



## Exploring Exchange Coupling in Ln-[1]Metallophenophane Compounds Using High-Field EPR

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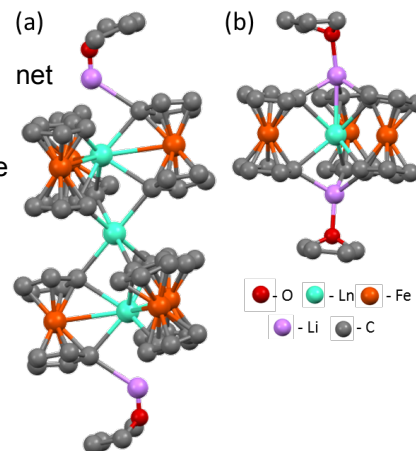
### Introduction

Single-molecule magnets (SMMs) are discrete molecules that exhibit slow relaxation of magnetization of purely molecular origin. In recent years, strategies towards increasing the operating temperatures of SMMs have focused on judicious tailoring of the ligand field environment surrounding lanthanide (Ln) ions, which can display significant magnetic anisotropy. However, relatively few examples of systems with strong Ln-Ln interactions exist. In the appropriate geometry, SMMs containing multiple strongly coupled anisotropic metal sites offer the advantage of effectively increasing the magnetic moment while simultaneously shutting down fast magnetization tunneling pathways.

Recently, a series of tri Ln-[1]metallophenophane compounds of the type  $[\text{Li}_2\text{Cl}(\text{THF})_6][\text{Li}_2\text{Ln}_3\text{Fc}_6(\text{THF})_2]$  have been developed [1], where Ln = Gd(III) (**1**), Tb(III) (**2**), and Dy(III) (**3**), and Fc = 1,1'-diferrocenyl. The linear chain-like structure, shown in **Fig.1**, contains two Ln ions in identical three-fold coordination environments at either end (A), and an octahedrally coordinated Ln ion (B) in the middle (A-B-A). Preliminary magnetic susceptibility measurements show that **1**, **2**, and **3** exhibit unusually strong ferromagnetic exchange coupling between the Ln ions.

### Experimental

In order to quantify the effects of exchange on the total magnetic anisotropy of the trimer, multi-frequency EPR measurements were performed on powders of **1**, **2**, and **3** and compared to their respective monomer analogues [2]; the structures are shown in **Fig.1**. All experiments were performed on the homodyne system coupled with the 15/17 T SC magnet in the EMR facility.



**Fig.1** (a) Trimer (**1**) and (b) Monomer (**2**). Each cyan Ln can be substituted for **1**, **2**, and **3**. Note that the monomer is identical to the end sub-units of the trimer.

### Results and Discussion

Both the monomer and trimer versions of compounds **2** and **3** proved to be EPR silent due to the inherently large zero-field splitting typically associated with Tb(III) and Dy(III), which exceeds the available frequency range, even in the highest frequency EPR spectrometers. Compound **1** on the other hand displays clearly resolved spectra. **Fig.2** shows a comparison between the monomer and trimer Gd(III) compounds. The results for the monomer are indicative of a weakly anisotropic spin  $S = 7/2$  moment, as expected for Gd(III). In contrast, the trimer shows a clear augmentation of the magnetic anisotropy, as the spectral density is spread further over the magnetic field range. Preliminary simulations of these spectra provide promising evidence of a strongly coupled total spin ground state of  $S = 21/2$ .

### Conclusions

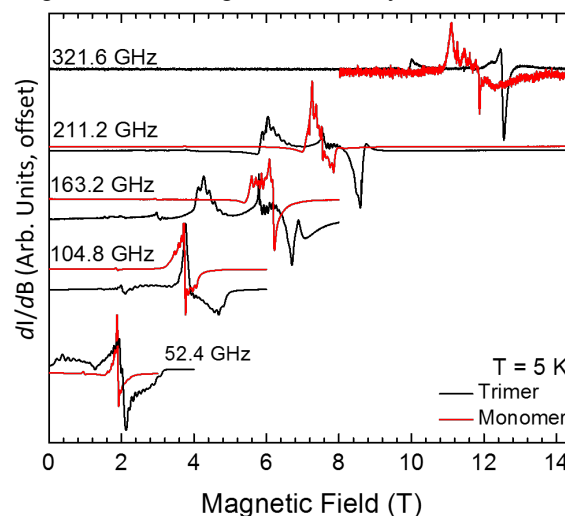
While measurements of **2** and **3** yielded no results, **1** shows evidence for strong exchange coupling between neighboring Ln ions in the trimer. In order to probe more anisotropic Ln ions such as Tb(III) and Dy(III), we have proposed further studies on heterometallic lanthanide complexes, in which one of the Gd(III) sites can be substituted for a more anisotropic ion.

### Acknowledgements

The NHMFL is supported by the National Science Foundation (NSF) through grants DMR-1157490 and 1644779, and the State of Florida. A portion of this work was also funded by NSF grant numbers CHE-1753014 and DMR-1610226.

### References

- [1] Latendresse, T.P., *et al.*, J. Am. Chem. Soc., **139**, 14877 (2017).
- [2] Latendresse, T.P., *et al.*, Angew. Chem. Int. Ed., **57**, 8164 (2018)



**Fig.2** Stacked EPR powder spectra of **1** for both the trimer (black) and monomer (red).