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Effects of central metal on electronic structure, magnetic properties, infrared and Raman spectra of double-decker phthalocyanine

Atsushi Suzuki*, Takeo Oku

The University of Shiga Prefecture, 2500 Hassaka, Hikone, Shiga 522-8533, Japan

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ABSTRACT

The effects of the central metal in double-decker metal phthalocyanine on the electronic structure, magnetic properties, and infrared and Raman spectra of the complex were investigated. Electron density distributions were delocalized on the phthalocyanine rings. The narrow energy gap and infrared peaks observed in the ultra-violet–visible–near infrared spectra of the systems were attributed to phthalocyanine ring–ring interactions the between overlapping π-orbitals on each ring. The chemical shift behavior of the phthalocyanine rings was separated by the deformation of their structure owing to nuclear magnetic interaction of the nuclear quadrupole interaction as determined by the electronic field gradient and asymmetric parameters. The magnetic parameters of principle g-tensors were dependent on the perturbation of the crystal field by the hybridization of the d-spin in the central metal conjugated with nitrogen ligands. In the case of the vanadyl system, the IR vibration modes were shifted by the soft vibration mode for resolving the symmetrical structure. Inactive Raman vibration modes arose from no-polarization on the phthalocyanine rings. Double-decker metal phthalocyanines have great advantages for the control of the magnetic mechanism for quantum spin entanglement in the relaxation process.

1. Introduction

The experimental realization of a nuclear magnetic resonance (NMR) quantum computer has been studied by a number of researchers. For example, nitrogen-vacancy color centers in diamond, pentafluorobutadienyl cyclopenta-dienyldicarbonyl-iron complexes, copper phthalocyanines, and nitrogen endohedral fullerene have been used to control quantum entanglement, quantization bits, and quantum calculations [1–3]. The magnetic behavior of magnetic interactions and the spin dynamics of organometallic transition complexes have been studied for application to spintronic devices, single molecular magnetism, and the entanglement of quantum spin in quantum calculations [4–11]. For instance, resonance frequency, spin dynamics based on the paramagnetic behavior and magnetic interaction of nuclear spin in copper phthalocyanine was independently used to control the entanglement of quantum spin in spin-lattice relaxation process [4]. The molecular design of endohedral metallofullerenes has been investigated for application to multi-quantum spin gates with decoupling pulses for quantum computers [5–11]. Experiment based on theoretical considerations of the magnetic behavior in these endohedral metallofullerene derivatives were carried out to elucidate the magnetic mechanism and spin dynamics of the spin-lattice relaxation. The magnetic mechanism and magnetic interaction were found to change upon chemical modification of the perturbation of metal-ligand crystal field, the central metal at the multi-state, the conjugation system, and electron donating and accepting groups. The chemical modification of organic transition complexes with multiplicity of quantum-spin, nuclear spin interaction, and spin-lattice relaxation is important for the control of spin gate entanglement in NMR quantum computers. Especially, the perturbation of the metal-ligand crystal field at the multi-state has been used to control the magnetic properties based on magnetic interaction at the multi-state and spin dynamics in the spin lattice relaxation process. The entanglement of nuclear spin as a quantum bit in superconducting circuits has been applied in a commercial quantum computer using superconducting flux qubits by the quantum computing company D-Wave Systems [12,13].

The performance of NMR quantum calculation using organometallic transition complexes in multi-states can be controlled by magnetic interaction involving hybridization of the d-spins and f-spins of the central metal under the ligand field. For instance, Rabi oscillations and coherent single nuclear spin manipulation have been experimentally demonstrated using an all-electrically controlled nuclear spin qubit transistor based on a single molecular magnet of double-decker terbium based

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* Corresponding author.
E-mail address: suzuki@mat.usp.ac.jp (A. Suzuki).

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phthalocyanine, through the use of the hyperfine Stark effect [14]. To improve spin multiplicity, spin dynamics, and entanglement in quantum spin, experimental investigations of the electronic structures and magnetic interaction of multi-decker phthalocyanines have been performed by NMR, alternating current magnetic susceptibility measurements, isothermal hysteresis curve measurements, scanning tunneling microscopy, and density functional theory [15–17]. Recently, experimental investigations and theoretical quantum calculations of the magnetic properties of bis(phthalocyaninato) terbium(III) double-decker phthalocyanine and quintuple-decker phthalocyanine and tris(phthalocyaninato) yttrium were performed for the development of single-molecule magnet and electron magnetic devices [18,19]. The single-molecular magnetic behavior of the terbium (III)-phthalocyaninato quintuple-decker complex was found to be strongly influenced by the magnitude of the terbium–terbium interaction with decreasing distance and quantum tunneling of the magnetization [19]. The magnetic relaxations and spin dynamics were dominated by the two-phonon Orbach mechanism. The magnetic relaxations were preferentially contributed from the direct process rather than the Raman process [20]. Experimental results and quantum chemical calculations elucidated the magnetic properties of the system based on electron delocalization and exchange repulsion of π-electrons in the phthalocyanine ring [21].

