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Investigation of Intramolecular Magnetic Interaction in Rare-earth-based Molecular Magnets

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Abstract

This research investigates the intramolecular magnetic interactions in the excited states of rare-earth-based molecular magnets, aiming to develop a novel strategy for controlling the quantum states of these molecular magnets. By examining the magnetic interactions in compounds with highly anisotropic rare-earth elements and photo-excited cyclic π systems, this study highlights potential applications in high-density recording media and quantum sensors. The novel interaction between the localized f electronic system (**J**) and the photo-excited cyclic π system (**L**) represents significant scientific progress, offering a new mechanism to control bistable quantum states through excitation and deexcitation processes. Such control is crucial for advancements in nanomagnet-based technology. Computational tasks were performed using GAUSSIAN for structural optimization and time-dependent property analysis, ORCA for detailed spectroscopic and magnetic property exploration, and OpenMOLCAS for estimating intramolecular interactions and calculating electronic structures in both ground and excited states.

1. Basic Information

(1) Collaborating JHPCN Centers

Tohoku
Osaka

(2) Theme Area

Large scale computational science area

(3) Research Areas

Very large-scale numerical computation

(4) Project Members and Their Roles

- Anas Santria (Osaka University):
Administration and execution
- Naoto Ishikawa (Osaka University):
Result confirmation

2. Purpose and Significance of the Research

This research aims to study the intramolecular magnetic interaction in the excited state of rare-earth-based molecular

magnets and propose a new strategy to control the quantum states of molecular magnets.

Examining the intramolecular magnetic interaction in compounds containing highly anisotropic rare-earth via its magnetic interaction to a photo-excited cyclic π promising future applications in developing high-density recording media and quantum sensors. The strategy to probe the interaction between the localized f electronic system (**J**) and the photo-excited cyclic π system (**L**) gives significant scientific progress since this interaction is a new type of electronic interaction. In addition, the interaction can potentially control the bistable quantum state through the excitation-deexcitation process, which becomes even more significant in the field of nanomagnet-based technology.

3. Significance as JHPCN Joint Research Project

The JHPCN Joint Research Project plays an important role in advancing our study. One of its primary contributions is the provision of high-performance computing resources, data storage, and bandwidth. These resources are critical for enabling the research team to carry out large-scale calculations efficiently and effectively. Access to advanced computational infrastructure not only meets the immediate needs of the study but also accelerates scientific progress and technological innovation within the broader field of molecular magnets.

The importance of this project extends beyond mere computational support. The research holds significant promise for enhancing our understanding of rare-earth-based molecular magnets. These insights could lead to the development of new strategies for quantum state control, a frontier area with vast potential applications in technology and material science. By overcoming the computational challenges inherent in such advanced research, the support from JHPCN becomes a cornerstone for realizing the full potential of these scientific endeavors.

4. Outline of Research Achievements up to FY2022 (Only for continuous projects)

N/A

5. Details of FY2023 Research Achievements

Our project involves computational tasks conducted using three software packages: GAUSSIAN, ORCA, and OpenMOLCAS. GAUSSIAN was employed at the Density-Functional Theory (DFT) level for structural optimization and Time-Dependent Density-Functional Theory (TDDFT) for investigating properties under time-dependent potentials. ORCA was utilized to explore physical and spectroscopic properties beyond GAUSSIAN's capabilities, such as magnetic circular dichroism (MCD), electron spin repulsion (ESR), and magnetic properties. OpenMOLCAS was employed with serial and parallel computing to estimate intramolecular interactions and calculate electronic structures of both ground-state and excited-state configurations.

The elucidation of the ground-state electronic structure within the 4f electronic system is of paramount importance for the study of lanthanide(III) porphyrinato/phthalocyaninato complexes and their magnetic properties. The information derived from this investigation is instrumental in achieving the primary objectives of our research project, particularly considering the energy range of 1-100 cm^{-1} , where degeneracy splitting is influenced by the ligand field. Determining the sublevel structure is a challenging task in both theoretical and experimental studies.

