EX23703

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.[1] 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),[2] 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 a different direction and value depending on the initial state of the z-component of **J** (J_z), i.e., antiferromagnetic for J_z = ± 13/2 and J_z = ± 11/2, while for J_z = ± 15/2 is ferromagnetic.[3] Based on that, it is possible to change the type of interaction by several methods, such as modifying the coordination environment. This information is a significant finding in developing molecular devices that utilize the single-molecule magnet (SMM) properties.

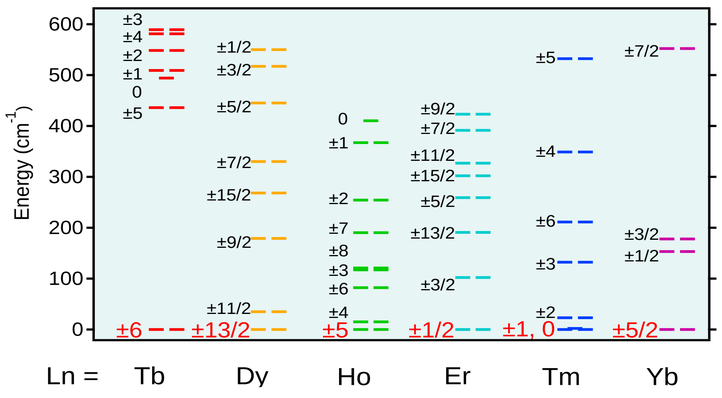


Fig 1. The ground multiplet state of Pc_2Ln^-.

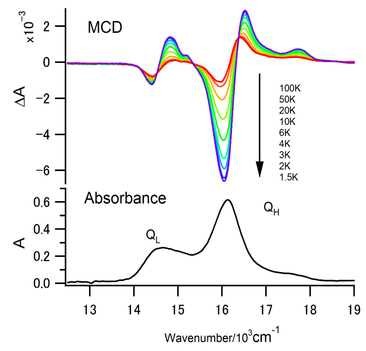


Fig 2. MCD and absorption spectra of Pc_2Tb^-

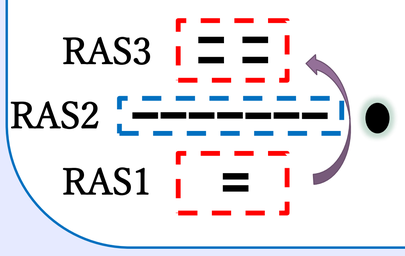
(1) N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.*, **2003**, 125, 8694-8695.
(2) K. Kizaki, H. Ozawa, T. Kobayashi, R. Matsuoka, Y. Sakaguchi, A. Fuyuhiro, T. Fukuda, N. Ishikawa. *Chem. Commun.*, **2017**, *53*, 6168–6171.
(3) K. Kizaki, A. Santria, N. Ishikawa, *Inorg. 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[4] 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.[5] The basis set 6-31G(d,p) was used for C, H, N, and O atoms,[6] while Stuttgart RSC 1997 basis sets were employed for metal ion.[7] 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.[8]



(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.

4. Previous Work

[Dy(Pc)Cyclen]$^+$

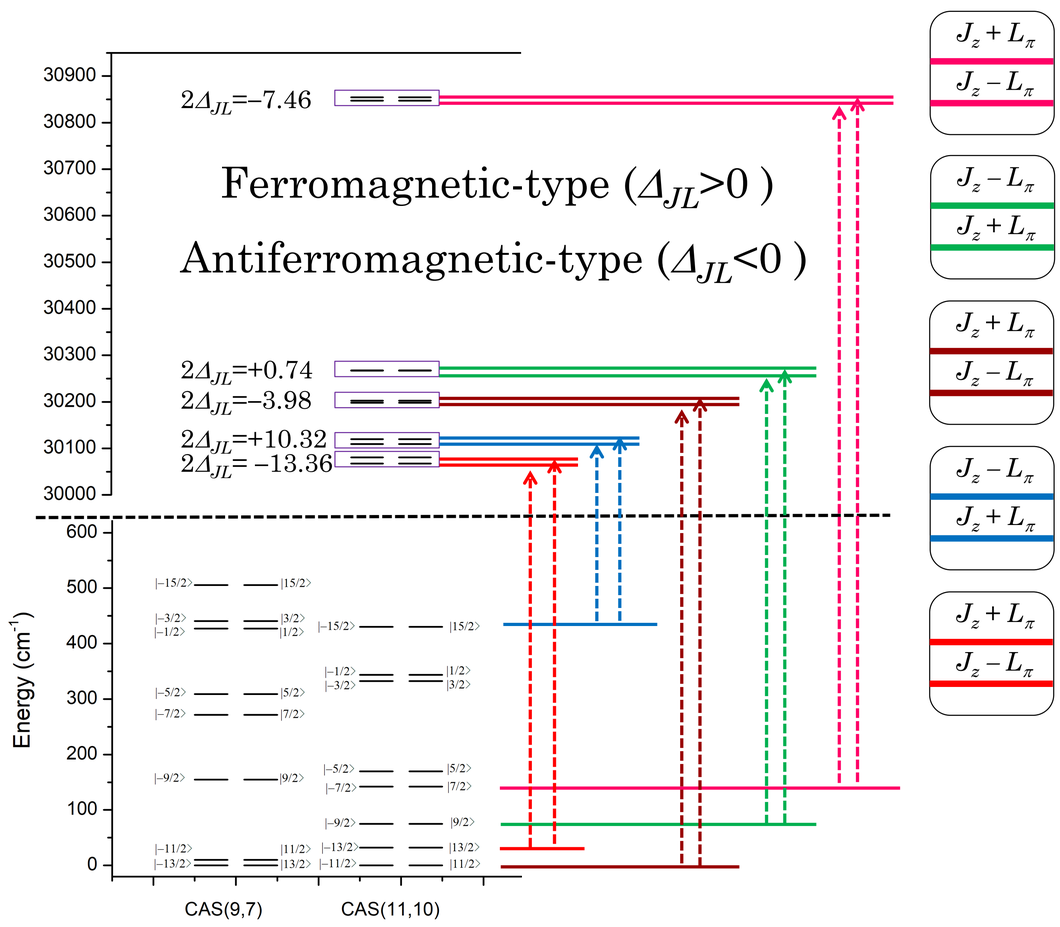
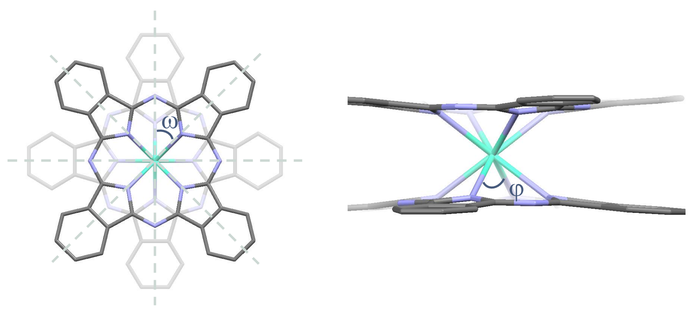


