Supporting Information

HERFD-XANES and RIXS study on the electronic structure of trivalent lanthanides across a series of isostructural compounds

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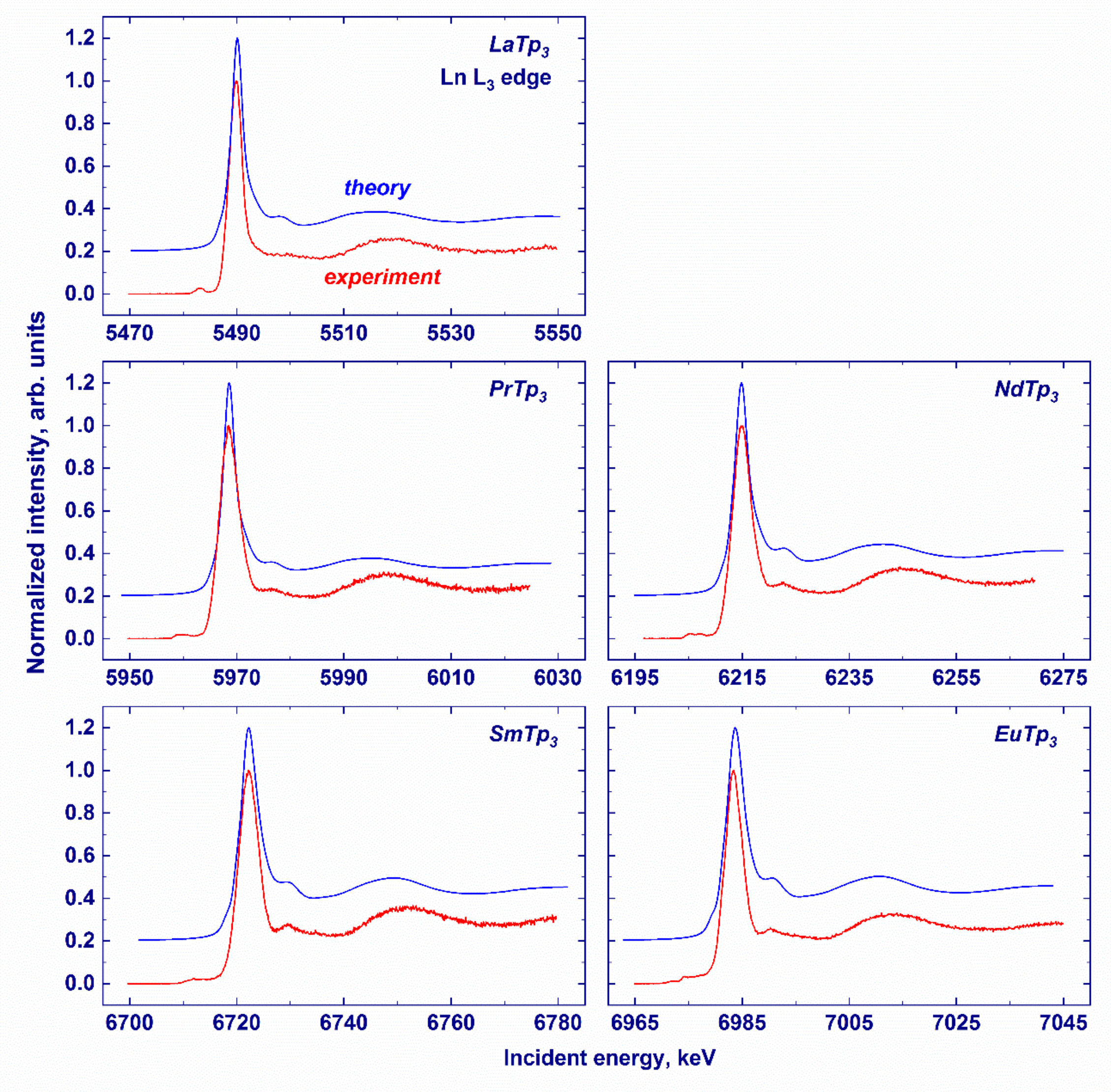

Figure S1. Comparison of experimental Ln^{3+} L$_3$-edge HERFD-XANES spectra of LnTp$_3$ compounds (Ln = La, Pr, Nd, Sm, and Eu) and those calculated by the FDMNES code (bottom and top spectra, respectively). For the sake of clarity, the spectra have been scaled to the same maximum height and offset along the Y-axis. Theoretical spectra have been shifted along the X-axis to align the white lines in the theoretical and experimental spectra.

