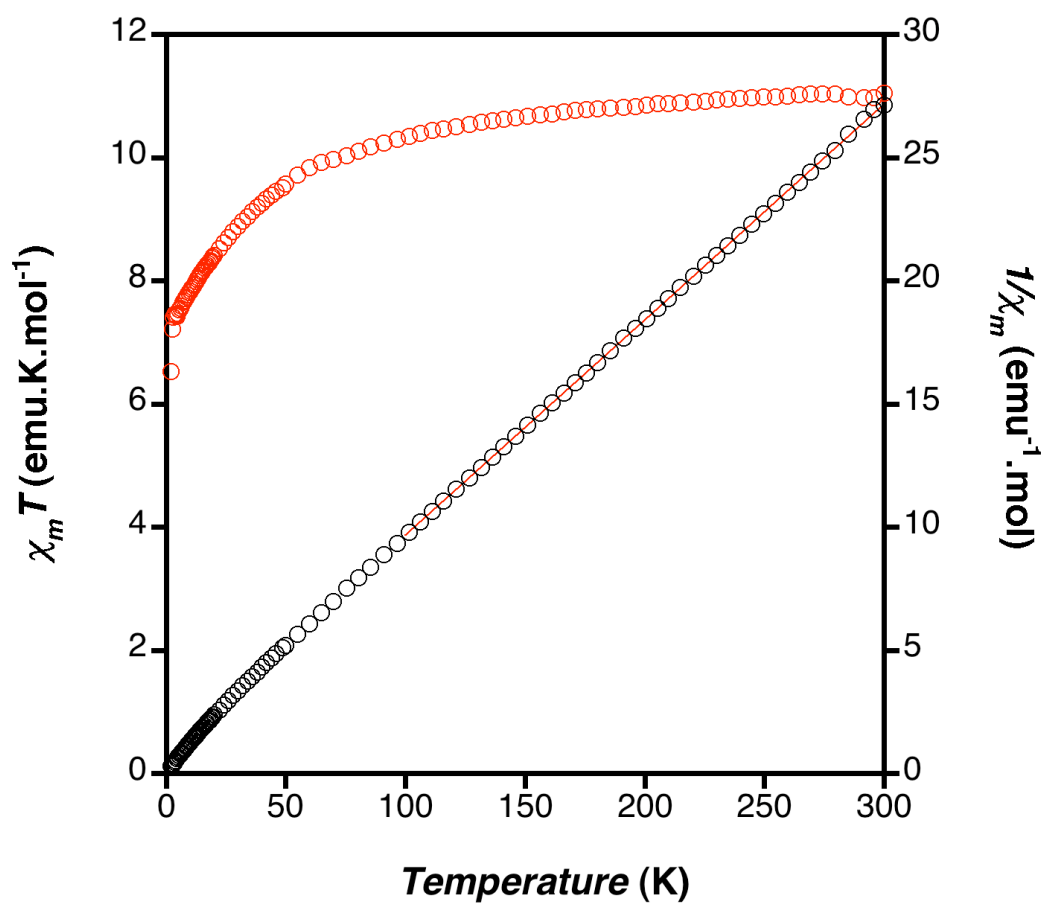


Supplementary information

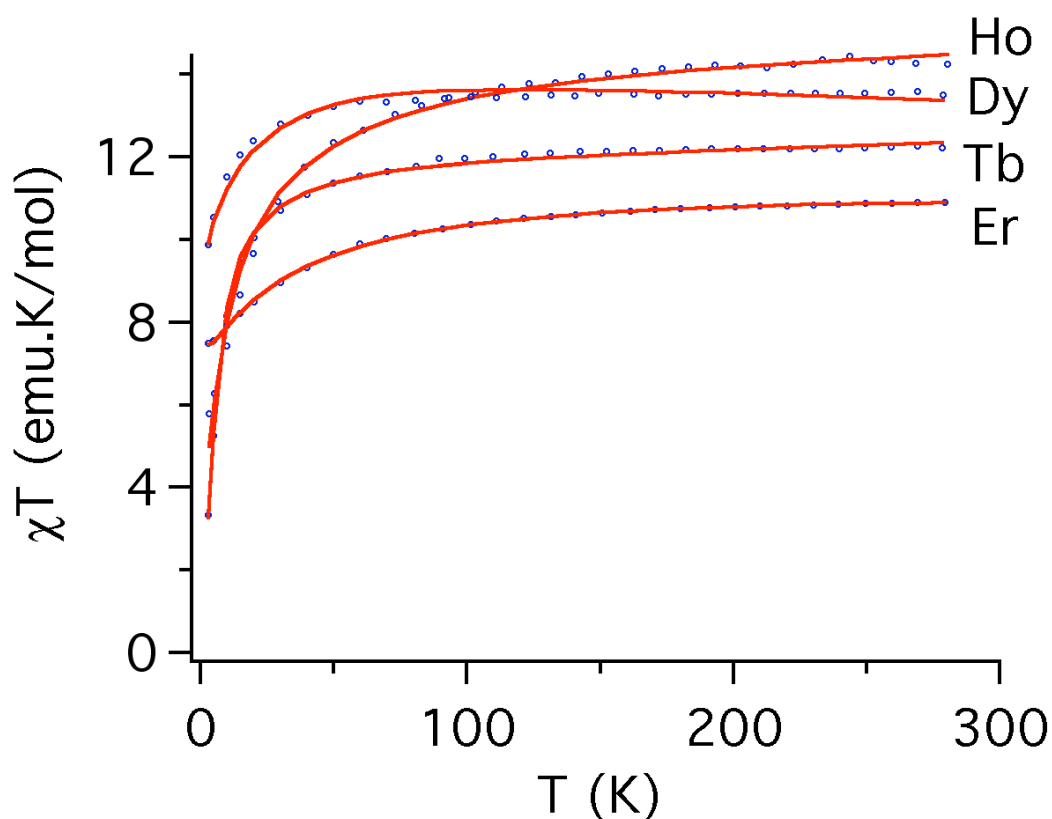
Experimental procedure:

All chemicals and solvents were employed as supplied. $[\text{ErW}_{10}\text{O}_{36}]\text{Na}_9 \cdot 35\text{H}_2\text{O}$ (**1**) was synthesized following a previously described procedure with slight modifications (see main text). In a first stage, $\text{Er}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ (2.180 g; 3.8 mmol) was dissolved in 30 ml of HCl (0.1 M) and heated at 80°C during 30 min giving rise to a colorless solution. Simultaneously, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (50 g, 152 mmol) was dissolved in distilled water (100 ml) with continuous stirring, pH was adjusted to 7.2 with acetic anhydride and the resulting solution was heated to 90°C (B). After that, (A) was dropwise added to the hot stirred tungstate solution (B). After being vigorously stirred for 1 hour, the mixture was filtered rapidly and left to evaporate at room temperature. Three weeks later, needle shape pale pink crystals of **1**, suitable for X-ray single crystal diffraction, were obtained. Yield 71%. IR (KBr): 937 (s), 849 (s), 787 (m), 706 (m), 588 (w), 548 (m), 490 (w).

