Karlsruhe Institute of Technology

Structural Characterization and Cryogenic Fluorescence Properties of Unique Hexanuclear Lanthanide Containing Polyoxometalates

Vanikrishna Ajithkumar Njayappallil[1], Masooma Ibrahim[2], Senthil Kumar Kuppusamy[3], Aravind Raveendranathan[2], Christopher Anson[1], Mario Ruben[234], Annie K. Powell[123]

1. *Institute of Inorganic Chemistry (AOC), Karlsruhe Institute of Technology (KIT),Karlsruhe, Germany*
2. *Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
3. *Institute of Quantum Materials and Technologies (IQMT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
4. *Institute of Supramolecular Science and Engineering, Université de Strasbourg, Strasbourg, France*

Introduction

Polyoxometalates (POMs) are a large class of metal-oxo nanoclusters usually composed of early transition metals in their high oxidation states (e.g., V^{5+}, Mo^{5+}, Nb^{5+}, Ta^{5+}, Mo^{6+} and W^{6+}). These species have been known for nearly two centuries and are famous for their redox properties, larger sizes, high negative charges, nucleophilicity and robust shell topologies.[1] The scope and properties of POMs can be expanded by the introduction of transition and rare earth metals. The nucleophilic oxygen rich sites on lacunary POMs can act as inorganic polydentate ligands to coordinate to 3d and 4f metal ions to form 3d-4f POM hybrids. The affinity of lanthanide ions towards oxo groups, as well as their properties in areas such as optics, catalysis and magnetism, places rare earth-based POMs as a promising all-inorganic-based route to novel materials.[2,3] Here, we introduce unique hexanuclear lanthanide containing POMs, **$\{Ln_6(SiW_9)_2\}$**, which have unique structural and luminescence properties.

Structure

The metalloligand approach using trilacunary Keggin POMs towards lanthanides (Ln^{3+}) leads to the formation of sandwich type 4f-based POM hybrids **$[\{W_9SiO_{34}\}_2\{Ln_6(\mu\text{-}OH)_3(OH_2)_9\}]^{5-}$, (Ln= Nd, Pr, Sm, Eu and Gd)** (Figure 1). Here, the six Ln^{3+} ions are linked through oxygen atoms between two SiW_9 units to give a 6:2 ratio which is uncommon. The synthesis is a straightforward one-pot method. All five analogues are isostructural and form a very robust 3D framework.

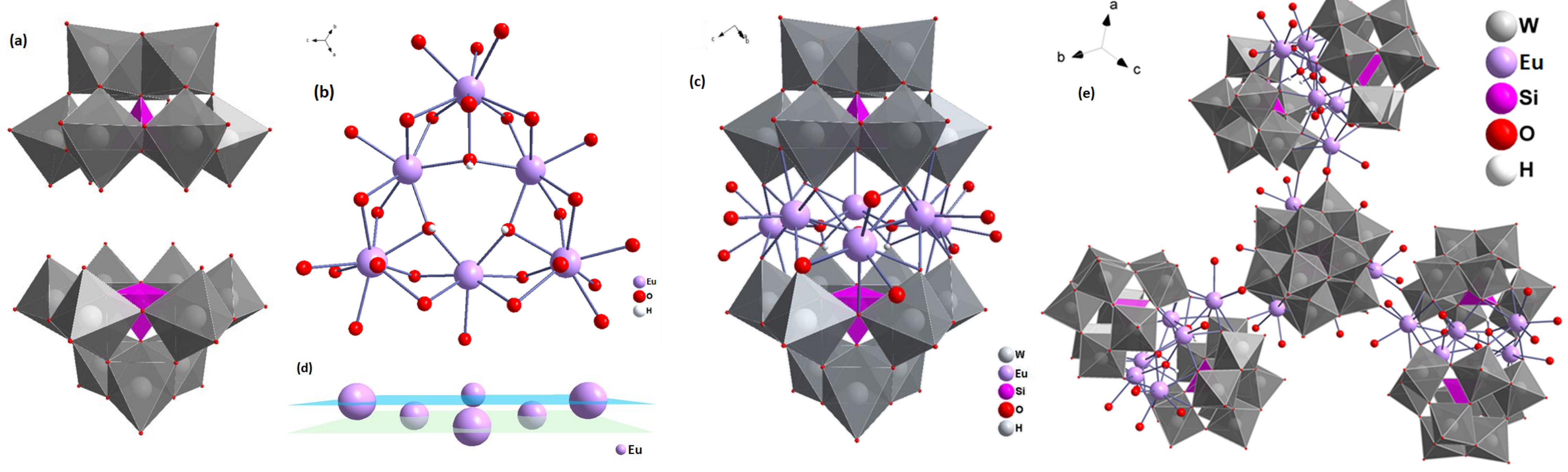

Figure 1. (a) Two SiW_9 building blocks of **$\{Eu_6(SiW_9)_2\}$**, (b) Eu_6-core linked through oxygen atoms, (c) $\{Eu_6(SiW_9)_2\}$ core, (d) two planes containing 3 Eu^{3+} ions each (e) $\{Eu_6(SiW_9)_2\}$ 3D framework