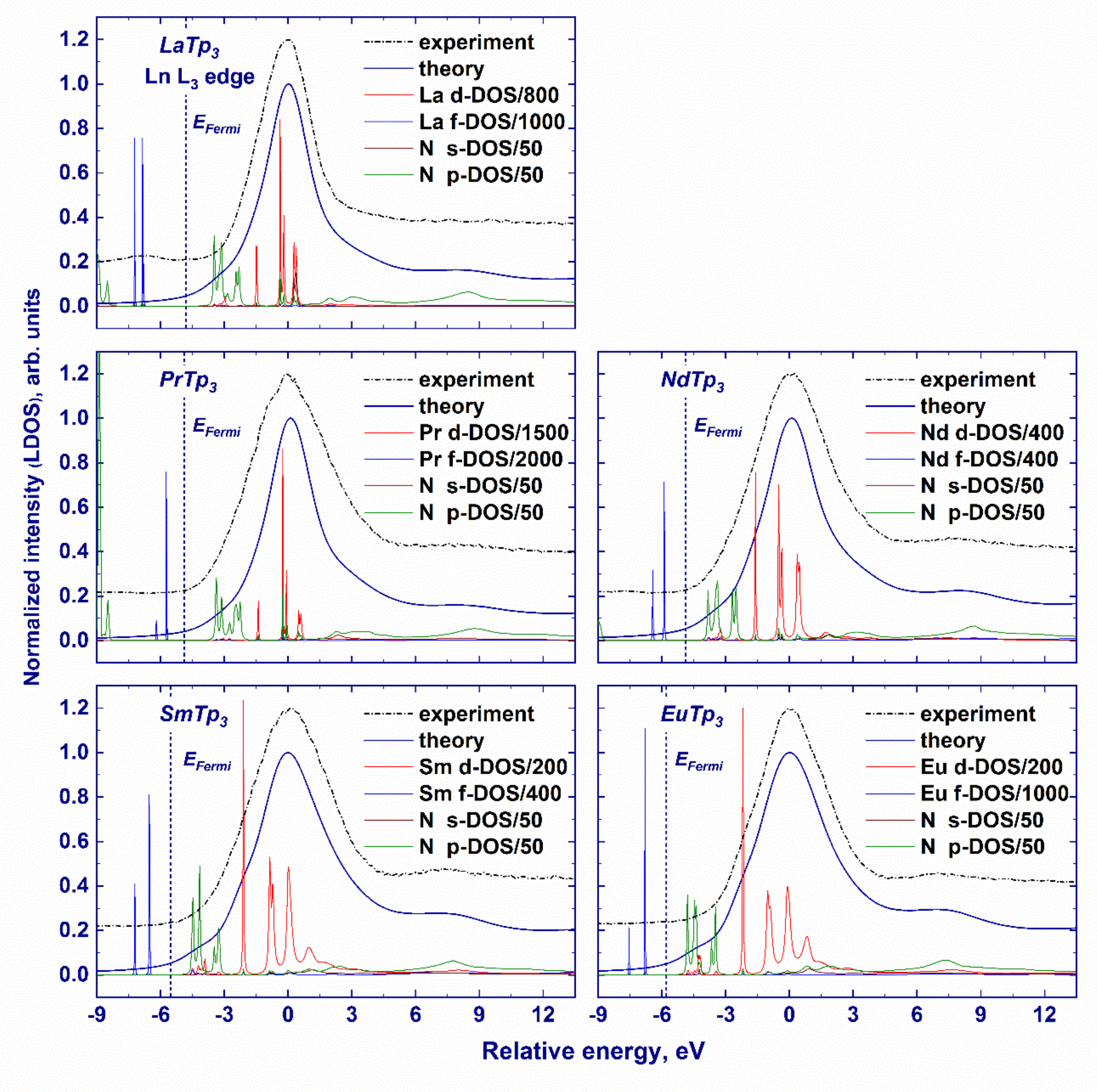

Figure S2. The finite difference computed LDOS (Ln^{3+} cation d and f-orbitals, N atom s and p-orbitals) and normalized XANES spectra of the LnTp$_3$ compounds (Ln = La, Pr, Nd, Sm, and Eu). The experimental spectra are provided with the dashed-dotted lines. The spectra intensities gave been scaled to the same maximum height while LDOS are presented in arbitrary units (note that the LDOS are scaled by the factors indicated in the legend). All of the theoretical curves are shown in the unified energy scale, zero of which corresponds to the position of the white line.

The Fermi level positions are marked with vertical dashed lines. The experimental spectra are aligned along the X-axis to fit the theoretical data.

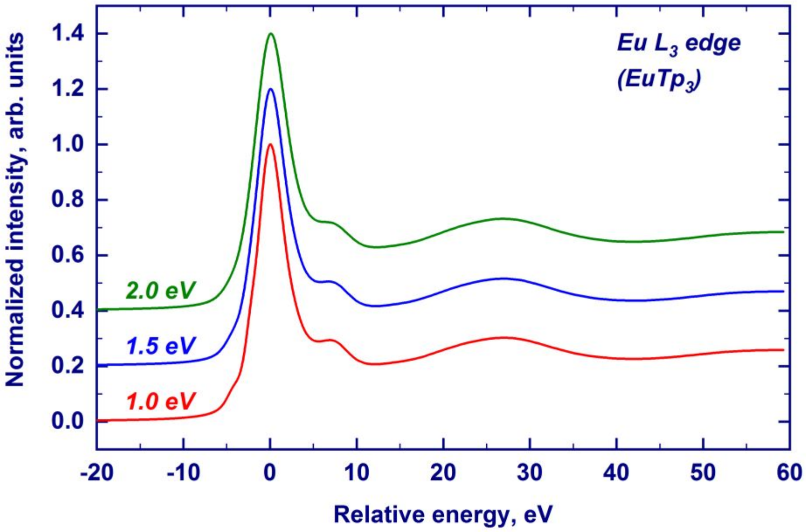

Figure S3. XANES spectra of the $EuTp_3$ L_3-edge absorption calculated with FDMNES code at different Gaussian convolution parameters. The convolution parameters Γ_{hole} and Γ_{max} were set to be 1.2 and 15 eV, respectively. All of the curves are shown in the unified energy scale, zero of which corresponds to the position of the white line.

