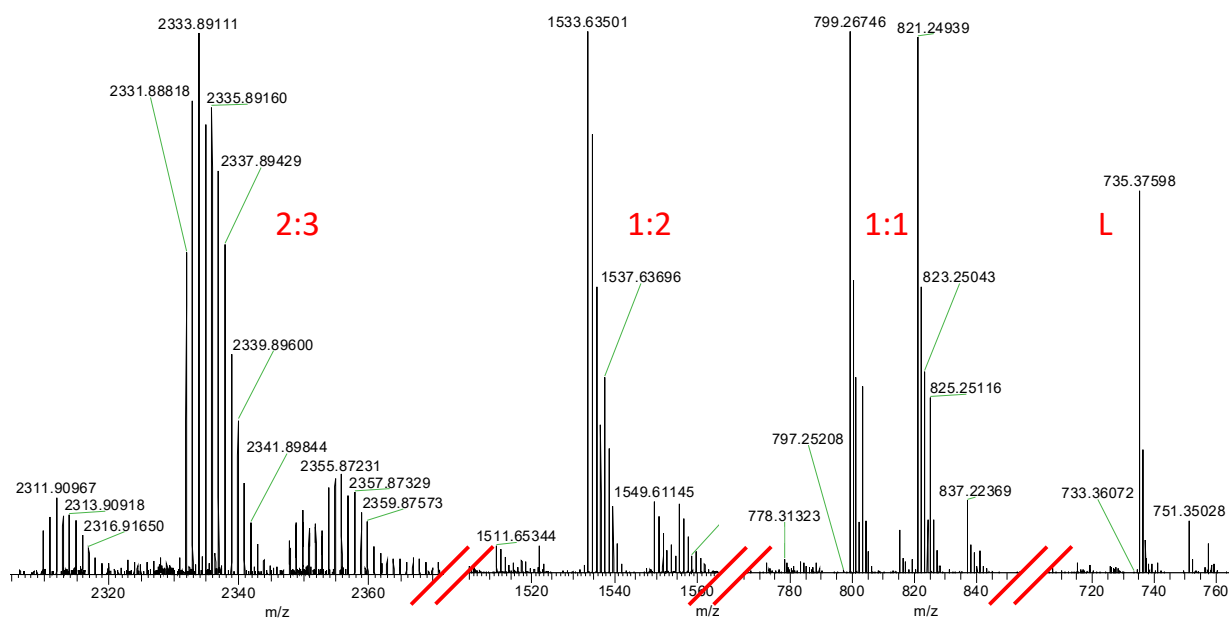


Figure S8. An example of the characteristic isotopic distribution introduced by the presence of 1 or more Zr(IV) ions, aiding peaks assignment.