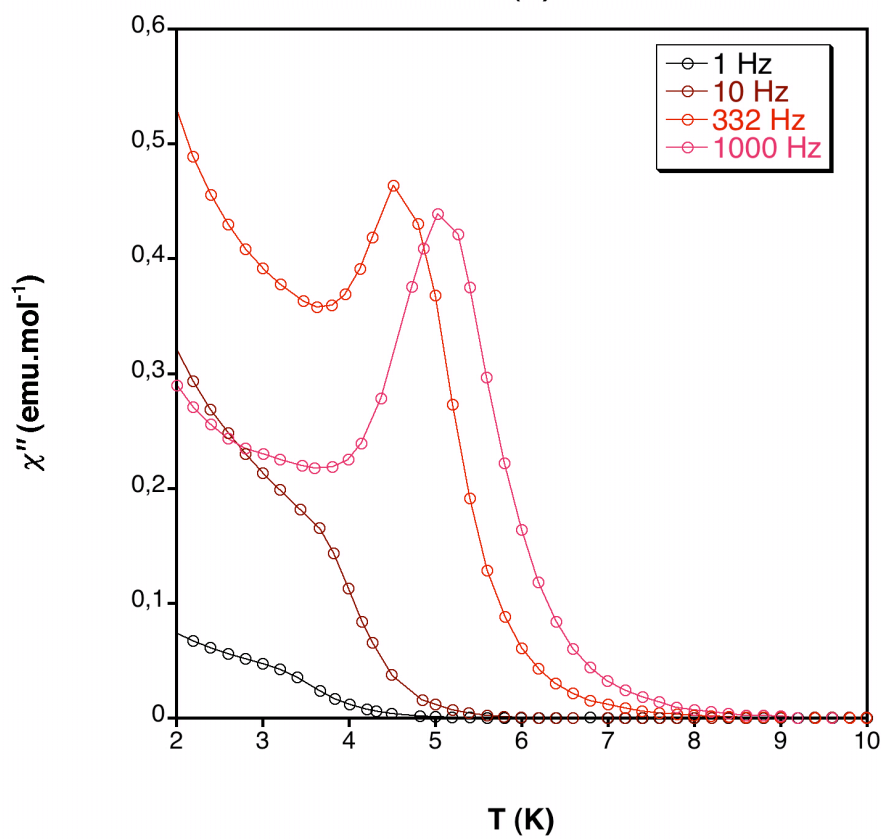
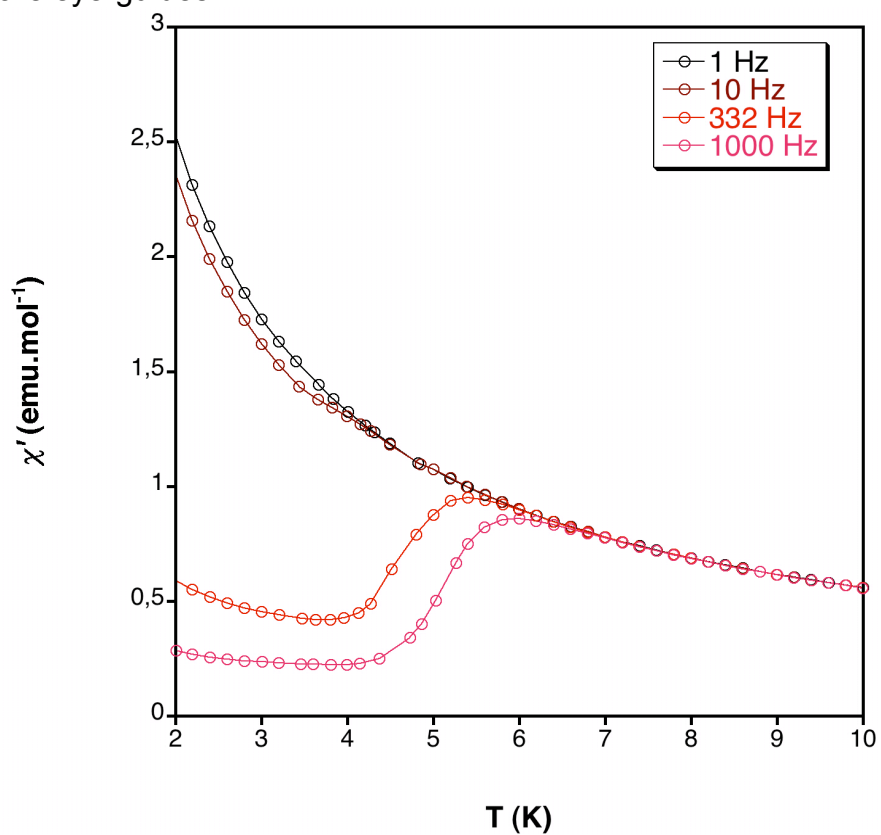
SI 1. $\chi_M T$ product (*left*) and χ_M^{-1} (*right*) temperature dependence of **1** in the 2-300 K range. Solid red line represents the best fitting to Curie-Weiss law in the high temperature regime.