To uncover the sublevel structure (ground-state) of the 4f system, we determined the ligand-field splitting parameters for Pc_2Ln^- (Ln=Gd, Tb, Dy) and $[\text{Ln}(\text{TPP})(\text{L})]^+$ (Ln = Dy; L=crown-ether, aza-crown-ether) complexes using a similar RASSCF method to that applied in $[\text{Ln}(\text{TPP})(\text{cyclen})]^+$ (Ln = Tb, Dy, Ho, Er, Tm, and Yb) complexes. [Dalton Trans., 2019, 48,7685] We selected seven orbitals with n (n=7,8,9) electrons as an active space, designated as RAS2(n, 7), in the C_1 point group with A irreducible representations, including 21 configurations. Within this space, we successfully positioned seven 4f orbitals ($4f_{3+}$, $4f_{2+}$, $4f_{1+}$, $4f_0$, $4f_{1-}$, $4f_{2-}$, $4f_{3-}$) between the highest-occupied π orbital and the lowest-unoccupied π orbital. Subsequently, the calculations were extended to the RASSI and SINGLE_ANISO modules to reveal the ligand-field splitting structure of the $J=7/2$, 6, and $15/2$ multiplets. These calculations generated spin-orbit (SO) states, including the lowest SO states associated with the ground multiplets of $J=15/2$ (Dy), $J=6$ (Tb), and $J=7/2$ (Gd).

Tables 1 and 2 present the obtained sublevel structure of the $J=7/2$ (Gd), $J=6$ (Tb), and $J=15/2$ (Dy) ground states for Pc_2Ln^- (Ln=Gd, Tb, Dy) and $[\text{Ln}(\text{TPP})(\text{L})]^+$ (Ln = Dy; L=crown-ether (12C4), aza-crown-ether(aza12C4)) complexes, using the ANO-RCC basis set. Notably, the doublets with $J_z = \pm 6$, $J_z = \pm 13/2$, $J_z = \pm 11/2$, and $J_z = \pm 15/2$ are the lowest states for Pc_2Tb^- , Pc_2Dy^- , DyTPP12C4^+ , DyTPPazaCrown^+ , respectively, indicating a large axial magnetic anisotropy with an easy axis perpendicular to the ligand plane. For

Pc_2Gd^- , the lowest J_z remains uncertain due to minimal energy splitting (less than 2 cm^{-1}). In the case of DyTPPaza12C4^+ , the two lowest doublets are energetically close, suggesting that slight changes in coordination or computational conditions can influence the lowest doublet. [Dalton Trans., 2024, 53, 628]

Table 1. Energy level of the Pc_2Ln^- (Ln=Gd, Tb, Dy) complexes from CAS(n,7)/RASSI/Single_Aniso calculations.

Pc_2Gd^-		Pc_2Tb^-		Pc_2Dy^-	
Energy (cm ⁻¹)	States	Energy (cm ⁻¹)	States	Energy (cm ⁻¹)	States
0.00	$ \pm 7/2\rangle$	0.00	$ \pm 6\rangle$	0.00	$ \pm 13/2\rangle$
0.81	$ \pm 5/2\rangle$	328	$ \pm 5\rangle$	93	$ \pm 15/2\rangle$
1.35	$ \pm 3/2\rangle$	561	$ \pm 4\rangle$	101	$ \pm 11/2\rangle$
1.61	$ \pm 1/2\rangle$	688	$ \pm 3\rangle$	260	$ \pm 9/2\rangle$
		742	$ \pm 2\rangle$	416	$ \pm 7/2\rangle$
		762	$ \pm 1\rangle$	541	$ \pm 5/2\rangle$
		767	$ 0\rangle$	621	$ \pm 3/2\rangle$
				660	$ \pm 1/2\rangle$

Table 2. Energy level of the $[\text{Dy}(\text{TPP})(\text{L})]^+$ (L=12C4, aza12C4) complexes from CAS(9,7)/RASSI/Single_Aniso calculations.

