

Ab Initio Study of Intramolecular Magnetic Interaction in Photoexcited Rare-earth-based Macrocyclic Complexes

Anas Santria

Graduate School of Science, Osaka University

1. Introduction

Rare-earth-based complexes with delocalized electrons in macrocyclic ligands have significant importance in various fields of research. Their magnetic, optical, and electronic properties have been studied intensively to fulfill the high demand for ultrahigh-density data storage, magnetic sensor, and quantum computing applications. Despite numerous studies, an essential innovation is still needed to control their quantum states. So far, two methods have been used to control their quantum states: a magnetic field and an electric current. The magnetic field is not suitable for controlling a few molecules because the other molecules in large areas can be affected. Another technique, using an electric current, is a technique that is often used. This effort is through the use of scanning tunneling microscopy (STM) probes onto those that have previously deposited on metallic substrates such as gold (Au), lead (Pb), and other conductances. Unfortunately, this effort is limited to the cases where STM is involved.

A new type of electronic interaction was observed in the excited state of the molecular compounds having large magnetic anisotropies, bisphthalocyaninato lanthanide(III) complexes, Pc_2Ln^- [1]. In these compounds, the interaction occurs between the total angular momentum (\mathbf{J}) of the lanthanide ion and the orbital angular momentum (\mathbf{L}) of cyclic π system (phthalocyaninato), as shown in Figure 1. It was found that the interaction, referred to as “ \mathbf{J} – \mathbf{L} interaction”, can be in a ferromagnetic-type or an

antiferromagnetic-type manner. Since the interaction can change the energy ordering of the sublevel structure in the ground state via photogeneration of \mathbf{L} , the quantum state of molecular magnets is expected can be controlled by this interaction through the excitation–deexcitation process.

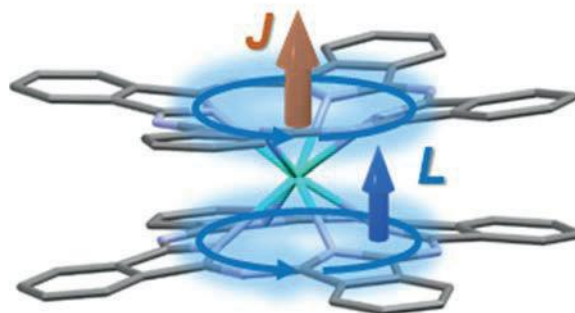


Figure 1 : \mathbf{J} – \mathbf{L} interaction in Pc_2Ln^-

This paper uses a computational chemistry approach to report how the \mathbf{J} – \mathbf{L} interaction occurs in various rare-earth-based macrocyclic complexes. Two questions are set as follows. First, how to determine the \mathbf{J} – \mathbf{L} interaction in lanthanide complexes with porphyrin as aromatic ligand? Second, does changing rare-earth-metal ion has any effect on the \mathbf{J} – \mathbf{L} interaction? To answer these questions, we chose several lanthanide ions such as Tb, Dy, Ho, Er, Tm, Yb ions as the metal center and a non-aromatic macrocyclic cyclen compound as the second ligand.

2. Computational Methods

The initial geometries of $[\text{Ln}(\text{TPP})(\text{cyclen})]^+$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{and Yb}$; $\text{TPP} = 5,10,15,20$ -

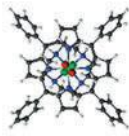
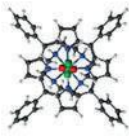
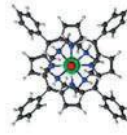
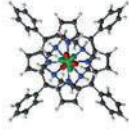
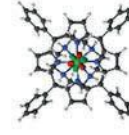
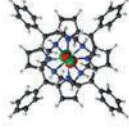
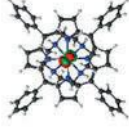

