Supporting Information
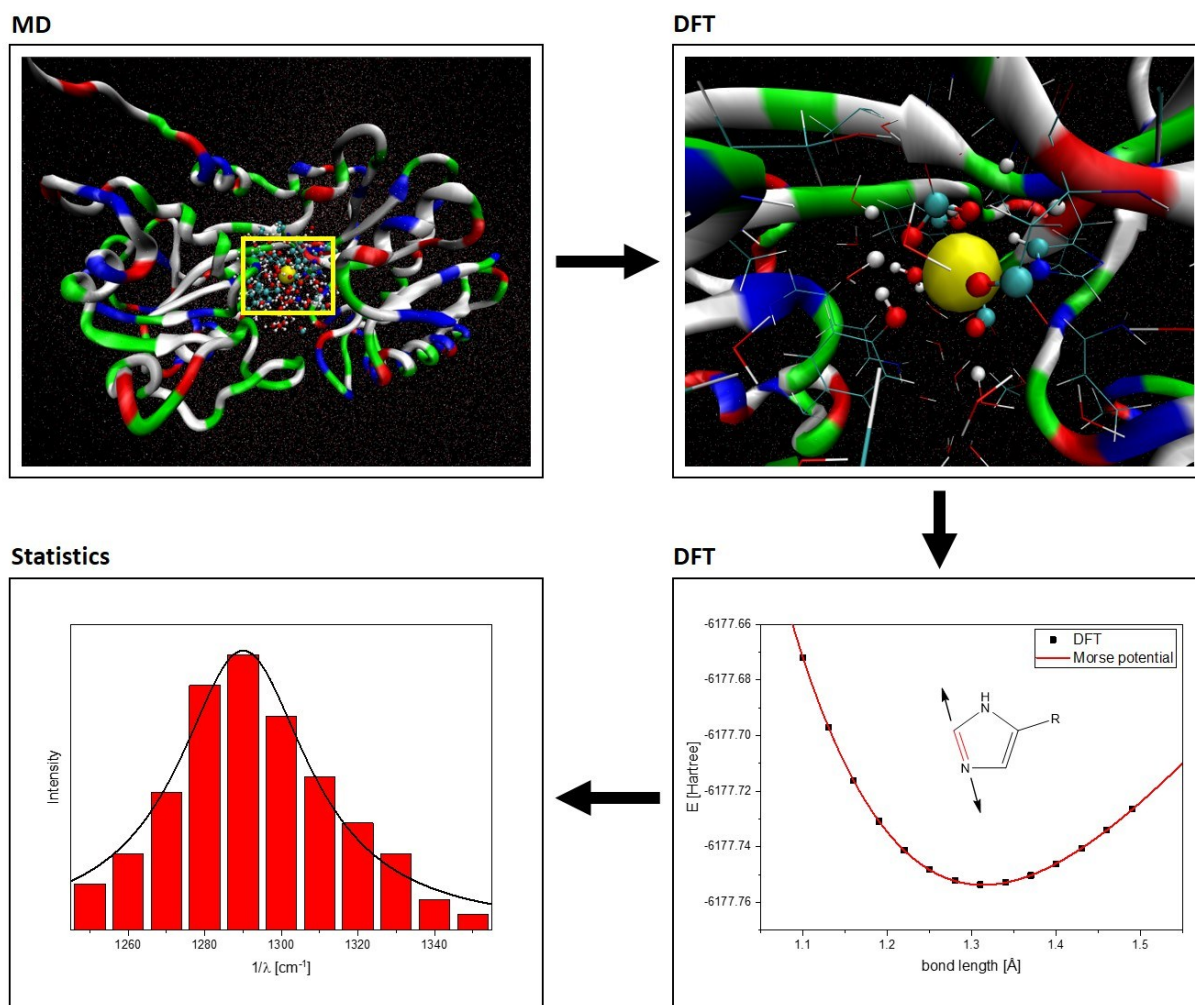
MD

DFT

Statistics

DFT

Fig. 1 Schematic representation of the process to compute vibrational modes using a combination of MD and DFT.
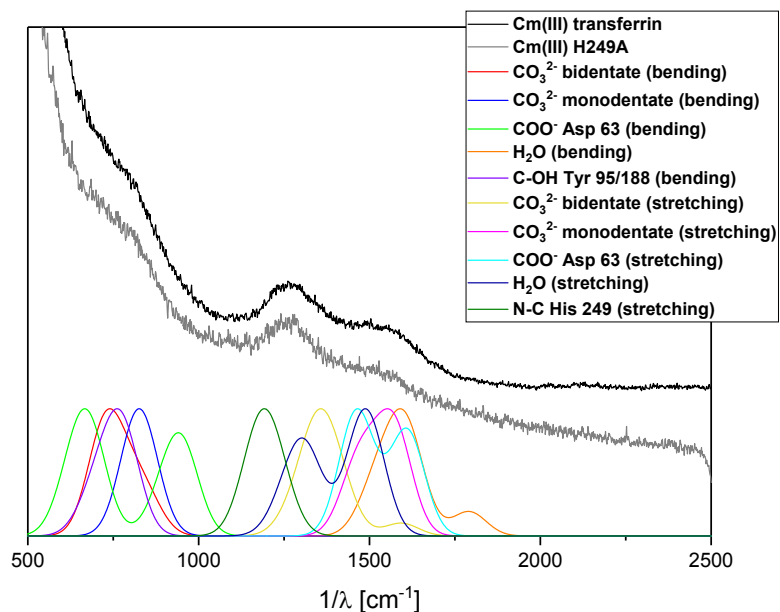
Fig. 2 Comparison of the measured VSB spectra of Cm(III) transferrin and Cm(III) H249A with calculated vibrational frequencies from DFT optimizations (Tyr 95 and Tyr 188 protonated, OH⁻ is neglected).
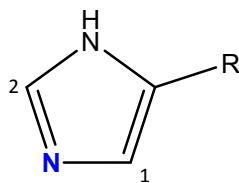

Fig. 3 Labelling of the atoms in His 249 (directly coordinating N is labelled in blue).

Table 1 Coordination numbers (CN) from MD simulation and bond-distances/vibrational frequencies (stretching vibration) from DFT optimizations (Tyr 95 and Tyr 188 protonated, OH⁻ is neglected).

	CN	bond length [Å] from DFT	bond length [Å] from MD
COO⁻ Asp 63	1.2	2.42 / 3.41	2.31
OH Tyr 95	1.0	2.75	2.84
OH Tyr 188	0.9	2.90	2.97
N-C His 249	0.9	2.98	2.87
H_2O	1.9	2.46	2.44
CO_3^{2-} (bidentate)	1.8	2.50	2.27
CO_3^{2-} (monodentate)	1.1	2.33	2.20

Table 2 Vibrational frequencies (stretching and bending vibration) of the coordinating transferrin groups from the DFT optimizations (Tyr 95 and Tyr 188 protonated, OH$^-$ is neglected).

	vibration [cm^{-1}]
COO$^-$ Asp 63 (stretching)	1467/1611
COO$^-$ Asp 63 (bending)	670/937
OH Tyr 95 (stretching)	1158/3393
OH Tyr 188 (stretching)	1201/3041
C-OH Tyr 95/Tyr 188 (bending)	756
N-C His 249 (stretching)	1298/1490
H$_2$O (stretching)	3285
H$_2$O (bending)	1591
CO$_3^{2-}$ (bidentate; stretching)	1357
CO$_3^{2-}$ (bidentate; bending)	792
CO$_3^{2-}$ (monodentate; stretching)	1549
CO$_3^{2-}$ (monodentate; bending)	815