Fig 3. The ground and excited doublet spin-orbit states of $[DyPc(cyclen)]^{+}$.

5. Research Progress

(a) Geometry Structure Optimization

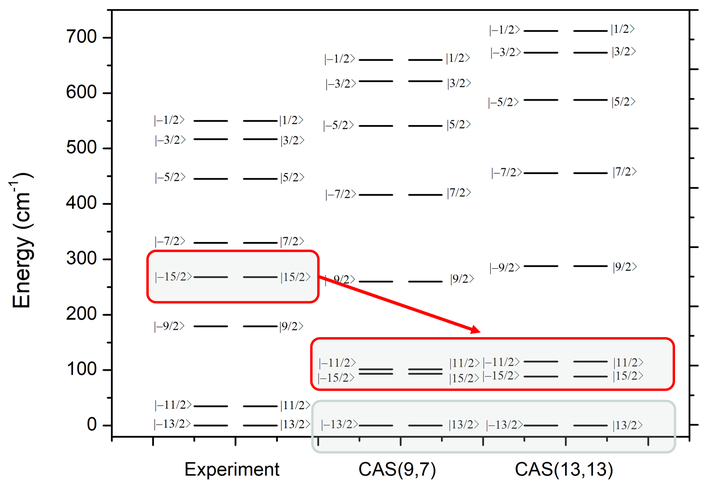
Program : Gaussian 16; Level : B3LYP
Basis set : Stuttgart RSC 1997 (Dy)
6-31G(d,p) (C, H, N)



	Calc.	Exp.[9]
Dy–N(average)	2.44 Å	2.42 Å
Interplanar distance (d_N)	2.81 Å	2.80 Å
Skew angle (ω)	45.00°	43.86°
Opening angle (φ)	109.63°	109.41°

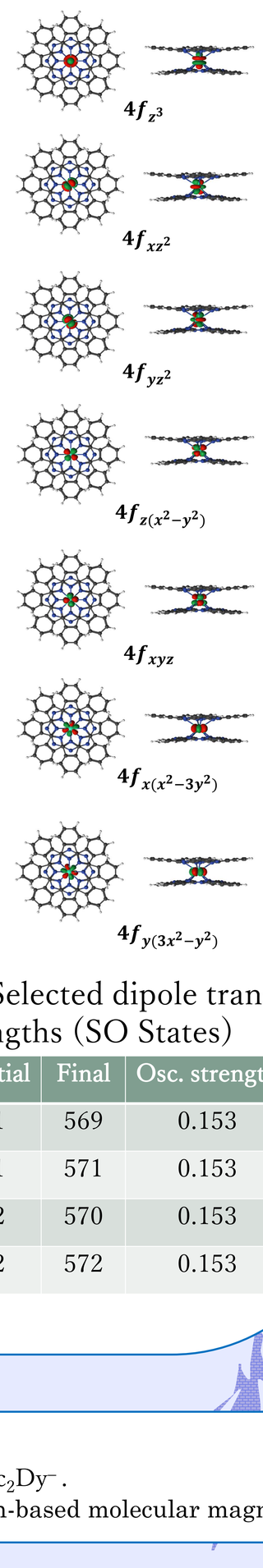
(b) Ground Multiplet State of Pc_2Dy^-

Program : OpenMOLCAS V.20.06
Basis set : ANO-RCC-VTZP (Dy)
ANO-RCC-VDZ (C_{close}, N_{close})
ANO-RCC-MB ($C_{distant}$, $N_{distant}$, H)



(9) R. Marx, et al., *Chem. Sci.*, **2014**, 5, 3287-3293.

(c) The 4f orbitals



(d) Selected dipole transition strengths (SO States)

Initial	Final	Osc. strength
1	569	0.153
1	571	0.153
2	570	0.153
2	572	0.153

6. Future Works

(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

This work is supported by the "Joint Usage/Research Center for Interdisciplinary Large-scale Information Infrastructures (JHPCN)". All calculations have been done using the supercomputer system SQUID at the Cybermedia Center, Osaka University.