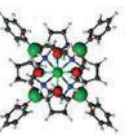
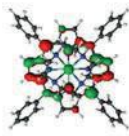
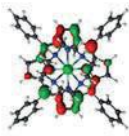
tetraphenylporphyrinato; cyclen = 1,4,7,10-tetraazadodecane) were obtained from experimental structures [2]. These structures were then modified using the Avogadro program [3] to ensure appropriate bond lengths, angles, orientation, and molecular symmetry. Subsequently, geometry optimization process was conducted using *Gaussian 16*, revision C.01 [4] at the B3LYP level of theory. The basis set 6-31G(d,p) was used for C, H, N, and O atoms [5], while Stuttgart RSC 1997 basis sets were employed for metal ion [6]. 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 [7].

3. Results and Discussion

3.1 Ground-States

The ground-state electronic structure of $[\text{Ln}(\text{TPP})(\text{cyclen})]^+$ complexes was determined using self-consistent field (SCF) calculations followed by the CASSCF method. In CASSCF calculations, the seven 4f orbitals with varying electron occupancy, specifically n ($n = 8(\text{Tb}), 9(\text{Dy}), 10(\text{Ho}), 11(\text{Er}), 12(\text{Tm}), 13(\text{Yb})$) electrons were successfully placed in between the typical occupied π and two degenerate unoccupied π^* orbitals of porphyrin. Because the molecule structures were designated to have C_2 symmetry, those 4f orbitals are distributed into irreducible representations (irrep) A and B, i.e., irrep A for $4f_{2+}$, $4f_{2-}$, and $4f_0$ orbitals, while irrep B for $4f_{3+}$, $4f_{3-}$, $4f_{1+}$, and $4f_{1-}$ orbitals, as shown in Table 1. Furthermore, the typical highest occupied molecular orbital (HOMO) of the porphyrin was found to belong to irrep A, while the lowest unoccupied molecular orbital (LUMO) belonged to irrep B.

Table 1. Molecular orbitals of $[\text{Ln}(\text{TPP})(\text{cyclen})]^+$ under C_2 symmetry viewed along z-axis.

Lanthanide		
Irrep A		
		
Irrep B		
		
Porphyrin		
Irrep A		
Irrep B		

To obtain the multilevel ground-state electronic structures of six lanthanide ions in $[\text{Ln}(\text{TPP})(\text{cyclen})]^+$, further calculations such as RASSI and Single Aniso were then carried out. For each lanthanide complex, a total of $2J+1$ substates were obtained, where J is the total angular momentum. Specifically, there are 13 substates for Tb, 16 substates for Dy, 17 substates for

Ho, 16 substates for Er, 13 substates for Tm, and 8 substates for Yb. These substates arise from the $J = 6$ (Tb), $J=15/2$ (Dy), $J=8$ (Ho), $J=15/2$ (Er), $J=6$ (Tm), and $J=7/2$ (Yb), as shown in Figure 2.

In addition to determining the number of substates, the composition of wave functions for each substates was also determined. In the cases of Tb, Ho, and Tm, the lowest substates were found to be composed of a mixture of $+J_z$ and $-J_z$ (J_z represents the z component of J). Sequentially, the lowest substate for Tb, Ho, and Tm is mainly composed of $|\pm 6\rangle$, $|\pm 4\rangle$, and $|\pm 6\rangle$. For Tb, the second lowest substate is separated by a very small energy gap (less than 1 cm^{-1}) from the lowest substate, whereas for Ho and Tm, there is a significant energy gap between the two lowest substates. On the other hand, Dy, Er, and Yb complexes exhibit doubly degenerate $+J_z$ and $-J_z$ substates. The lowest substates for these lanthanide complexes are $| -11/2 \rangle$ and $| +11/2 \rangle$ for Dy, $| -1/2 \rangle$ and $| +1/2 \rangle$ for Er, and $| -5/2 \rangle$ and $| +5/2 \rangle$ for Yb. These findings are consistent with previous experimental report [8], validating the accuracy of the computational approach. In this stage, the primary objective is to provide information regarding the wavefunctions pertaining to the the lowest substates of the ground state. This crucial information serves as the fundamental basis for determining the **J-L** interaction.

