

Effect of heavier element on the ultra-low frequency phonons in Nd(III) based luminescent nanomagnets

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The ultralow-frequency (ULF) vibrations in the sub-terahertz (sub-THz) region are explored due to their potential applications in various fields such as - aerospace industry and information technology.^{1,2} Combining such ability in the molecular complexes allows us to incorporate other physical properties like luminescence, magnetism etc. With the above aim, we prepared two supramolecular assemblies with the pseudohalides [Nd^{III}(phen)₃(NCX)₃]·0.3EtOH (X = S, **1-S**; Se, **1-Se**), crystallizing in the centrosymmetric triclinic *P*-1 space group, and characterized them extensively through various spectroscopy, and quantum chemical calculations for both compounds (**Figure 1a**).

The powdered samples for both assemblies exhibit minimum THz-wave absorption of 0.59 THz (19.7 cm⁻¹) for **1-Se** and 0.65 THz (25.7 cm⁻¹) for **1-S** (**Figure 1b**). We found out that the THz-wave absorption is redshifted upon heavy element substitution. Further monocrystals of both compounds also have ULF Raman scattering in the sub-THz (below one terahertz) region (**Figure 1c**). As a result, we discovered that both complexes reveal exceptionally low-frequency Raman shifts, which also shifts towards the low-frequency region for selenium-containing assemblies. The quantum chemical calculations were performed on the optimized geometry to visualize the vibrations indicating the nature of these vibrations to be of pendulum type. Additionally, near-infrared (NIR) emission from the Nd(III) centre is also studied with varying temperatures revealing ratiometric thermometric behaviour. They also reveal field-induced single-molecule magnetic properties.

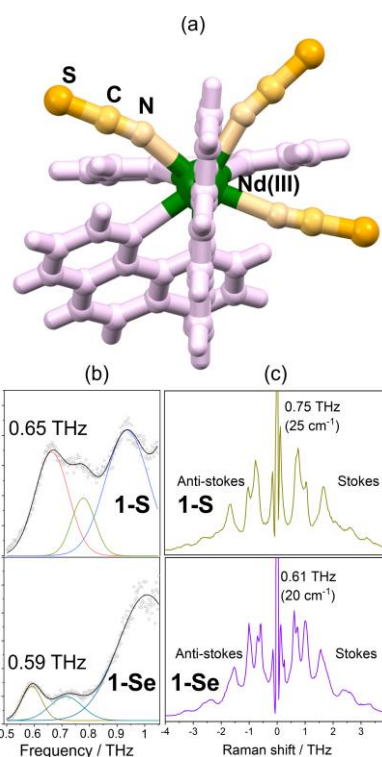


Figure 1. Crystal structure of **1-S** with assigned elements name (a), terahertz signal from **1-S** and **1-Se** (b), and Raman shift of **1-S** and **1-Se** in the specified region (c).

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