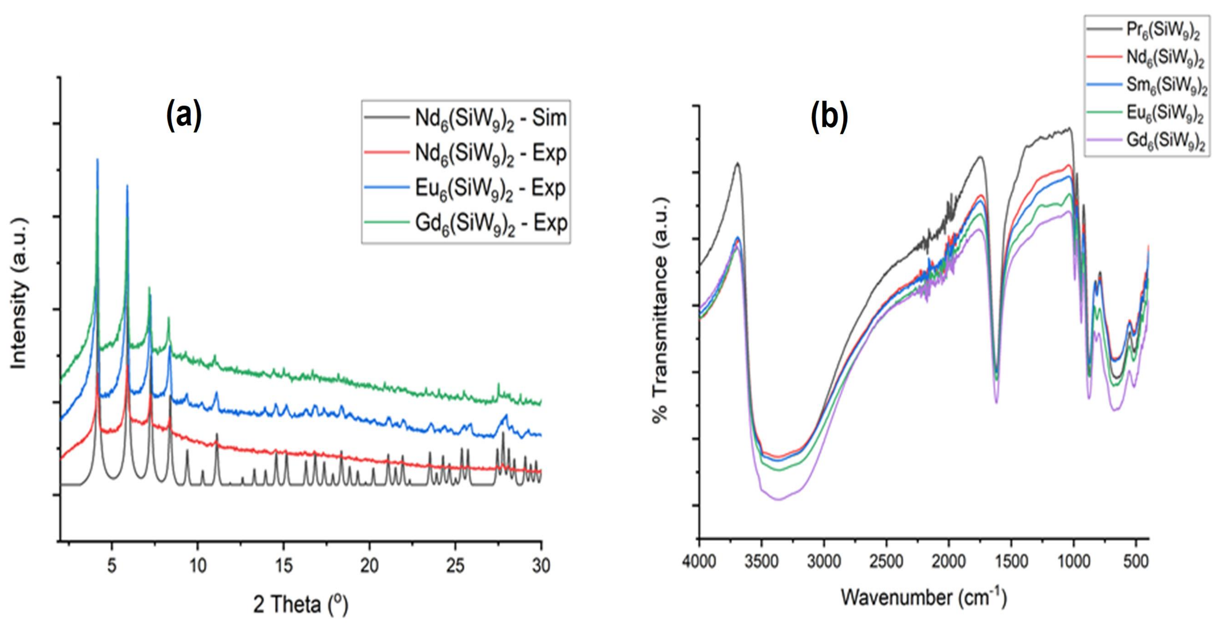

Figure 2. (a) PXRD pattern and (b) FT-IR spectral characterization of **$\{Ln_6(SiW_9)_2\}$**

Temperature-Dependent Fluorescence Analysis at Cryogenic Temperatures in $Eu_6(SiW_9)_2$ System

The Antenna effect: The O→M (**W**) charge transfer in the POM ligand causes intersystem crossing (ISC) that allows the transition from Singlet to Triplet states. The energy is then transferred to the $^5D_0$ excited state, followed by the emission to the J (0-6) levels of the ground term ^7F ($^5D_0 \rightarrow {}^7F_J$) of Eu^{3+}.

- The highest excitation was found at 396 nm (Figure 3. (c)).
- The temperature-dependent analysis at 2K, 77K, 180K and 300K was done and there are some distinct observations at low temperature (2K).
- The $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ transitions at 2K shows a missing peak compared to the other temperatures at 77K, 180K and 300K (Figure 3. (a), (b)).
- Comparing the spectroscopic analysis of **$Gd_6(SiW_9)_2$** in RT reveals the energy levels of the LMCT in **$Eu_6(SiW_9)_2$** (Figure 3. (e)).
- The energy of the $^5D_0$ level in Eu^{3+} is 17,230 cm^{-1} and that of the triplet energy level of the ligand is 22,573 cm^{-1}.
- The lifetime was found to be 277.18 μs and 274.15 μs at 2K and 300K respectively.

