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# Exploring the Ground and Excited States Structure of Rare-Earth-Based Molecular Magnets

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# Introduction

In the realm of rare-earth-based complexes with aromatic ligands, a captivating phenomenon awaits discovery – the ground and excited states within the complexes. These complexes possess an intriguing feature, at the ground state, various magnetic anisotropies can occur as depicted in Figure 1. Pioneering the exploration of this mesmerizing domain, Ishikawa et al, unveiled the behavior of a single molecule magnet, revealing a profound magnetic anisotropy.<sup>1</sup> This phenomenon emerges when the central metal of a phthalocyaninato (Pc) complex takes the form of either Tb or Dy. At the excited state, observed experimentally with magnetic circular dichroism (MCD) spectroscopy (Figure 2),<sup>2</sup> the complex unveils itself as a captivating system, coupling the orbital angular momentum (L) derived from Pc with the total angular momentum (J) derived from the 4f electrons. In our recent study, it was found that the coupling in the excited state of dysprosium monophthalocyaninato complex can have <u>a different</u> <u>direction and value depending on the initial state of the z-component of  $J(J_z)$ , i.e.,</u> antiferromagnetic for  $J_{z=} \pm 13/2$  and  $J_{z=} \pm 11/2$ , while for  $J_{z=} \pm 15/2$  is ferromagnetic.<sup>3</sup> Based on that, it is possible to change the type of interaction by several methods, such as <u>modifying the coordination environment</u>. This information is a significant finding in <u>developing molecular devices</u> that utilize the single-molecule magnet (SMM) properties.





#### Ln = Tb Yb Tm Dv Ho

Fig 1. The ground multiplet state of  $Pc_2Ln^2$ .

Fig 2. MCD and absorption spectra of Pc<sub>2</sub>Tb<sup>-</sup>

(1) N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, J. Am. Chem. Soc., 2003, 125, 8694-8695. (2) K. Kizaki, H. Ozawa, T. Kobayashi, R. Matsuoka, Y. Sakaguchi, A. Fuyuhiro, T. Fukuda, N. Ishikawa. Chem. Commun., 2017, 53, 6168–6171.

(3) K. Kizaki, A. Santria, N. Ishikawa, Inorg. Chem. Front., 2023, 10, 915–925.

#### 2. Objective

This research aims to comprehensively understand the electronic structure of the ground and excited states in rare-earth-based molecular magnets.

### 3. Method

The initial geometries of  $Pc_2Ln^-$  were obtained from experimental structures. These structures were then modified using the Avogadro program<sup>4</sup> to ensure appropriate bond lengths, angles, orientation, and molecular symmetry. Subsequently, the geometry optimization process was conducted using *Gaussian 16*, revision C.01 at the B3LYP level of theory.<sup>5</sup> The basis set 6-31G(d,p) was used for C, H, N, and O atoms,<sup>6</sup> while Stuttgart RSC 1997 basis sets were employed for metal ion.<sup>7</sup> To obtain electronic structures, spin-orbit states, and oscillator strength of the optimized geometries, the complete active space self-consistent field (CASSCF)/restricted active space state interaction (RASSI)/SingleAniso calculations were performed in OpenMolcas version 22.06.<sup>8</sup>

# 5. Research Progress

(a) Geometry Structure Optimization Program : Gaussian 16; Level : B3LYP Basis set : Stuttgart RSC 1997 (Dy) 6-31G(d,p) (C, H, N)

# (c) The 4f orbitals









(4) M.D. Hanwell, et al., *journal of Cheminformatics*, **2012**, *4*, 1-17. (5) M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, 2019. (6) G. A. Petersson, et al., J. Chem. Phys., 1991, 94, 6081-6090. (7) M. Dolg, et al., J. Chem. Phys., 1989, 90, 1730-1734. (8) (a) I. F. Galvan, et al., J. Chem. Theory Comput., 2019, 15, 5925-5964; (b) P. A. Malmqvist, et al., J. Phys, Chem., 1990, 94, 5477-5482; (c) P. A. Malmqvist, et al., Chem. Phys. Lett., 2002, 357, 230-240.



| Dy-N(average)                | $2.44~{ m \AA}$ | $2.42~{ m \AA}$ |
|------------------------------|-----------------|-----------------|
| Interplanar distance $(d_N)$ | $2.81{ m \AA}$  | $2.80~{ m \AA}$ |
| Skew angle ( $\omega$ )      | 45.00°          | 43.86°          |
| Opening angle (q)            | 109.63°         | 109.41°         |

Calc.

Exp.

(b) Ground Multiplet State of Pc<sub>2</sub>Dy<sup>-</sup> Program : OpenMOLCAS V.20.06 Basis set : ANO-RCC-VTZP (Dy) ANO-RCC-VDZ ( $C_{close}$ ,  $N_{close}$ ) ANO-RCC-MB (C<sub>distant</sub>, N<sub>distant</sub>, H)







Fig 3. The ground and excited doublet spin-orbit states of [DyPc(cyclen)]<sup>+-</sup>.

(1) Find the other SO states associated with the Q bands of  $Pc_2Dy^-$ . (2) Calculate the ground and excited states of other rare-earth-based molecular magnets.

### 7. Acknowledgements

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