$[\text{Dy}(\text{TPP})(12\text{C4})]^+$		$[\text{Ln}(\text{TPP})(\text{aza}12\text{C4})]^+$	
Energy (cm ⁻¹)	States	Energy (cm ⁻¹)	States
0.00	$ \pm 11/2\rangle$	0.00	$ \pm 15/2\rangle$
2.56	$ \pm 13/2\rangle$	32.09	$ \pm 13/2\rangle$
105.69	$ \pm 9/2\rangle$	71.21	$ \pm 5/2\rangle$
188.94	$ \pm 7/2\rangle$	103.39	$ \pm 11/2\rangle$ $ \pm 3/2\rangle$
202.31	$ \pm 5/2\rangle$	115.66	$ \pm 1/2\rangle$
324.88	$ \pm 1/2\rangle$	229.91	$ \pm 9/2\rangle$ $ \pm 11/2\rangle$
333.57	$ \pm 3/2\rangle$	251.70	$ \pm 5/2\rangle$ $ \pm 3/2\rangle$
388.78	$ \pm 15/2\rangle$	261.65	$ \pm 7/2\rangle$

For excited state calculations, we included several highest-occupied π orbitals and lowest-unoccupied π orbitals as RAS1 and RAS3, respectively, to the RASSCF calculations. The number of configurational interaction (CI) roots used in these calculations was 49, 195, and 780 for Pc_2Gd^- , Pc_2Tb^- , and Pc_2Gd^- , respectively. With this number of CIs, hundreds to thousands of spin-orbit SO states were obtained. Among the hundred or thousand states, the lowest SO doublets are correspond to the $J = 7/2$, $J = 6$, $J = 15/2$ ground multiplets of Gd^{3+} , Tb^{3+} , Dy^{3+} , as listed in Tables 3 and 4. For the $[\text{Dy}(\text{TPP})(\text{L})]^+$ complexes, SO doublets related to π - π^* transitions are roughly $31,000 \text{ cm}^{-1}$ above the ground SO doublets, as listed in Table 3, while for Pc_2Ln^- are about $36,000 \text{ cm}^{-1}$ separated from the lowest states, as listed in Table 4. (Note: the introduction of RAS1 and RAS3 active spaces could potentially lead to different splitting pattern in the ground multiplet, especially for the lowest two doublets of DyTPP12C4^+ . In this case, $|\pm 11/2\rangle$ can be the second lowest state, and $|\pm 13/2\rangle$ can be the lowest state, which contrasts with the ground-state calculation results in Table 2). These calculations provide further evidence supporting the existence of **J-L** interaction between the orbital angular momentum generated by the π system of the ligand and the total angular momentum of these complexes. The results show that the J_Z values vary by approximately $L_Z(\pi)$ due to the changes in L_Z from π - π^* electronic transitions. This results in pairs of doublets with opposite changes in J_Z , indicating different type of **J-L** interactions. For dysprosium complexes, in the lower energy

doublet, the angular momentum decreases by $L_Z(\pi)$ while in the higher energy doublet, it increases by $L_Z(\pi)$, demonstrating an antiferromagnetic-type interaction where the antiparallel arrangement is more stable than the parallel. In contrast, for the gadolinium and terbium complexes, in the lower energy doublet, the angular momentum increase by $L_Z(\pi)$, while in the higher energy doublet, it decreases by $L_Z(\pi)$, demonstrating a ferromagnetic-type interaction where the parallel arrangement is more stable than the antiparallel.

Table 3. Energy level of the $[\text{Dy}(\text{TPP})(\text{L})]^+$ ($\text{L}=\text{12C4}$, aza12C4) complexes from CAS(13,11)/RASSI/Single_Aniso calculations.