Experimental studies on the magnetic properties and electronic structure of multi-decker phthalocyanines using NMR, ultraviolet–visible (UV–vis), near infrared (NIR), infrared (IR), Raman, and near edge X-ray absorption fine structure spectroscopy analysis have been reported [22,23]. Especially, the electronic structure and magnetic interaction can be determined from the isotropic chemical shift observed in ^{13}C NMR and ^{1}H NMR, while the vibration modes seen in IR and Raman spectra derive from the magnetic interaction and spin dynamics in the relaxation process. The dynamic relaxation processes of quadruple-decker phthalocyanine complexes with terbium or dysprosium ions as magnetic centers have been found to depend on the magnetic interaction based on f–f interactions. The spin relaxation phenomena and nuclear spin driven quantum tunneling of magnetization of these complexes have also been discussed using experimental results and a theoretical model [24]. The magnetic relaxation phenomena based on quantum tunneling magnetizations in the quadruple-decker phthalocyanines has been measured using alternate current magnetic susceptibility data and the numerically calculated Zeeman diagram of the f-electronic centers [25]. IR spectroscopic investigations of the oxidized forms of these complexes have revealed characteristic electronic transitions and fingerprint regions. The observed bands were assigned to π–π^* transitions in π-electronic systems having narrow molecular orbital energy gap [26]. The switching of the single-molecule magnetic properties and self-assembly of terbium–porphyrin double-decker complexes has been studied for application in molecular spintronics [27].

The electronic structure and magnetic behavior of double-decker phthalocyanine complexes with unoccupied electron spin in the central metal on the phthalocyanine ring in cation, anion, and radical states have great advantages for the development of spintronic devices, single-molecule magnets, and quantum calculation. Especially, double-decker phthalocyanine complexes having a d-spin transition metal ion of scandium, yttrium, or vanadyl atoms as their central metal exhibit crystal field splitting with multi-degeneracies of d spin orbitals under the ligand field. In the case of d-spin in the transition metal ion, quantum chemical consideration based on perturbation theory requires investigation of the electronic structure and magnetic interaction of the nuclear quadrupole interaction, which can be determined by EFG and η, and IR and Raman vibration modes. For complexes containing f-spin transition metal ions, experimental measurements must be carried out at extremely low temperature owing to their short relaxation time, making it difficult to detect experimental results with quantitative analysis. Quantitative analysis of the magnetic mechanism must consider the incorporation of high level sections on the crystal field.

The purpose of this research is to investigate the effects of the central metal in double-decker phthalocyanine on its electronic structure, magnetic and optical properties, and IR and Raman vibrations. Especially, the effects of central metals such as vanadium, scandium, and yttrium as d-spin transition metal ions on the magnetic parameters is investigated through quantum chemical calculation of the chemical shift of ^{13}C, ^{1}H, ^{14}N NMR spectra, UV–vis–NIR spectra, excitation processes, and IR and Raman vibration modes. The magnetic mechanism will be discussed on the basis of nuclear spin interaction, spin–local interaction, nuclear–spin interaction, nuclear quadrupole interaction based on EFG and η related to electronic and charge density distribution caused by overlapping π-orbitals on the deformed phthalocyanine rings.

2. Calculation method

The isolated molecular structures of multi-decker metal phthalocyanines in $M(Pc)_2$, (M = V, Sc, Y) at neutral and doublet states were optimized by *ab-initio* quantum chemical calculations using unrestricted Hartree–Fock (URHF) as a unrestricted open shell self-consistent field (SCF) calculation and by density functional theory (DFT) calculation using the Gaussian 03 program with Becke's unrestricted three-parameter hybrid functional B3LYP (UB3LYP) [28,29] method in order of STO-3G*, 3-31G*, 6-31G*, and LANL2MB as the basis set. The highest occupied molecular orbital (HOMO), HOMO-1, the lowest unoccupied molecular orbital (LUMO), LUMO+1, and the HOMO–LUMO band gap (E_g) were calculated. Mulliken atomic charges, electron density distributions, and the electrostatic potential (ESP) on the phthalocyanine ring were estimated by Mulliken population analysis. After calculating the optimized structures and electron structures near frontier molecular orbital, the isotropic chemical shifts of ^{13}C, ^{1}H, ^{14}N NMR spectra, principle g-tensors, V-tensors of EFG, and η of ^{13}C, ^{14}N, ^{45}Sc, and ^{89}Y atoms in the double decker phthalocyanines were calculated by DFT using gauge-independent atomic orbitals (GIAO) [30] with a hybrid functional UB3LYP method and LANL2MB as the basis set. The IR and Raman vibration modes and frequencies of the optimized structures at the ground state were calculated by DFT with UB3LYP with LANL2MB using frequency calculations. UV–vis–NIR spectra and excited processes of the optimized structures were calculated by time dependent DFT (TDDFT) with UB3LYP with LANL2MB as the basis set [31]. The TDDFT intense excitation energies, oscillator strengths, and transition process expressed in terms of the frontier molecular orbitals were also computed.

3. Results and discussion

The electronic structures of $V(Pc)_2$, $Sc(Pc)_2$ and $Y(Pc)_2$ at HOMO and LUMO were calculated by DFT with hybrid functional calculation UB3LYP using LANL2MB as the basis set. The optimized structures, electron density distributions, and energy levels at the HOMO and LUMO of $V(Pc)_2$, $Sc(Pc)_2$, and $Y(Pc)_2$ are shown in Fig. 1 and Table 1. As shown in Fig. 1(a)–(c), the optimized structures of $V(Pc)_2$, $Sc(Pc)_2$, and $Y(Pc)_2$ were sandwich structures with degeneration of the energy levels around the frontier orbital. The optimized structures were slightly perturbed by chemical modification as the central metal diameter varied. The deformation of the structure caused by the changes in chemical bond and angle between the central metal and nitrogen ligand influenced the energy levels near the frontier orbital and band gap. The length of the chemical bond between the metal and nitrogen and the angle of the N—M—N bonds

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