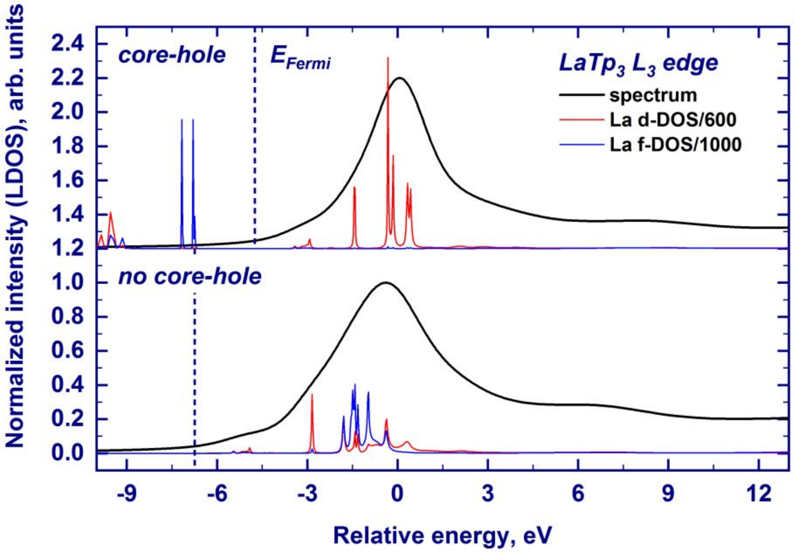

Figure S4. The finite difference computed LDOS (Ln^{3+} cation d and f-orbitals) and normalized XANES spectra of the $LaTp_3$ compound including a core-hole (top panel) and without it (bottom panel). The spectra intensities gave been scaled to the same maximum height while LDOS are presented in arbitrary units (note that the LDOS are scaled by the factors indicated in the legend). All of the theoretical curves are shown in the unified energy scale, zero of which corresponds to the position of the white line. The Fermi level positions are marked with vertical dashed lines.