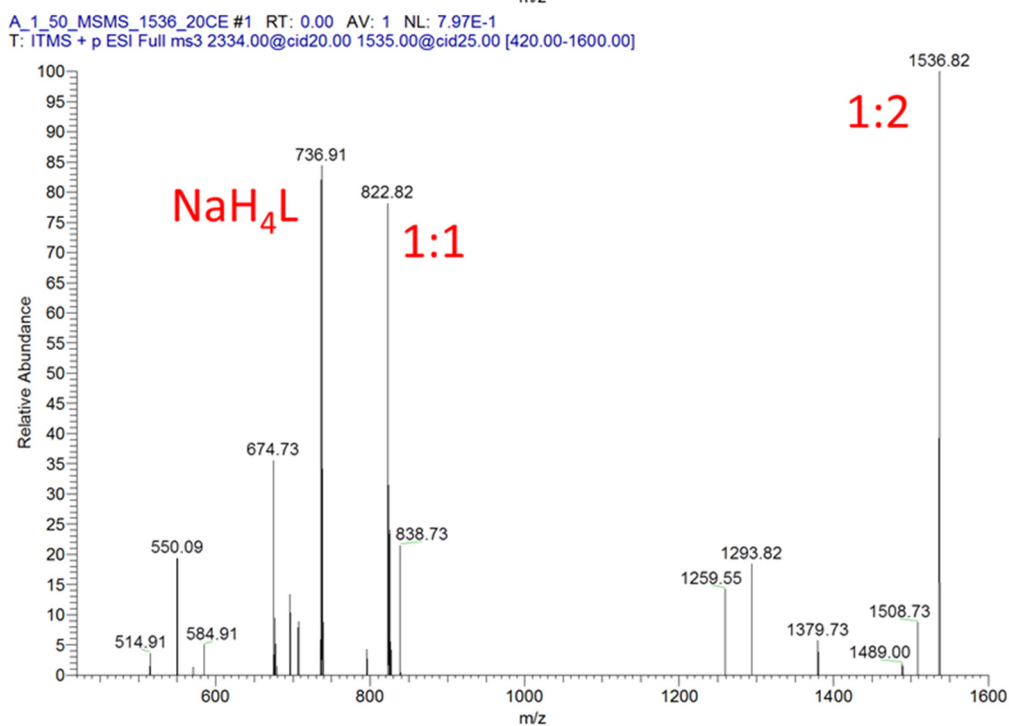
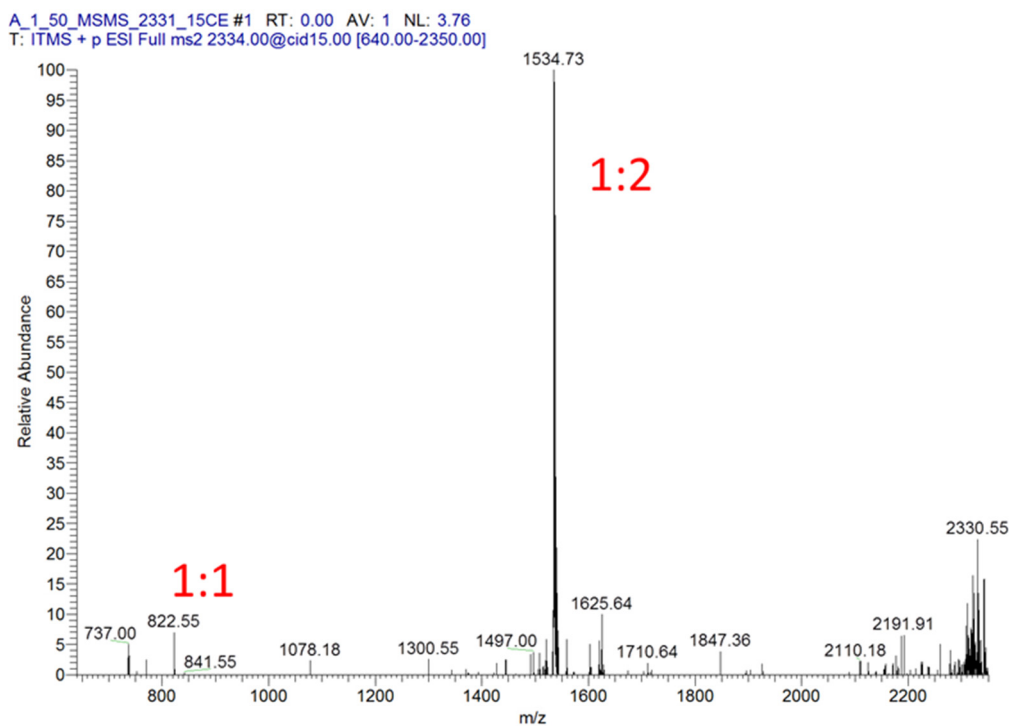


Figure S9. Top: MS-MS spectra showing how the 2:3 peak (m/z 2331) is broken down into 1:2, 1:1 and L not coordinated to Zr(IV). Bottom: 1:2 peak (m/z 1536) can be broken down into 1:1 and L not coordinated to Zr(IV) as well.