$[\text{Dy}(\text{TPP})(\text{12C4})]^+$		$[\text{Ln}(\text{TPP})(\text{aza12C4})]^+$	
Energy (cm^{-1})	States	Energy (cm^{-1})	States
0.00	$ \pm 11/2\rangle$	0.00	$ \pm 15/2\rangle$
17.39	$ \pm 9/2\rangle$	35.25	$ \pm 13/2\rangle$
47.14	$ \pm 13/2\rangle$	77.09	$ \pm 5/2\rangle$
65.89	$ \pm 7/2\rangle$	115.08	$ \pm 11/2\rangle$
78.95	$ \pm 13/2\rangle$	130.90	$ \pm 1/2\rangle$
203.96	$ \pm 3/2\rangle$	248.27	$ \pm 9/2\rangle$
217.61	$ \pm 1/2\rangle$	272.91	$ \pm 5/2\rangle$ $ \pm 3/2\rangle$
340.16	$ \pm 15/2\rangle$	287.48	$ \pm 7/2\rangle$
31170	$J_Z - L_Z(\pi)$	31568	$J_Z - L_Z(\pi)$
31781	$J_Z + L_Z(\pi)$	31723	$J_Z + L_Z(\pi)$

Table 4. Energy level of the Pc_2Ln^- ($\text{Ln}=\text{Gd}$, Tb , Dy) complexes from CAS((n+4),13)/RASSI/ Single_Aniso calculations.

Pc_2Gd^-		Pc_2Tb^-		Pc_2Dy^-	
Energy (cm^{-1})	States	Energy (cm^{-1})	States	Energy (cm^{-1})	States
0.00	$ \pm 7/2\rangle$	0.00	$ \pm 6\rangle$	0.00	$ \pm 13/2\rangle$
1.14	$ \pm 5/2\rangle$	336	$ \pm 5\rangle$	94	$ \pm 15/2\rangle$
1.89	$ \pm 3/2\rangle$	578	$ \pm 4\rangle$	97	$ \pm 11/2\rangle$
2.27	$ \pm 1/2\rangle$	710	$ \pm 3\rangle$	250	$ \pm 9/2\rangle$
		767	$ \pm 2\rangle$	405	$ \pm 7/2\rangle$
		789	$ \pm 1\rangle$	534	$ \pm 5/2\rangle$
		794	$ 0\rangle$	620	$ \pm 3/2\rangle$
				661	$ \pm 1/2\rangle$
37653.0	$7/2+Lz(\pi)$	36671	$6+Lz(\pi)$	36792	$13/2-Lz(\pi)$
37653.4	$7/2-Lz(\pi)$	36679.2	$6-Lz(\pi)$	36797	$13/2+Lz(\pi)$
37653.1	$5/2+Lz(\pi)$	37006.9	$5+Lz(\pi)$	36863	$15/2-Lz(\pi)$
37653.3	$5/2-Lz(\pi)$	37013.5	$5-Lz(\pi)$	36873	$15/2+Lz(\pi)$
37653.1	$3/2+Lz(\pi)$	37250.6	$4+Lz(\pi)$	36909	$11/2-Lz(\pi)$
37653.2	$3/2-Lz(\pi)$	37253.5	$4-Lz(\pi)$	36913	$11/2+Lz(\pi)$
37653.1	$1/2+Lz(\pi)$	37382.7	$3+Lz(\pi)$	37084	$9/2-Lz(\pi)$
37653.2	$1/2-Lz(\pi)$	37385.1	$3-Lz(\pi)$	37089	$9/2+Lz(\pi)$
		37387.1			
		37432.9	$2+Lz(\pi)$	37255	$7/2-Lz(\pi)$
		37444.9	$2-Lz(\pi)$	37260	$7/2+Lz(\pi)$
				37385	$5/2-Lz(\pi)$
				37387	$5/2+Lz(\pi)$
				37463	$3/2-Lz(\pi)$
				37468	$3/2+Lz(\pi)$
				37504	$1/2-Lz(\pi)$
				37510	$1/2+Lz(\pi)$