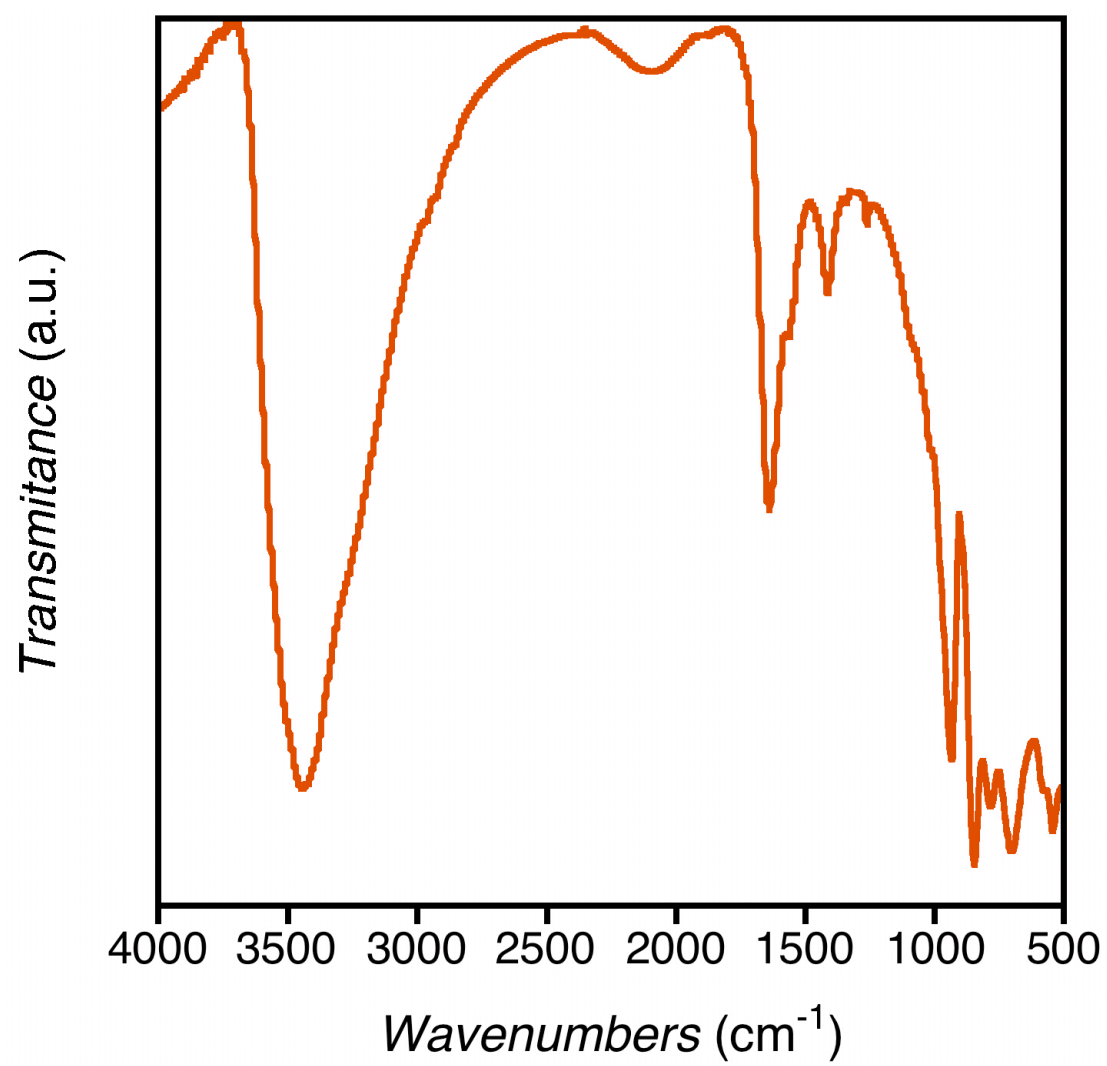
SI 2. Experimental (blue opened circles) and theoretical (red line) temperature dependence of the susceptibility for the LnW_{10} family ($\text{Ln} = \text{Ho}, \text{Dy}, \text{Tb}$ and Er). Due to the large number of ligand-field parameters to be determined, we needed to use a procedure similar to that developed by Ishikawa (Ishikawa, N., *J. Phys. Chem. A* **2003**, *107*, 5831-5835). In this model, the temperature dependence of magnetic susceptibilities of several isostructural lanthanide complexes is fitted simultaneously. This fit yields a set of common LF parameters for all lanthanide complexes with a linear dependency with the number of f electrons.



SI 3. Low-frequency In-phase (*up*) and out-of-phase (*down*) dynamic susceptibility of **1**. From left to right: 1 100, 332, 3200 and 1000 Hz. Solid lines are eye-guides



SI/ 4. Infrared spectrum of **1**.



SI 5. Perspectives showing the cationic framework build up by sodium ions octahedrally coordinated to water encapsulating the polyoxometalate.

