Abstract of Thesis

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Title	Interaction between Highly-Anisotropic 4f System and Photo-Excited Cyclic π –systems in Lanthanide-Porphyrin Complexes with Varied Non-Aromatic Ligands (さまざまな非芳香族配位子を持つランタニド-ポルフィリン錯体における高異方性4f電子系と光励起環状π電子系間の相互作用)

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It has been long known that 18π electrons-tetrapyroles compounds such as phtalocyanine and porphyrin acquire angular momentum denoted as **L** in excited states due to the π–π* electronic transition. When they form coordination compounds with trivalent lanthanides (Ln), there expected to be an electronic interaction between **L** and the total angular quantum number (denoted as **J**) of Ln. Such interaction, symbolized as Δ_{JL}, has been investigated using variable-temperature variable-magnetic field (VT-VH) magnetic circular dichroism (MCD) by our groups as the first research group who did the investigation[1-5]. The value of Δ_{JL} were found to be determined by performing least-square fitting of the simulated $\mathcal{A}_1/\mathcal{D}_0$ ratios to the experimental ratios in which $\mathcal{A}_1$ corresponds to the A-term signal of MCD and $\mathcal{D}_0$ is associated with the oscillator strength.

The first studies were done for phthalocyanine complexes with Ln being Tb and Dy in Ln-phthalocyanine homoleptic double-decker $[Ln(Pc)_2]^-$, it was found that the interaction in the Tb case was ferromagnetic while that of the Dy complex showed both ferromagnetic and antiferromagnetic interaction[1,2]. When one Pc was replaced with 1,4,7,10-tetraazacyclododecane (cyclen) as a non-aromatic ligand yielding heteroleptic [Tb(Pc)Cyclen]Cl, two bands in visible wavelength as the lowest π–π* band showed the ferromagnetic-type interaction in the Tb complex[3] while antiferromagnetic in Dy case.

The investigation of Δ_{JL} was also performed for porphyrin cases specifically tetraphenylporphyrinato (TPP) complexes with Tb and Dy, namely [Ln(TPP)Cyclen]Cl previously[4,5]. Contrast to Pc ligand, three bands were observed called Q(0,0) and Q(1,0) bands located in the range of visible wavelength (500-600 nm) and B(0,0) band which is detected on higher energy around 400 nm. These bands have different spectral characters: B band is sharp and intense while Q bands have relatively lower intensity. B band has total angular momentum $\Delta_L = \pm 1$ and Q bands have $\Delta_L = \pm 9$. All of those bands generated three A-term spectral shape in MCD spectra, where different **L** and Δ_{JL} were determined and calculated. From those reports, it was concluded that the interaction was antiferromagnetic in the Dy complex while in the Tb complex, the electronic interaction was antiferromagnetic in B(0,0) band and ferromagnetic in Q(0,0) and Q(1,0) bands.

In this doctorate research, the question to be answered was set as follows: *Is there any impact from the second ligands toward the* L_z *value and also the* Δ_{JL} *in Ln-TPP in B band and in Q bands?* From that question, there are some aspects to be examined. First, does variation of electronegativity of the tetradentate site (in the second ligand with similar symmetry) alter the Δ_{JL} in the complexes? Second, to what extend does L_z depend on the symmetry as well as different atoms of the second ligand? Third, do B and Q bands of porphyrin have same tendency to perturbation by different non-aromatic ligands in heteroleptic complexes?

All of those questions are explored by changing cyclen with three different ligands: 1,4,7,10-tetraoxacyclododecane or 12-crown-4 ether, 1-aza-4,7,10-trioxacyclododecane or 1-aza-12-crown-4 ether, and 2,2′-Ethylenebis(nitrilomethylidene)diphenol, *N*,*N*′-Ethylenebis(salicylimine) or salen. 12-crown-4 ether and 1-aza-12-crown-4 ether are two ligands having cyclododecane structure, similar to

cyclen. This is to investigate the effect from cyclododecanes ligands with different atoms in the tetradentate binding pocket. In 12-crown-4 ether the symmetry is analogous to cyclen while in 1-aza-12-crown-4 ether, the symmetry is slightly reduced with an amine replacing one oxygen. The symmetry is further lowered when cyclododecane ring structure is cleaved by having salen ligand as the non-aromatic ligand. Besides that, the coordinating atoms in salen are more varied as well.

The complexes designed to fulfill the above mentioned purposes above are denoted herein after as [Ln(TPP)Crown]Cl, [Ln(TPP)Azacrown]Cl, and [Ln(TPP)Salen]Cl with Ln is Y, Tb, or Dy. All of them were first synthesized and analyzed in this research project. There has been no report on the compounds until now.

In the case of [Y(TPP)Crown]Cl and [Y(TPP)Azacrown]Cl, measurements were performed to determine L_z. Positive A-term pattern corresponding with B(0,0), Q(0,0), and Q(1,0) bands were detected and the intensity were unchanged at lowered temperature, associated with the diagmagnetic nature of Y. In [Tb(TPP)Crown]Cl and [Tb(TPP)Azacrown]Cl, temperature-dependent positive A-term profiles, in which all bands became more intense with diminished temperature due to the ferromagnetic character of the **J–L** interaction, were observed. On the other hand, [Dy(TPP)Crown]Cl and [Dy(TPP)Azacrown]Cl demonstrated reversal of normal A-term spectral shape as temperature was reduced especially on B(0,0) band and this is related with antiferromagnetic nature of the **J–L** interaction. Furthermore, even though the L_z value is practically unchanged from cyclen, 12-crown-4 ether, and 1-aza-crown-4 ether, there is substantial differences in Δ_{JL} values with different non-aromatic ligands and such variation is more apparent in Q bands than in B band.

