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Review

Multiple-decker phthalocyaninato Tb(III) single-molecule magnets and Y(III) complexes for next generation devices

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ABSTRACT

A new magnetic relaxation phenomenon for an Ising dimer of a Tb-phthalocyaninato triple-decker SMM $Tb_2(obPc)_3$ (**1**) is reported. In Argand plots, the magnetic relaxation splits from a one-component system into a two-component system (temperature-independent and temperature-dependent regimes) in a dc magnetic field. There was clear evidence that the magnetic relaxation mechanisms for the Tb^{3+} dimer depended heavily on the temperature and the dc magnetic field. The relationships among the molecular structure, ligand field, ground state, and SMM properties in a direct current (dc) magnetic field are discussed. Furthermore, in order to investigate the stability of the complexes in vacuum evaporation (dry) process and the control of their surface morphology after transferring to a surface, we studied the lanthanoid-phthalocyaninato triple-decker molecule Y_2Pc_3 deposited on a Au(1 1 1) surface using a low-temperature scanning tunneling microscope. It is important to both understand and control the quantum properties of Ln-Pc multiple-decker SMMs with an external field and the monolayer or multi-layer structures on a substrate for next generation devices, such as magnetic information storage.

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1. Introduction

Metal complexes of phthalocyanine (Pc) and its derivatives, e.g., metal-Pc (MPc), double-decker (MPc_2) or triple-decker (M_2Pc_3), with metal atoms in the cavity of the Pc ligands or as linkers have found applications in gas sensing devices, photovoltaic materials, light-emitting diodes, solar and fuel cells, and so on [1–3]. For most applications, the properties of the molecular devices are influenced by the quality of the nanostructures and thin films; thus, the orientation and assembly of the molecules must be precisely controlled. The introduction of scanning tunneling microscopy/spectroscopy (STM/STS) made it possible to characterize surface morphology and electronic structure even at the atomic level. The first STM observation involving Pc complexes revealed the inner structure of an isolated molecule of a CuPc/Cu(1 0 0) system [4], and CuPc and CoPc molecules were discriminated via dark and bright contrast spots in the center of the molecules. The bright contrast was explained to be due to the d orbital of the Co atom which contributed to the STM tunneling current [5,6]. Similar investigations have been performed on surface assemblies of MPc (M = Cu, Co, Fe, Pb, Pd, and Mn) on different substrates, and physical properties, such as the Kondo effects in magnetic ion Pc molecules, have been explored [7–16]. These experiments were mainly performed on thin films on metal/semiconductor substrates in ultrahigh vacuums. For investigations in solution and under ambient conditions, Pc molecules with alkyl substituents adsorbed on a graphite surface, which formed perfect thin films or alkane lamellae, were used as a buffer layer to immobilize the planar molecules [17,18]. Finally, most research has focused on single-decker Pc ligand molecules.

Double-decker Pc sandwich complexes (MPc_2) are important components in molecular electronic sensors, electrochromic displays, field-effect transistor devices, etc. [19–27]. Lanthanoid double-decker complexes ($LnPc_2$) consist of a Ln^{3+} ion and two Pc ligands, each having a formal charge of −2 with a closed shell π electron system. It is known that one-electron oxidation of the anion radical occurs at the ligand, resulting in a neutral complex with an open shell π electron system [28,29]. $LnPc_2$, therefore, has two spin systems: an unpaired π electron on one of the Pc ligands and a Ln^{3+} ion with 4f electrons. MPc_2 with various substituents have been synthesized [30–38]. At the same time, the Pc ligand can form triple-decker complexes composed of three Pc^{2-} ligands and two Ln^{3+} ions (Ln_2Pc_3) [39–42], resulting in a neutral complex with a closed shell π electron system [43,44]. $LnPc_2$ and Ln_2Pc_3 have different properties due to their different electronic structures.

Since organic macromolecules often decompose via thermal evaporation methods, most of the STM results have concerned surface assemblies of $Er[(C_{12}H_{25}O)_8Pc]_2$ [45], $Pr(PcOC8)_2$ [46], (Nc)Eu(α-TPPc) [47], and Tb-octa-alkoxyl-substituted Pc double-decker complexes [48] and triple-decker complexes. [{Pc(15C5)$_4$}Lu{Pc(15C5)$_4$}Lu(PcOC8)] [49], (TPP)Eu(CRPc)Eu(CRPc) [50], and [(Pc)Dy(PcOC8)Dy(Pc)] [51] are prepared by placing a droplet of a solution of the complexes on the substrate to form two-dimensional thin films. Because the adsorbed molecules are thermally unstable, no high resolution STM images have been obtained at room temperature. Therefore, much research is needed to understand surface assemblies, electronic properties, and physical properties of Pc sandwich complexes. STM and STS are good tools for such work because extreme conditions, such as high magnetic fields, low sample temperatures, and atomic-level resolution, can be achieved. With these techniques, sample preparation on metal/semiconductor surfaces is important.