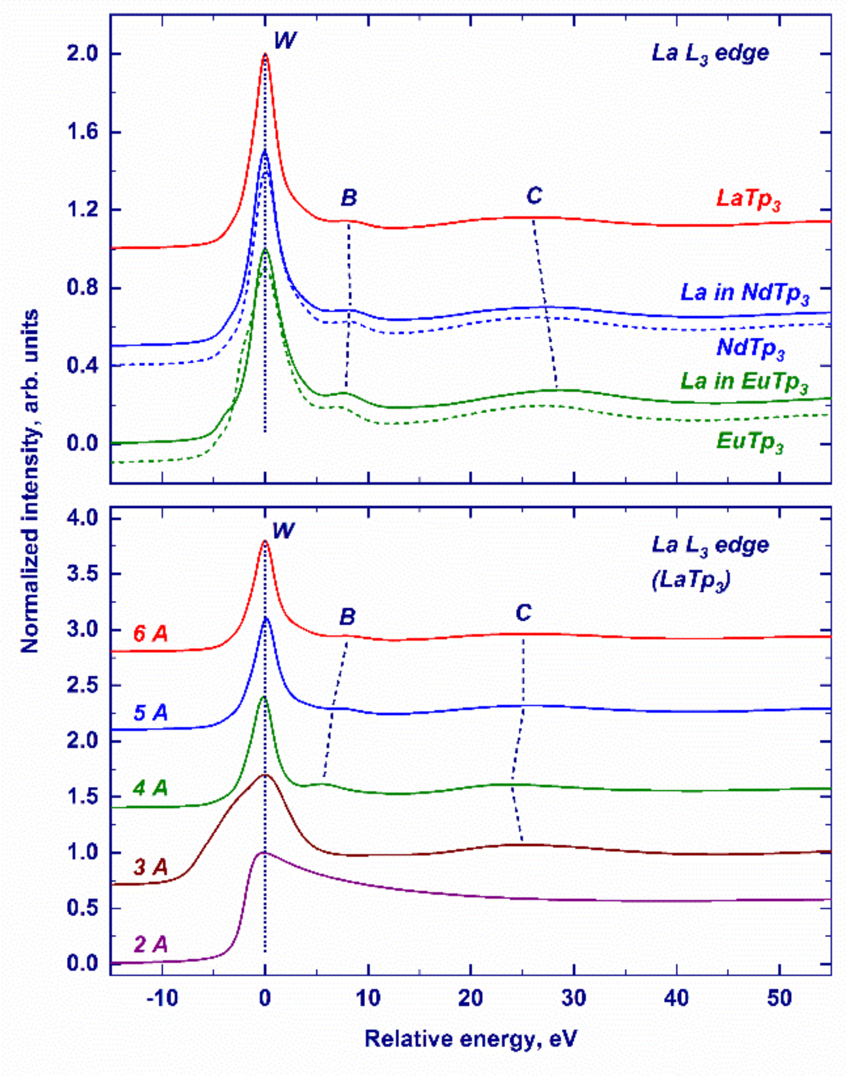

Figure S5. Finite difference computed XANES spectra of the La^{3+} in the Tp_3 structure corresponding to the $LaTp_3$, $NdTp_3$ and $EuTp_3$ compounds (top panel). Finite difference calculated XANES spectra of the $LaTp_3$ substance with different radius of the cluster (the corresponding radius value in Angstroms is provided in figure; bottom panel). The calculated spectra of $NdTp_3$ and $EuTp_3$ (dotted lines) are provided for comparison. For the sake of clarity, the spectra have been scaled to the same maximum height and offset along the Y-axis. All of the curves are shown in the unified energy scale, zero of which corresponds to the position of the white line (marked with a **W**). Other spectral features (pre-edge structure and two post edge peaks) are marked with **B** and **C**, respectively. Dashed and dotted lines are guides to the eye.