6. Details of FY2023 Research Achievements

Our calculations provide compelling evidence for **J-L** interactions between the π system of the ligand and the total angular momentum of the complexes. Specifically,

we observed that J_z values fluctuate with $Lz(\pi)$ changes due to $\pi-\pi^*$ transitions, leading to pairs of doublets with opposite J_z changes. This indicates different types of **J-L** interactions: an antiferromagnetic-type interaction in dysprosium complexes, where the lower energy doublet's angular momentum decreases by $Lz(\pi)$ and the higher energy doublet's angular momentum increases by $Lz(\pi)$; and a ferromagnetic-type interaction in gadolinium and terbium complexes, where the opposite pattern is observed.

Building on our current progress, future research will focus on several areas to further advance our understanding of **J-L** interaction:

Expanded Active Spaces: Further explore the impact of different active space configurations on the splitting patterns of ground multiplets. This can refine our understanding of the electronic structures and interactions in various complexes.

Detailed Mechanistic Studies: Conduct in-depth analyses of the mechanisms behind the observed **J-L** interactions. Understanding these interactions at a fundamental level could open new avenues for designing materials with specific magnetic properties.

Experimental Validation: Collaborate with experimentalists to validate our computational predictions through spectroscopic and magnetic measurements. This will help to confirm the theoretical models and potentially uncover new phenomena.

Broader Range of Complexes: Extend the calculations to a broader range of rare-earth-based complexes and ligands to

generalize the findings. This can help in discovering novel complexes with desirable electronic and magnetic properties.

Technological Applications: Investigate the potential technological applications of these findings, particularly in areas such as quantum computing, magnetic resonance imaging (MRI) contrast agents, and molecular magnets. *Improved Computational Techniques:* Continuously refine computational techniques and methodologies to enhance accuracy and efficiency. This includes leveraging advances in hardware and software to tackle more complex systems.

By addressing these future prospects, we aim to advance the field of rare-earth chemistry and contribute to the development of new materials with tailored properties for various scientific and industrial applications.

7. List of Publications and Presentations

(1) Journal Papers (Refereed)

[1] L.C. Adi, A. Santria, N. Ishikawa, Tuning of the Antiferromagnetic-type Interaction in Photo-Excited Single-Decker Porphyrin-Lanthanide Complexes with Different Crown Capping Ligands, *Dalton Trans.*, Vol. 53, pp. 628-639, Nov. 2023. [Journal Q1]

[2] A. Santria, N. Ishikawa, Identification of a small interaction between the spin-only 4f-electronic system of trivalent Gd ion and a photo-excited cyclic π electronic system. [*under review Inorg. Chem.*]

(2) Proceedings of International Conference Papers (Refereed)
N/A

(3) Presentations at International conference (non-refereed)
[1] Anas Santria, Naoto Ishikawa, "Exploring the J-L Interaction in Dysprosium-Phthalocyaninato Complexes: Insights from Ab Initio CASSCF Calculations", The 9th International Symposium on Applied Chemistry (ISAC), pp. 41, Dec. 2023.

(4) Presentations at domestic conference (non-refereed)
[1] S. Hamano, A. Santria, N. Ishikawa, Magnetic Circular Dichroism Temperature Dependence of Porphyrin-Cerium Sandwich Complexes for the purpose of Study of 5f- π interaction. The 17th Annual Meeting of Japan Society for Molecular Science 2023, Osaka, September 12-15, 2023.

[2] A. Santria, N. Ishikawa, Exploring Weak Electronic Interaction in the π - π^* Excited State of Gadolinium(III) Monoporphyrinato Complex using Magnetic Circular Dichroism Spectroscopy. The 73rd Conference of Japan Society of Coordination Chemistry, Ibaraki, September 21-23, 2023.

(5) Published open software library and so on.
N/A

(6) Other (patents, press releases, books and so on)
N/A