

## Supporting Information

### **X-ray-Induced Sample Damage at the Mn L-edge: A Case Study for Soft X-ray Spectroscopy of Transition Metal Complexes in Solution**

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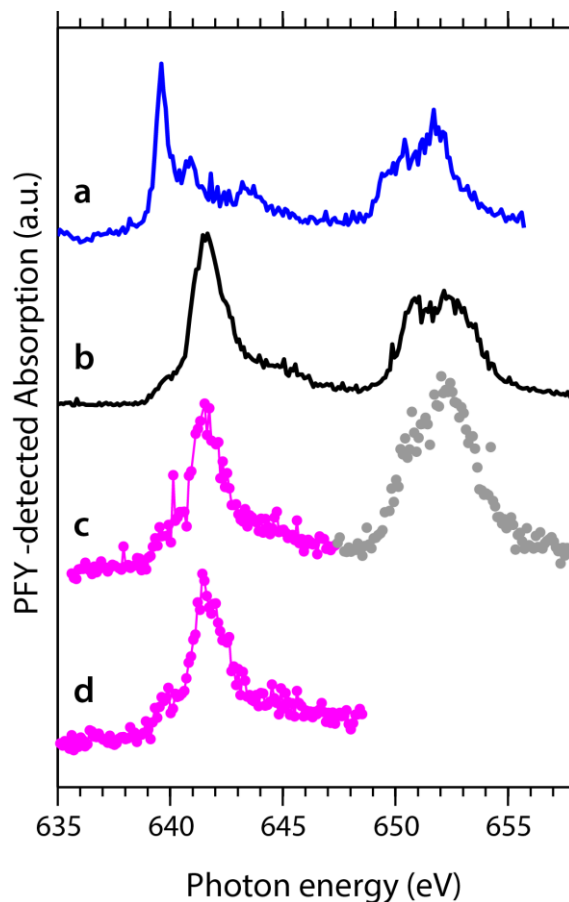
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## 1. Preparation of Solution Samples

### 1.1 Identification of Mn<sup>III</sup> Species in Sample B

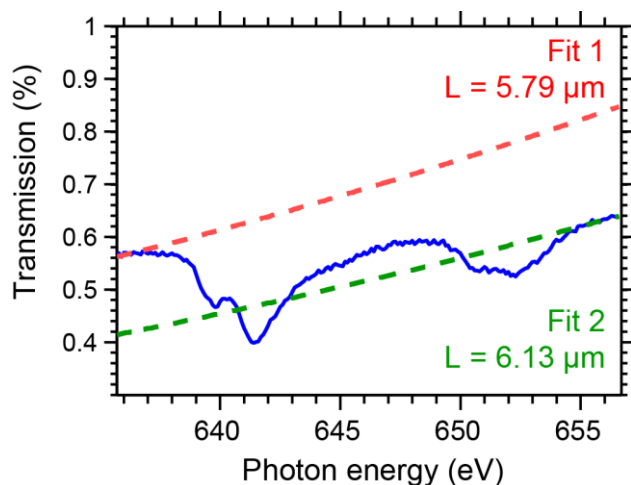
The spectroscopic shift of the L<sub>3</sub>-edge absorption maximum of high spin Mn<sup>II</sup>, Mn<sup>III</sup> and Mn<sup>IV</sup> species was shown earlier to be a reliable indicator of the oxidation state of high-spin Mn complexes (refs. S1-S2). Applying this observation to the shape of the L<sub>3</sub>-edge of spectrum “c” in Fig. 3 supports the notion that the spectrum of Sample B measured at low doses shows the clear signature of a Mn<sup>III</sup> species. With a different experimental setup based on partial-fluorescence yield detected XAS (refs. S1-S2) we found equivalent clear indications that solubilizing Mn<sup>II</sup>(acac)<sub>2</sub> in acetylacetone leads to chemical changes of the sample, resulting in a solution sample of a Mn<sup>III</sup> species (see Fig. S1). The spectrum of this species is similar to that measured for Mn<sup>III</sup>(acac)<sub>3</sub> in solution of acetylacetone. With this, we are confident that we can treat sample B as chemically equivalent to sample A, as assumed throughout our analysis in the main paper.



**Figure S1.** Assignment of sample B, as introduced in the main paper, via comparison of L-edge XAS, measured in partial fluorescence yield (PFY)-detected mode. Spectra (a) and (b) are the spectra of  $\text{Mn}^{\text{II}}(\text{acac})_2$  in ethanol and  $\text{Mn}^{\text{III}}(\text{acac})_3$  in acetylacetone, as published in refs. S1-S2, respectively. Spectra (c) and (d) are measured for a  $\text{Mn}^{\text{III}}$  species that results from solubilizing solid  $\text{Mn}^{\text{II}}(\text{acac})_2$  in acetylacetone, i.e. equivalent to the preparation of sample B in the main paper. In spectrum (c), we note a potential overestimation of the  $L_2$ -edge intensity (gray) which possibly originates in a change of the experimental conditions. In spectrum (d) the liquid sample injection broke down at 649 eV. The spectrum shape and the position of the  $L_3$ -edge main features in (c) and (d) are similar with those of  $\text{Mn}^{\text{III}}(\text{acac})_3$  in acetylacetone (b). The axis of the incident photon energy was calibrated with the same constant energy shift for all spectra via the sharp  $L_3$ -edge absorption maximum of  $(\text{Mn}^{2+})_{\text{aq}}$  as done before (refs. S1, S2, S3).