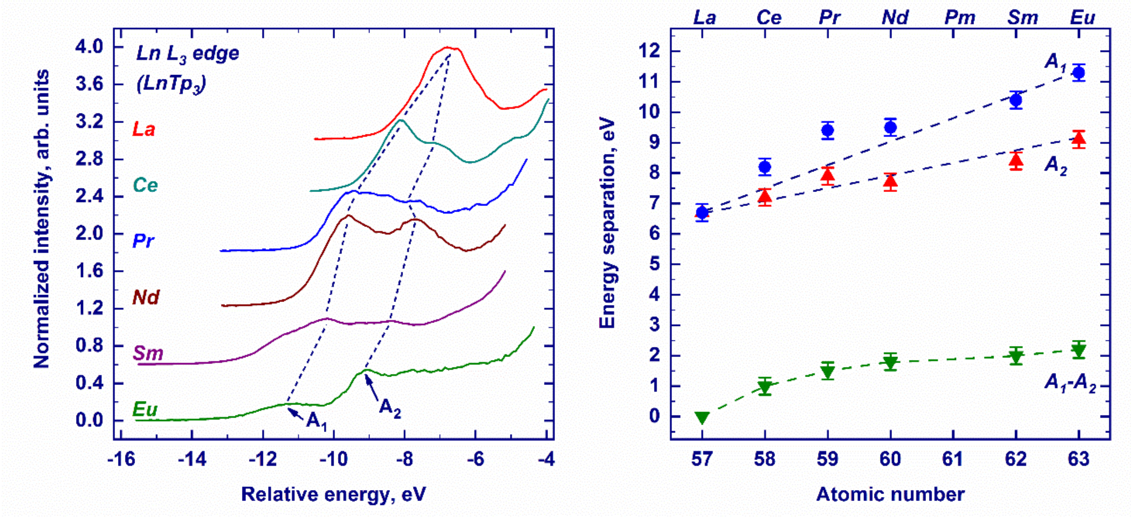

Figure S6. (Left panel). Experimentally measured pre-edge regions of the Ln^{3+} L_3-edge absorption in the $LnTp_3$ compounds (Ln = La, Ce, Pr, Nd, Sm, and Eu). The curves are shown in a unified energy scale, with zero corresponding to the position of the white line. A_1 and A_2 labels represent low and high energy quadrupolar features, respectively. (Right panel). The energy separation between the white line and the resonance energy of the quadrupolar transition features **A_1** (blue filled circles) and **A_2** (red filled apex-up triangles). **A_1−A_2** (green filled apex-down triangles) is the energy separation between the A_1 and A_2 features observed in the HERFD-XANES spectra. Dashed lines are guides to the eye.