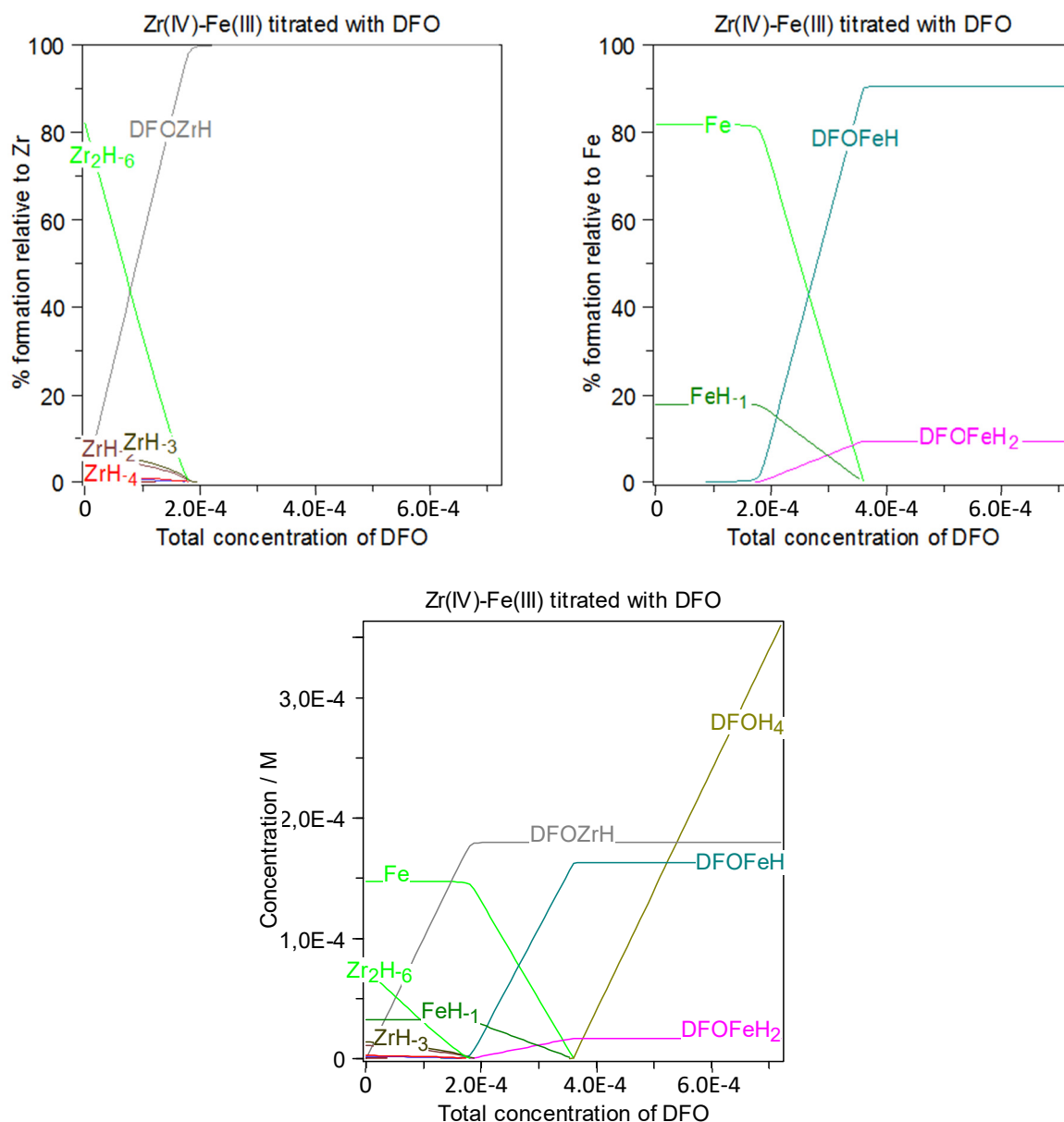


Figure S10. Outlook of experiment a): 1:1 $\text{Fe}^{3+}:\text{Zr}^{4+}$ solution titrated with increasing equivalents of DFO (0 to 4 eqs). Concentrations and full thermodynamic set of constants from ref 13. Top left: the first equivalent of DFO selectively and exhaustively binds Zr^{4+} (no spectral changes involved). Top right: the second equivalent of DFO exhaustively binds Fe^{3+} (all spectral change must happen here). Bottom: global outlook of the experiment showing no $\text{Fe}^{3+}/\text{Zr}^{4+}$ competition for DFO and end of the experiments at 2 added equivalents of DFO (last two equivalents of ligand remain free and cause no spectral change). Progressive spectral changes from 0 to 4 equivalents were instead reported (Figure 3 of ref. 13).

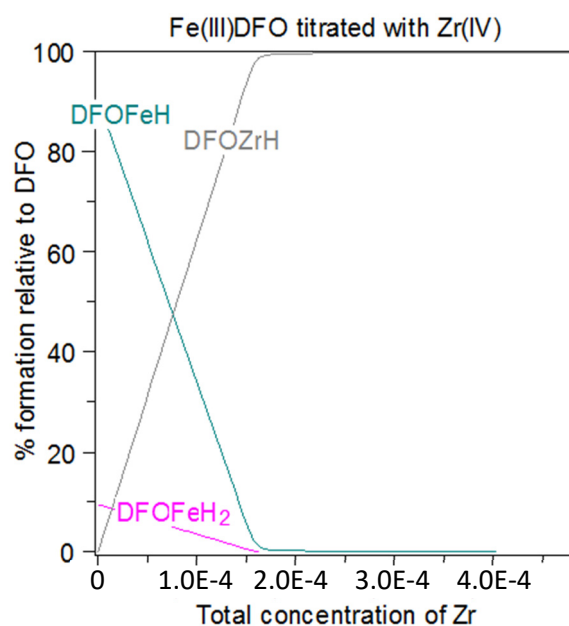


Figure S11. Outlook of experiment b): 1:1 Fe^{3+} :DFO solution titrated with Zr^{4+} (0 to 3 eqs). Concentrations and full thermodynamic set of constants from ref 13. 1 equivalent of Zr^{4+} should displace Fe^{3+} entirely causing discoloration of the solution. Spectral changes were instead observed up to 3 eqs of added Zr^{4+} (ref. 13). No $\text{Fe}^{3+}/\text{Zr}^{4+}$ competition is present in any case: Zr^{4+} quantitatively displaces the Fe(III) complex.