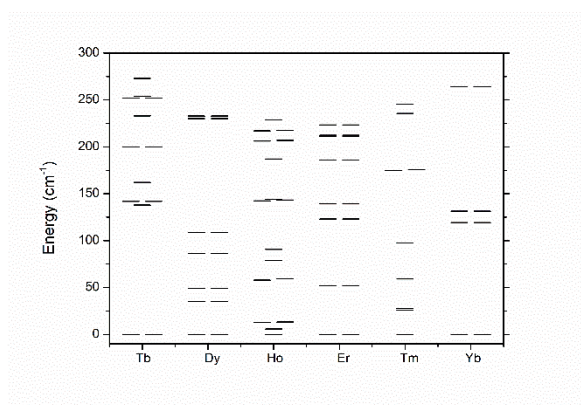


Figure 2 : Multilevel ground-state structure of $[\text{Ln}(\text{TPP})(\text{cyclen})]^+$.

3.2 Excited-states

Using the results from the ground-state calculations as an initial guess, the CASSCF calculations for the excited states were carried out. Two highest-occupied π orbitals (HOMOs) and two lowest-unoccupied π orbitals (LUMOs) were added to the active space so that the total electrons and orbitals become $n+4$ and 11, respectively. In addition, RASSI and Single Aniso modules with the specific keyword for generating spin-orbit (SO) states, dipole transition strengths, and other physical properties were then executed.

For $[\text{Tb}(\text{TPP})(\text{cyclen})]^+$, with a spin multiplicity of 7 and 119 CIROOTs, a total of 833 SO states were generated. Among these states, two excited doublets associated with the Q-band were identified, as depicted in Figure 3. The lower- and higher excited doublet SO states are separated by $26,929 \text{ cm}^{-1}$ and $26,938 \text{ cm}^{-1}$ from the lowest ground state, respectively. At the lowest ground state, the L_z is equal to 2.94 and S_z is 2.96. These values indicate that J_z is equal to 5.9, consistent with the ground-state calculation. Notably, the sum of L_z and S_z for the excited doublet SO states deviates from that of the ground state, i.e., 10.21 and 1.72 for the lower- and higher-excited doublet SO states, respectively. These deviations correspond to the orbital angular value of the porphyrin system (L_π) at the Q-band, as previously reported [9]. At the lower excited doublet SO state, L_π demonstrates positive sign, while at the higher excited doublet SO state, it exhibits a negative sign. Since L_π has the same sign as J_z at the lower excited doublet SO states (more stable), the interaction is interpreted as a ferromagnetic-type manner (see Figure 3). For the magnitude of the interaction, represented as Δ_{JL} , can be determined by calculating half of the energy between the lower- and higher-excited doublet SO states. In this case, Δ_{JL} was obtained to be approximately 4.5 cm^{-1} .

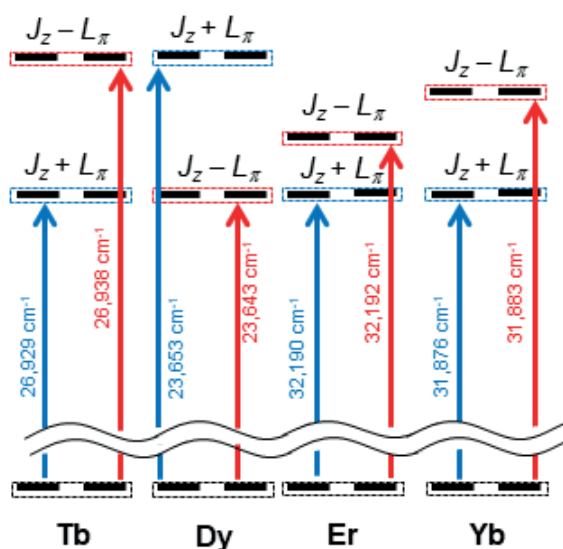


Figure 3 : Schematic energy diagram of the spin-orbit states associated with the Q-band of $[\text{Ln}(\text{TPP})(\text{cyclen})]^+$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Er}$ and Yb).

