HEXAGONAL BIPYRAMIDAL Dy(III) SINGLE-MOLECULE MAGNETS: FROM HIGH MAGNETIC REVERSAL BARRIER TO OUTSTANDING PCS TAGS FOR NMR

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Large magnetic anisotropy (MA) is a fundamental requirement for both high-performance single-molecule magnets (SMMs) and pseudocontact shift (PCS) tags. Thus, achieving strong easy-axis MA through chemical design is a central goal in SMM, which can similarly be used to enhance PCS in NMR by maximizing through-space dipolar interactions. To date, the most effective mononuclear SMMs are based on dysprosium(III) ions ($4f^9$) in highly axial crystal fields, typically realized via pseudo-two-coordinate strategy or sandwich-like ligand approach. In this talk, we will present a mononuclear hexagonal bipyramidal Dy^{III} complex ($[Dy(L^E)(4\text{-MeO-PhO})_2](BPh_4)\cdot 3THF$) with nearly perfect D_{6h} local symmetry, using a hexaaza macrocyclic Schiff base ligand and finetuned axial alkoxide/phenol-type ligands (Figure 1). This complex presents a large easy-axis MA with effective magnetic reversal barrier of 1338(3) K. When preserved in tetrahydrofuran-d_8 solution, the solution 1H NMR spectra at room temperature reveal remarkably large PCS exceeding -540 ppm. The remarkable solution stability and huge MA opens the possibility to engineer new highly performant PCS tags.

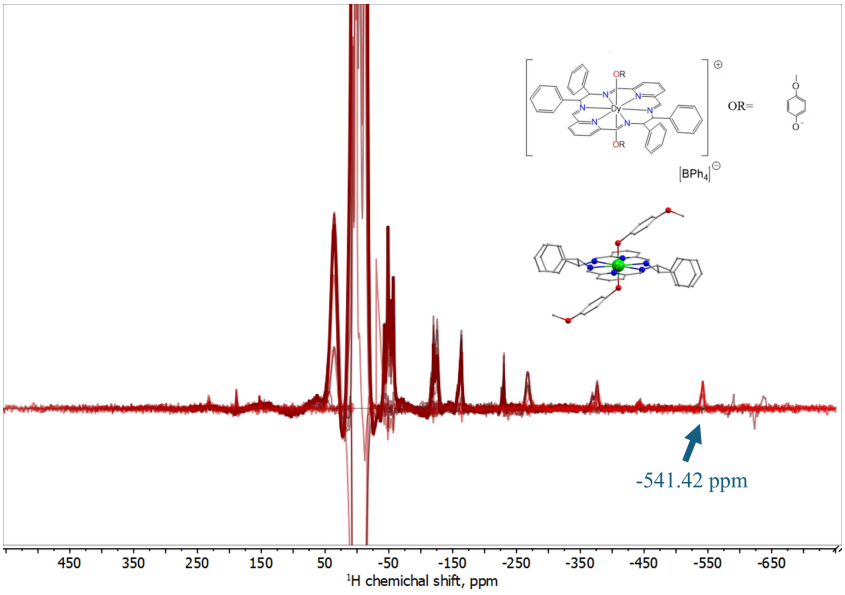

Figure 1. Experimental 300 MHz ^{1}H-NMR spectrum recorded at 293 K and 7 T in tetrahydrofuran-d_8.

[1] Z.-H. Li, Y.-Q. Zhai, W.-P. Chen, Y.-S. Ding, Y.-Z. Zheng. *Chem. Eur. J.* **2019**, *25*, 16219.