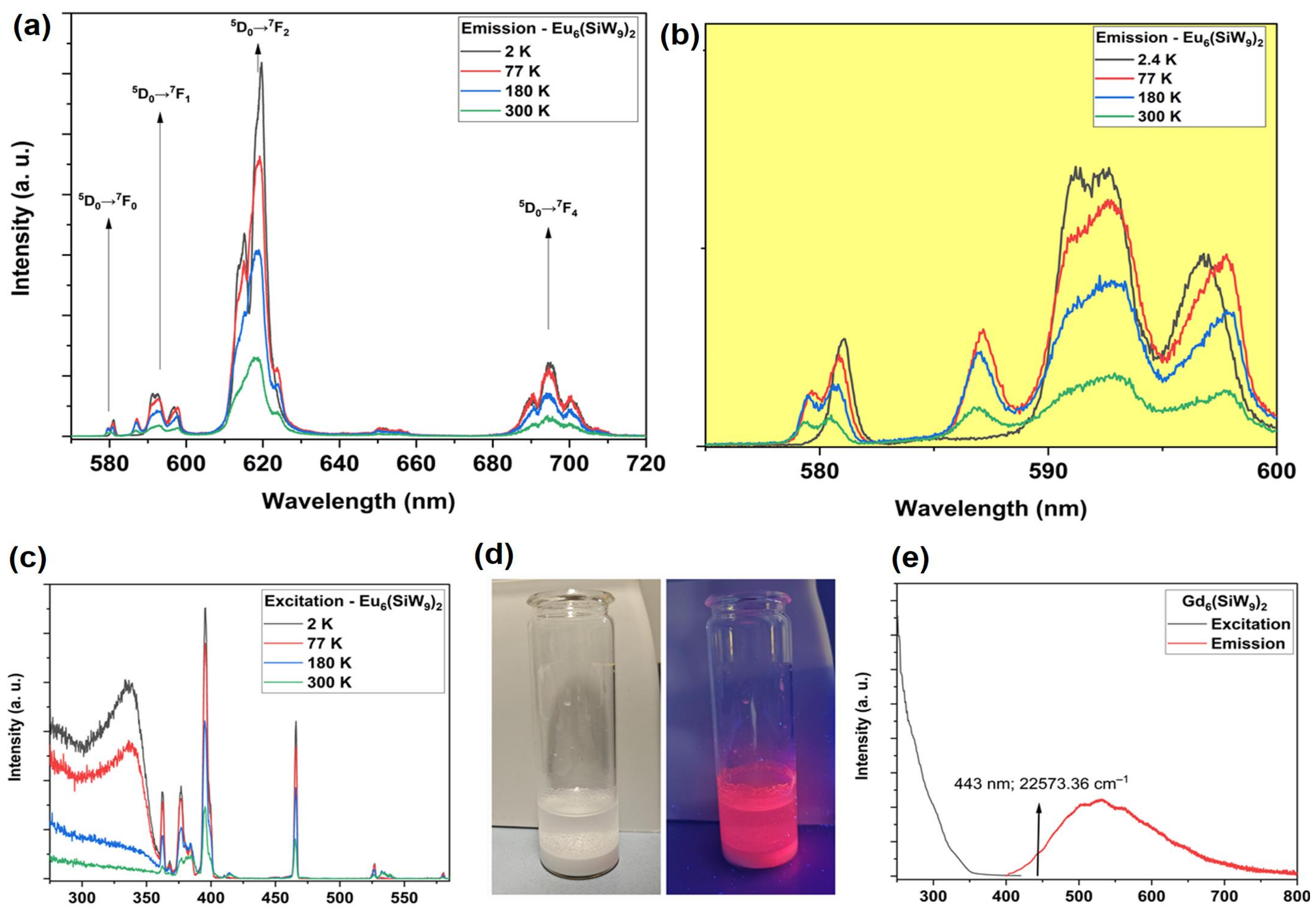

Figure 3.

Conclusion and Outlook

- A series of hexanuclear lanthanide-containing sandwich-type POM-hybrids, **$\{Ln_6(SiW_9)_2\}$**, has been successfully synthesized using a one-pot method for the first time.
- Temperature-dependent fluorescence spectroscopic measurements within the temperature range of 2–300 K have been conducted on **$\{Eu_6\}$**. Our future plans involve conducting further studies to thoroughly analyze and comprehend the collected data.
- The objective is to explore the catalytic potential of all **$\{Ln_6\}$** compounds.
- The magnetic properties of the paramagnetic **$\{Ln_6\}$** POMs will be extensively investigated. This investigation will include the exploration of magneto-caloric effects as well as potential applications of these compounds as contrast agents.

References

1. *Polyoxometalates*, **2023**, *2*, 9140022.
2. *J. Phys. Chem. A,* **1997,***101,* 5046-5053.
3. *Coord. Chem. Rev.*, **2015**, 295,1–45.

Acknowledgment

Karlsruhe Institute of Technology (KIT) for funding and Prof. Dr. Dieter Fenske and Dr. Olaf Fuhr for all the measurement of the crystallographic data.