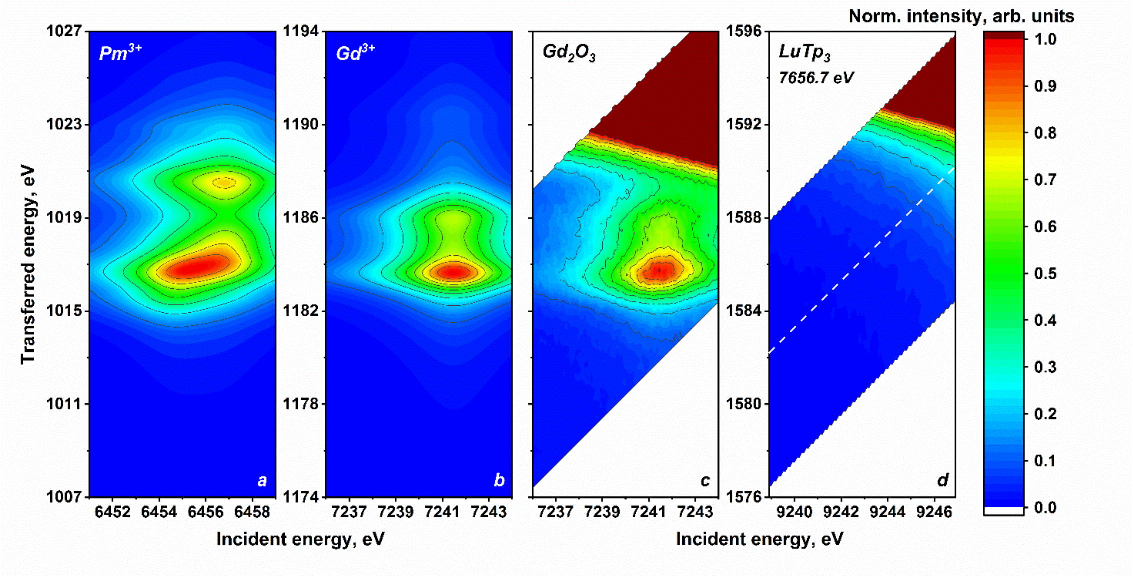

Figure S7. Atomic multiplet calculated (a, b) and experimentally measured (c, d) 2p3d RIXS planes for the lanthanide trivalent cations (Ln = Pm, Gd, and Lu). Experimental planes were measured for the Gd_2O_3 and $LuTp_3$ compounds. For the sake of clarity, the RIXS planes have been scaled. The position of the HERFD-cut for $LuTp_3$ is marked with a dashed line. Emission energy which was used to record the corresponding HERFD-cut is provided in the top left corner. Owing to the absence of the experimental data on Pm^{3+} the L_3 (6459 eV) and M_5 (1027 eV) edge energies were added to the corresponding theoretical values for this lanthanide to rescale X and Y axes, respectively.