In the case of $[\text{Dy}(\text{TPP})(\text{cyclen})]^+$ complex, a combination of spin multiplicity 6 and 189 CIROOTs results 1134 SO states. Among these states, the lowest doublet SO state exhibits $L_z = 3.43$ and $S_z = 1.75$, which yields $J_z = 5.18$, consistent with the values obtained in the ground state calculation. For the excited doublet SO states associated with the Q-band, the sum of L_z and S_z amounts to 1.28 for the lower excited doublet state and 9.38 for the higher excited doublet states. This indicates that the L_π has the opposite sign to J_z at the lower energy state, as shown in Figure 3. Consequently, in this complex, the coupling between \mathbf{J} and \mathbf{L} in of an antiferromagnetic-type nature. Furthermore, the lower- and higher excited doublet states are separated by $23,643 \text{ cm}^{-1}$ and $23,653 \text{ cm}^{-1}$ respectively, from the lowest SO state. As a result, Δ_{JL} was is estimated to be approximately 5.0 cm^{-1} .

A total of 1260 SO states were obtained for $[\text{Er}(\text{TPP})(\text{cyclen})]^+$ by combining a spin multiplicity of 4 with 315 CIROOTs. The lowest doublet SO state exhibits $L_z = 0.38$ and $S_z = 0.11$. The doublet states

associated with the Q-band are separated by $32,190 \text{ cm}^{-1}$ and $32,192 \text{ cm}^{-1}$, respectively, from the lowest doublet state. At the lower doublet excited SO state, the sum of L_z and S_z is only 0.11 larger than that of the ground-state (0.49). The difference, which was previously expected to be attributed to L_π , is significantly smaller compare to the cases of $[\text{Tb}(\text{TPP})(\text{cyclen})]^+$ and $[\text{Dy}(\text{TPP})(\text{cyclen})]^+$. Additionally, the Δ_{JL} value obtained is very small, approximately 1.0 cm^{-1} . Interestingly, this small difference was observed in a compound with a small J_z . Therefore, the small J_z may contribute to the small value of L_π that interact with J_z in the $[\text{Er}(\text{TPP})(\text{cyclen})]^+$. To further investigate this observation, it is necessary to perform calculation on $[\text{Yb}(\text{TPP})(\text{cyclen})]^+$ based on its electronic ground state. $[\text{Yb}(\text{TPP})(\text{cyclen})]^+$ possesses a primary $J_z = |\pm 5/2|$ at the lowest ground state, which lies between the lowest J_z values of $[\text{Dy}(\text{TPP})(\text{cyclen})]^+$ ($|\pm 11/2|$) and $[\text{Er}(\text{TPP})(\text{cyclen})]^+$ ($|\pm 1/2|$).

The calculation on $[\text{Yb}(\text{TPP})(\text{cyclen})]^+$ was performed using the same methodology as the other lanthanine(III) complexes. Setting the spin multiplicity to 2 with 119 CIROOTs resulted in 238 SO states. The analysis focused on the lowest doublet ground state and two doublet excited SO states associated with Q-band. At the lowest doublet ground SO state, the value of J_z was determined to be approximately 1.61, obtained from the sum of $L_z = 1.37$ and $S_z = 0.24$. The L_z value was then found to undergo changes at the two doublet excited SO states (lower doublet excited SO state = $31,876 \text{ cm}^{-1}$, higher doublet excited SO state = $31,883 \text{ cm}^{-1}$). The L_z is increased by approximately 3.9 at the lower excited SO states, while it reduced by approximately 4.18 at the higher excited SO state (Note: The S_z sign in the doublet excited SO states is kept positive as well as that in the lowest ground SO state). As discussed previously, the changes in L_z are attributed to the