In this review, recent developments in Ln-Pc multiple-decker single-molecule magnets (SMMs) on surfaces for next generation devices are presented. First, we describe strategies for preparing next-generation devices using SMMs. Section 2 focuses on preparation, characterization by using STM and STS, and FET properties of $LnPc_2$ SMMs adsorbed on surfaces as backgrounds. In Section 3, the relationships among the molecular structures, crystal fields, ground states, and SMM properties of Tb_2Pc_3 in a direct current (dc) magnetic field are discussed. Finally, in the last section, STM and STS studies of other surface-adsorbed Ln_2Pc_3 are reported. Specifically, the electronic structures of these complexes are described.

2. Strategy for next generation devices

Information technologies need new ways to process information. In principle, a single spin can be used as a 'bit' of information to prepare high-density storage and quantum computing devices [52–64]. Quantum tunneling of the magnetization (QTM) between double well potentials [6], which is a prominent characteristic property of single-molecule magnets (SMMs), underpins this concept [65–71]. In 1993, Mn_{12} clusters were reported by Hendrickson et al. to be the first SMMs. SMMs behave like magnets with frozen spins, and a potential exists across two energy barriers at low temperatures, known as the blocking temperature (T_B). In the case of 3d cluster SMMs, an easy axis-type magnetic anisotropy, which is represented by a negative zero-field splitting constant (D), occurs due to magnetic interactions among high-spin 3d metal ions in the clusters. At the same time, researchers have been studying complexes with higher T_B than that of the Mn cluster [73–77].

In recent years, lanthanoid-phthalocyaninato (Ln-Pc) sandwich complexes have been shown to be SMMs, and researchers have utilized their QTM and magnetic relaxation behavior [65–72]. SMM behavior results from the ligand field. Ishikawa et al. have reported that the SMM TBA^+ $[TbPc_2]^-$ ($TBA^+ = (C_4H_9)_4N^+$) has a long magnetization relaxation time [78–88]. Ln(III)-Pc molecules showing SMM behavior have significantly large axial magnetic anisotropies, which occur by a different mechanism than those for known 3d metal cluster SMMs [73–77]. In the case of Ln SMMs, on the other hand, the ligand field of the Ln ion controls the anisotropy. The ligand field potential around the Tb^{3+} ion ($4f^8$) with a total angular momentum (J) of 6 splits the ground multiplet so that the lowest sublevel has the largest J_z value ($|J_z| = 6$, corresponding to up/down spin states) and large energy gaps to the remaining sublevels (ca. 400 cm^{-1}) [78–88]. Thus, there is a small probability for a transition between $J_z = +6$ (up-spin state) and −6 (down-spin state) substates and hence a slow magnetization response to an applied magnetic field.

From studies involving vacuum evaporation method and the magnetic anisotropy in a specific direction on a surface, Vitali et al. were able to determine the electronic structure (SMM character) of $TbPc_2$ deposited on a Cu(1 1 1) surface in an ultrahigh vacuum (UHV) using a dry imprint technique [89]. On the basis of the properties of $LnPc_2$ SMMs, we think that $TbPc_2$ can be used as a 'bit' of information in high density storage technology by taking advantage of the single up-spin/down-spin property, which is equivalent to 2^1.

$TbPc_2$ SMMs can couple with magnetic impurities, including Tb^{3+} ions, and/or conducting electrons from the tunneling current in STS, which is known as the Kondo effect [90]. The magnetic properties of transition metal atoms in a host molecule can be elucidated via the Kondo resonance observed by using cryogenic STM [91–93]. Most of the previous studies on the Kondo effect have focused on magnetic atoms on open metal surfaces [94–104], and their Kondo temperatures (T_K) have been very low, meaning the spin-dependent transport properties are consequently lost under ambient conditions. Recent studies on molecular Kondo effects show that caging the magnetic atoms in a molecule can increase or decrease T_K [91–93,105]. In these cases, both the molecular structure [92,93] and the molecular conformation [91] play an important