In order to explore more how distorted symmetry alters the angular momentum and the interaction, cyclododecane-group ligands was changed with salen whose symmetry is lower than 1-aza-12-crown-4 ether. More distorted non-aromatic ligand did not change the pattern of electronic transition as positive A-term patterns were observed for B(0,0) band, Q(0,0) band, and Q(1,0) band. Furthermore, [Tb(TPP)Salen]Cl showed temperature dependence in all bands where the intensity of positive A-term increased with diminished temperature. On the other hand, in [Dy(TPP)Salen]Cl, negative A-term was observed in B(0,0) band but on the contrary, positive A-term was observed in Q bands without reversal to negative A-term. In the complexes with Y, Tb, and Dy, L_z values in B(0,0) band were similar to those with 12-crown-4 ether and 1-aza-12-crown-4 ether. Interestingly, L_z of Q(0,0) band of the salen complex is higher than in the complexes with cyclen, 12-crown-4 ether, and 1-aza-12-crown-4 ether. Thus, salen has more significant effect on the total angular momentum of porphyrin than the other non-aromatic ligands. The Δ_{JL} of B(0,0) band of [Tb(TPP)Salen]Cl and [Dy(TPP)Salen]Cl is in between that of the other complexes containing cyclododecane compounds. Contrast to that, Δ_{JL} in Q(0,0) band of [Tb(TPP)Salen]Cl is notably higher than the other complexes while in [Dy(TPP)Salen]Cl, Δ_{JL} is still in the range between that of [Dy(TPP)Crown]Cl as the lowest and [Dy(TPP)Cyclen]Cl as the highest.

In conclusion, different non-aromatic ligands always affect the electronic interaction in Tb and Dy. However, such alteration is more significant in Q band than in B band without necessarily change the L_z. As well as that, compared to B(0,0) band, Q(0,0) band is easier to be perturbed by lower symmetry of the second ligand as indicated by L_z values of B(0,0) which remained unchanged with different ligands while L_z in Q(0,0) increased when the second ligand is significantly more distorted. Moreover, between the two lanthanides, Tb is more prone to electronic interaction alteration with different non-aromatic ligands tuning than Dy.

様式 7

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

希土類イオンを磁性中心とする単分子磁石における分子内磁気相互作用の研究が、学術的観点からのみならず、エレクトロニクスやスピントロニクスなどへの応用の観点からも盛んに行われている。これらの研究は主に基底状態を対象としたものであり、励起状態に関する研究はほとんど進んでいない。本研究室において、これまでに希土類と大環状π電子系からなる分子系において、希土類４ｆ電子系の全角運動量Ｊと大環状π電子系の光励起状態の軌道角運動量Ｌとの間に磁気相互作用(J-L 相互作用)が存在することを見出している。

ポルフィリンは大環状π電子系を持ち、可視光のエネルギー領域に存在する 2 種類の励起状態において、いずれの場合も軌道角運動量を獲得する。本研究では、このポルフィリンに注目し、ポルフィリン―希土類の１：１錯体における J-L 相互作用について系統的な研究を行った。これまでの本研究室における先行研究においては、ポルフィリン、希土類イオン、サイクレンからなる錯体、[Ln(cyclen)(tpp)]Cl、(**1-Ln**、Ln=三価希土類、tpp = テトラフェニルポルフィン配位子)が合成され、ポルフィリン：希土類比が１：１の錯体における J-L 相互作用が初めて観測されている。ここで第 2 配位子として用いられたサイクレンは、配位原子として 4 つの窒素を持ち、ポルフィリンとの組み合わせによって 8 配位スクエアアンチプリズム構造をあたえる一方、π電子系のない飽和環状構造を持ち、ポルフィリンのπ電子系とは直接の相互作用をしない。

本研究においては、第二配位子の配位元素の違いおよび配位構造の対称性が J-L 相互作用にどのような影響を及ぼすかについて、系統的な研究を行った。この目的を達成するために、3 種類の新規錯体群を合成した。一つ目は、第二配位子として、12－クラウン－4 をもつ錯体、[Ln(12C4)(tpp)]Cl、(**2-Ln**)を得た。これにより、**1-Ln** の４つの配位窒素を酸素に置き換えたことによる J-L 相互作用への影響について研究を行った。二つ目に第二配位子として、アザ－12－クラウン－4 をもつ錯体、[Ln(aza12C4)(tpp)]Cl、(**3-Ln**)を得た。これにより、**2-Ln** の１つの酸素を窒素に置き換えたことにより、配位構造の対称性を低下させたことによる J-L 相互作用への影響について研究を行った。三つ目に、第二配位子としてさらに構造の相違が大きいサレンを持つ錯体、[Ln(salen)(tpp)]Cl、(**4-Ln**)を得た。これにより、さらに大きく配位環境を変化させた場合の J-L 相互作用への影響について研究を行った。

希土類イオンとして三価テルビウムおよび三価ジスプロシウムを用いた上記化合物(**2-Ln**、**3-Ln**、**4-Ln**)について、温度依存・磁場依存磁気円偏光二色性分光法(VT-VH-MCD)による測定を行い、ポルフィリンの第一、第二π－π*励起状態の励起状態における J-L 相互作用の観測・評価を行った。観測された MCD 強度の温度・磁場依存性に対して、ＪおよびＬの Zeeman 分裂と J-L 相互作用を含めた理論モデルによる解析を行い、J-L 相互作用の値を決定した。これにより、J-L 相互作用の大きさとポルフィリン上の軌道角運動量への第二配位子の構造と希土類の種類による依存性に明らかにした。以上の研究成果は希土類イオンの全角運動量と光励起環状π電子系の軌道角運動量との相互作用の理解に対して重要な知見を与えていると評価できる。よって、本論文は博士（理学）の学位論文をして十分価値のあるものと認める。