Utilization of diamagnetic Zn(II) ion to boost the anisotropic nature of Ln(III) ion in heterodinuclear Zn(II)–Ln(III) single-molecule magnets

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Kolekcja

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Streszczenie

A series of dimetallic Zn^{II}–Ln^{III} compounds of general formulae $[LnZn(L)_3(NO_3)_2]\cdot 2CH_3OH$ (Ln^{III} = Dy^{III} (**1**), Tb^{III} (**2**), Gd^{III}(**3**)) was prepared by stepwise reaction of compartmental ligand LH = ((E)-2-((pyridin-2-ylmethylene)amino)phenol) with Ln $(NO_3)_3\cdot xH_2O$ and Zn $(NO_3)_2\cdot xH_2O$ in the presence of triethylamine as base. The single crystal XRD analysis indicated that both metallic ions are connected to each other through phenolic oxygen atom from fully deprotonated ligand. Based on the SHAPE analysis, the Dy^{III} ion has nine coordination numbers with distorted spherical capped square antiprism geometry, while the Zn^{II} ion has six coordination numbers with distorted octahedral geometry. DC magnetic studies reveal the existence of antiferromagnetic interaction between the Zn^{II} and Ln^{III} metal centers. AC magnetic studies reveal that the complex **1** show field-induced single-molecule magnet (SMM) properties with an effective energy barrier of 155 K under an applied dc field of 0.1 T, whereas complex **2** does not show SMM behavior. Furthermore, we conducted DFT and ab initio CASSCF + RASSI-SO calculations to probe the single-ion properties of Ln(III) ions and to understand the role of the diamagnetic Zn^{II} ion in the magnetization relaxation in order to interpret the experimental observations. Ab initio calculations predict that the g_z values are strongly axial in nature in the ground state of Dy(III) ion in complex **1** and that allows the magnetic relaxation to occur via excited states with a U_{cal} of 380.8 K. DFT calculations discovered that the presence of the diamagnetic Zn(II) ion causes greater negative charges on the bridging oxygen atoms, which enhances the anisotropy of Dy(III) ion and thus reduces the quantum tunneling of magnetization (QTM) effects, and helps to achieve better SMM features for **1**.

Język

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