## 2. Data Analysis and Processing of Transmission Spectra

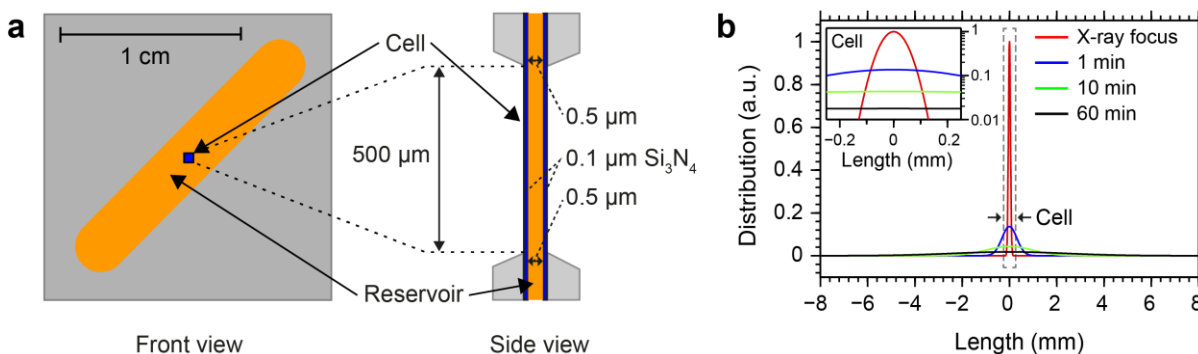
### 2.1 Data Processing



**Figure S2.** Determination of the jet thickness via fits with Henke's tables (refs. S4-S5) from the experimental transmission data. In order to account for drifts in the sample thickness during the scan, the thickness of the liquid sample was fitted once on the low- (fit 1) and once on the high-energy side (fit 2) of each spectrum (start and end of the scan, respectively). For each separate spectrum scan, the range of these two thickness values were used in the main paper to determine the uncertainty of the sample thickness. In this example, the thickness of the transmission cell increased continuously by 6% from around 5.8  $\mu\text{m}$  to around 6.1  $\mu\text{m}$  during the spectrum scan.

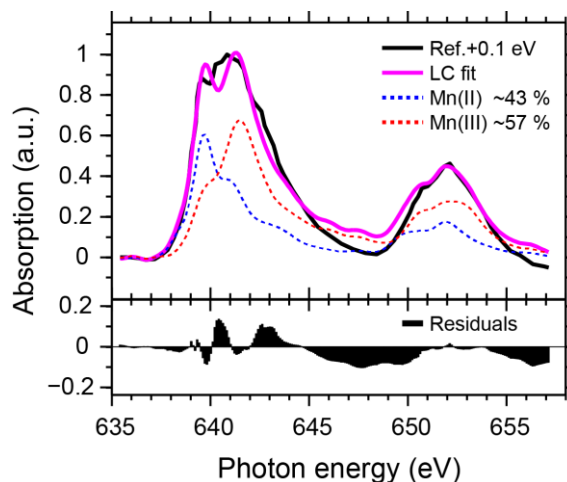
### 3. X-ray Damage

#### 3.1 Diffusion-Driven Sample Exchange with the Sample Reservoir



**Figure S3.** (a) Geometry and dimensions of the transmission cell and the sample reservoir, adapted from ref. S6. (b) Calculated relative probability distributions of a damaged molecule at different time points after the damage event. The curves show relative probability distributions, calculated for the two-dimensional diffusion of sample molecules at different times in the experiment (using  $D \sim 4 \cdot 10^{-6} \text{ cm}^2/\text{s}$  for  $\text{Mn}^{\text{III}}(\text{acac})_3$  in non-aqueous solution as discussed in the main paper) were convoluted with a 100 μm (fwhm) Gaussian profile of the x-ray beam. The inset shows the same data with a zoom to the length scale of the transmission cell (logarithmic scale on the y-axis). The differences in the cell-averaged probability density between the curves allow for estimating the order of magnitude by up to which dose-values may potentially be overestimated in the analysis of our main paper, where diffusion-driven sample exchange with the sample reservoir is neglected.

### 3.2 X-ray Damage in Reference Spectra



**Figure S4.** Assessment of the x-ray absorption spectrum of solid  $\text{Mn}^{\text{III}}(\text{acac})_3$  from ref. S7, using a linear combination of damage-free spectra of  $\text{Mn}^{\text{II}}(\text{acac})_2$  and  $\text{Mn}^{\text{III}}(\text{acac})_3$  in solution from ref. S3, as described in the main paper. The spectrum from ref. S7 was corrected for a linear absorption background and shifted by +0.1 eV to match with the calibrated spectra from ref. S3. The damage-free spectra from ref. S3 were broadened with a Gaussian convolution function with a spectral width (fwhm) of 0.7 eV to simulate the additional experimental broadening in ref. S7. The amount of  $\text{Mn}^{\text{II}}$  fitted within thin model is 43 % and that of  $\text{Mn}^{\text{III}}(\text{acac})_3$  is 57%.

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