presence of L_π . In this case, it was found that L_π aligns in a similar direction as J_z at the lowest doublet, as shown in Figure 3. This indicates a ferromagnetic-type interaction between J_z and L_π . Additionally, Δ_{JL} was determined to be approximately 3.5 cm^{-1} . These findings further support the previous hypothesis that L_π and Δ_{JL} are closely related to the size of J_z .

Efforts have been made to determine the **J-L** interaction in $[\text{Ho}(\text{TPP})(\text{cyclen})]^+$ and $[\text{Tm}(\text{TPP})(\text{cyclen})]^+$ using various spin multiplicity and numbers of CIROOT in the calculations. However, despite successfully exciting electrons from π orbitals to π^* orbitals, the identification of SO states associated with the π - π^* transition remains challenging. This difficulty arises because degenerate doublet excited SO states were not found in these complexes. Additionally, as depicted in Figure 2, the two lowest substates of the ground state do not exhibit degeneracy, leading to a lack of degeneracy in the excited states related to these substates as well. To overcome these challenges, a different computational approach or analysis method is required. Further investigations and refinements are needed to accurately determine the **J-L** interaction and understand the properties of the excited states in $[\text{Ho}(\text{TPP})(\text{cyclen})]^+$ and $[\text{Tm}(\text{TPP})(\text{cyclen})]^+$.

5. Conclusion

Through *ab initio* calculations, the interaction between **J** and **L**, referred to as “**J-L** interaction”, has been determined in $[\text{Ln}(\text{TPP})(\text{cyclen})]^+$. This interaction can manifest in two ways: ferromagnetic-type and antiferromagnetic-type interaction. Thus far, the ferromagnetic-type interaction has been observed in $[\text{Tb}(\text{TPP})(\text{cyclen})]^+$, $[\text{Er}(\text{TPP})(\text{cyclen})]^+$, and $[\text{Yb}(\text{TPP})(\text{cyclen})]^+$, while the antiferromagnetic-type interaction has been observed in $[\text{Dy}(\text{TPP})(\text{cyclen})]^+$. The magnitude of this interaction is obtained by calculating the half-energy separation between the two doublet excited spin-orbit states. It is important to note

that the magnitude of the J_z of the lanthanide ion can influence the strength of this interaction.

Acknowledgements

All calculations have been done using supercomputer system SQUID at the Cybermedia Center, Osaka University.

References

- (1) K. Kizaki, et al., *Chem. Commun.*, **53**, 6168-6171, (2017); T. Fukuda, et al., *Chem. Eur. J.*, **23**, 16357-16363, (2017).
- (2) A. Santria, et al., *Inorg. Chem.*, **56**, 10625-10632 (2017).
- (3) Avogadro: an open-source molecular builder and visualization tool. Version 1.1.1 ; M.D. Hanwell, et al., *Journal of Cheminformatics*, **4**, 1-17 (2012)
- (4) M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, 2019.
- (5) G. A. Petersson, et al., *J. Chem. Phys.*, **94**, 6081-6090, (1991).
- (6) M. Dolg, et al., *J. Chem. Phys.*, **90**, 1730-1734, (1989).
- (7) I. F. Galvan, et al., *J. Chem. Theory Comput.*, **15**, 5925-5964, (2019); P. A. Malmqvist, et al., *J. Phys. Chem.*, **94**, 5477-5482, (1990); P. A. Malmqvist, et al., *Chem. Phys. Lett.*, **357**, 230-240, (2002).
- (8) A. Santria, et al., *Dalton Trans.*, **48**, 7685-7692 (2019)
- (9) A. Santria, et al., *Inorg. Chem.*, **59**, 14326-14336 (2020).