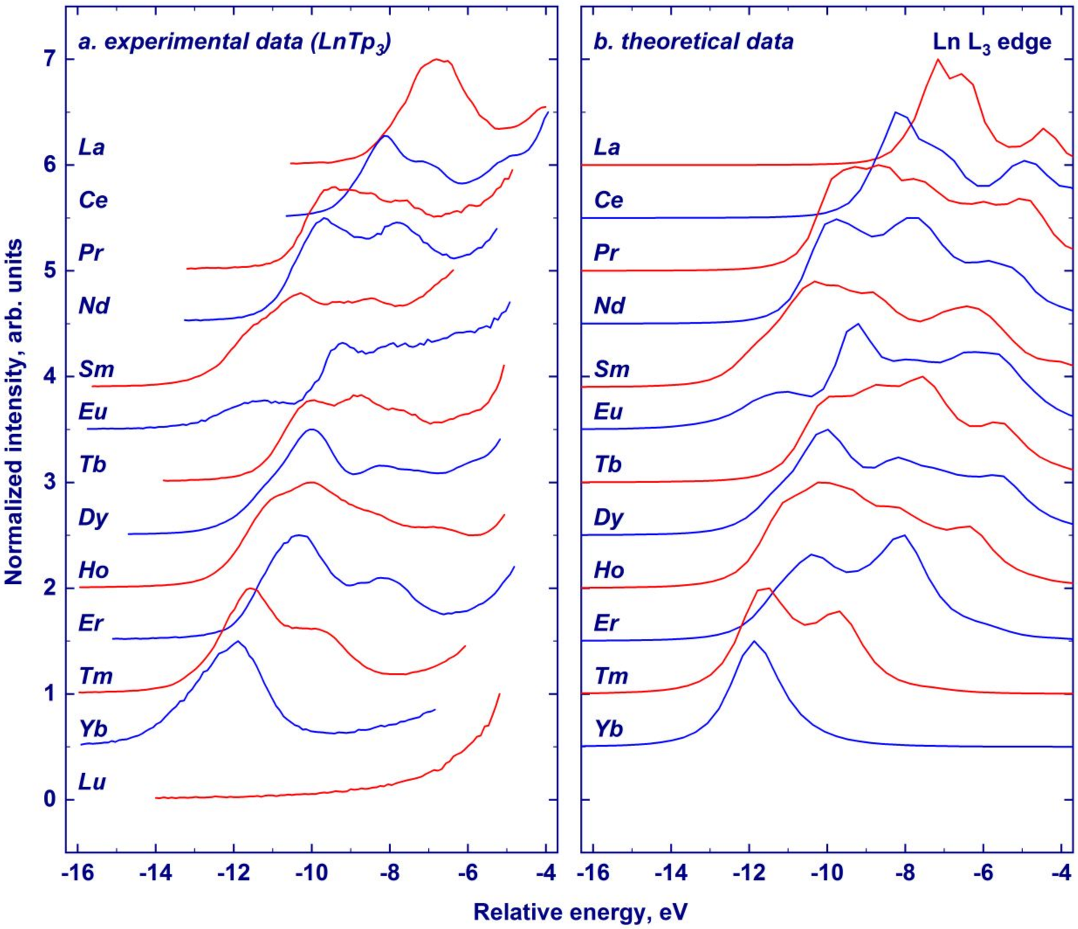

Figure S8. Experimentally measured (left panel) and atomic multiplet theory calculated (right panel) pre-edge regions of the XANES spectra of the Ln^{3+} L_3-edge absorption in the $LnTp_3$ compounds (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, and Lu). For the sake of clarity, the spectra have been scaled to the same maximum height and offset along the Y-axis. All of the curves are shown in the unified energy scale, zero of which corresponds to the position of the white line.

Table S1. The Lorentzian broadening parameters were used to calculate the RIXS planes for the $LnTp_3$ compounds using the Quanty code.

Element (Ln)	Lorentzian broadening FWHM, eV	
	Incident energy	Energy Transfer
La	3.41	0.82
Ce	3.48	0.87
Pr	3.60	0.92
Nd	3.65	0.96
Pm	3.75	1.02
Sm	3.86	1.07
Eu	3.91	1.13
Gd	4.01	1.19
Tb	4.12	1.25
Dy	4.17	1.31
Ho	4.26	1.38
Er	4.35	1.46
Tm	4.48	1.53
Yb	4.60	1.61

Atomic parameters calculations

As mentioned in the main text, we have used the code developed by Robert Cowan to calculate the parameters that enter the atomic Hamiltonian. The Slater integrals (F^k and G^k) are calculated using the radial wave functions obtained from Hartree-Fock calculations including mass-velocity and Darwin relativistic corrections (see page 201 from Cowan, R. D. *The Theory of Atomic Structure and Spectra*; Los Alamos series in basic and applied sciences, Univ. of California Press: Berkeley, Calif., 1981). The spin-orbit coupling constants are based on the expression derived for Blume and Watson using the radial function calculated previously (page 219 from Cowan, 1981). We list below the input file for the RCN program used to calculate the parameters for Pr^{3+}:

```
22 -9    2   10  1.0    5.E-06    1.E-09-2   130   1.0  0.65  0.0 0.50 0.0  0.7
   59           4f2              4F02
   -1
```