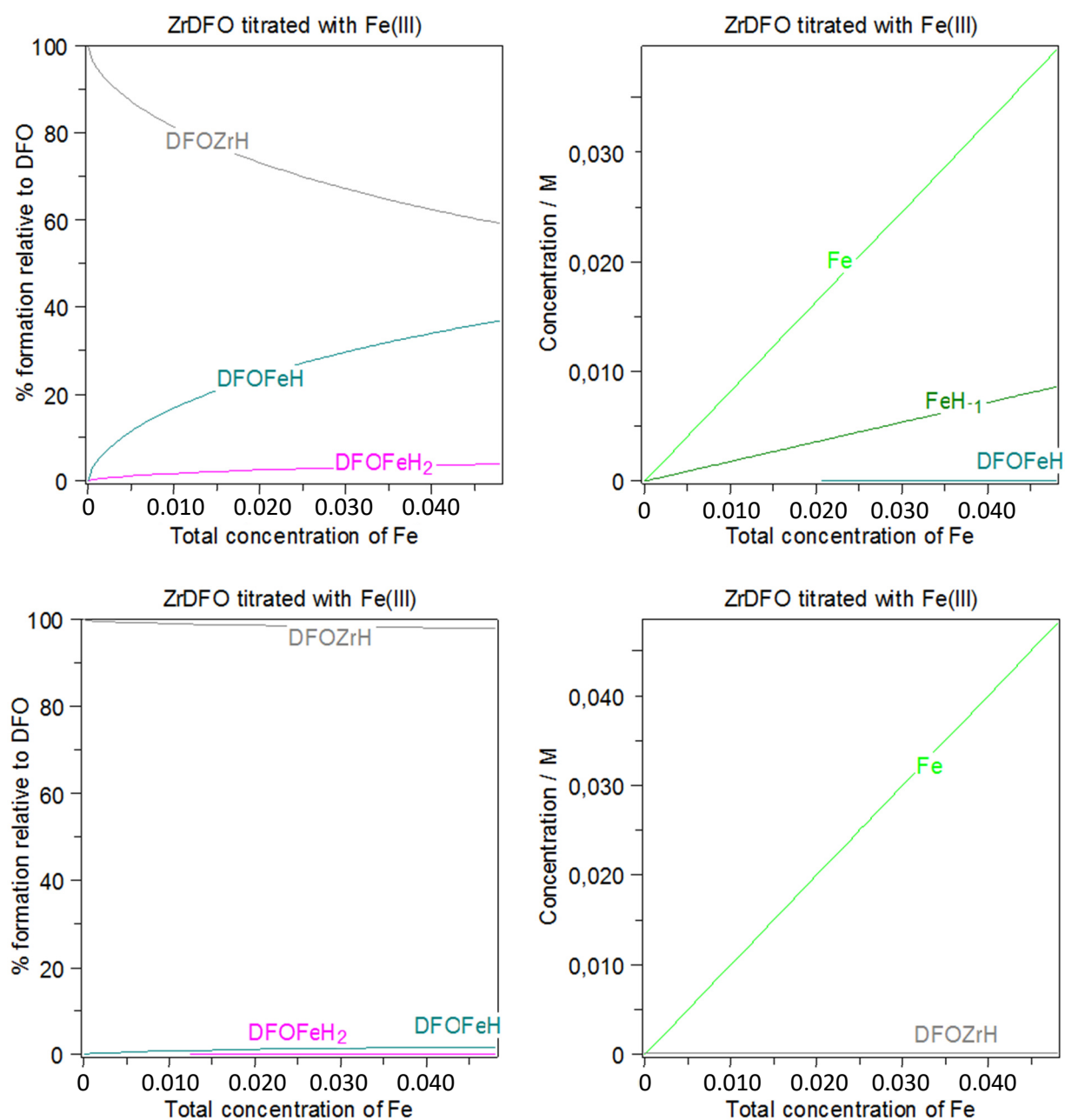


Figure S12. Outlook of experiment c): 1:1 Zr^{4+} :DFO solution titrated with Fe^{3+} (0 to 300 eqs). Concentrations and full thermodynamic set of constants from ref 13. Top: the real experiment displaying competition (the hydrolysis of Fe^{3+} and Zr^{4+} has been included in calculations). Bottom: same experiment ignoring hydrolytic equilibria for both metals: no dissociation of ZrDFO complex should occur, because Fe^{3+} does not compete with Zr^{4+} for DFO.