

Phthalocyanine Single-Molecule Magnets

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Single-molecule magnets (SMMs) have attracted much attention due to their potential applications in molecular spintronic devices. Rare earth SMMs are considered to be the most promising for application owing to their large magnetic moment and strong magnetic anisotropy. Phthalocyanines (Pcs) are large rings with 18π electron conjugation and have a wide range of applications in spintronics.

Keywords: single-molecule magnets ; rare earth elements ; phthalocyanines

1. Introduction

Single-molecule magnets (SMMs), with the slow relaxation of magnetization and quantum tunneling [1][2][3], are considered a significant discovery in the field of nanomagnetism [4]. SMMs are often used to fabricate nanoscale devices and high-density data storage media [5][6][7][8][9]. Notably, Mn_{12} [1] and Fe cluster [10] are the earlier discovered SMMs, which belong to $3d$ SMMs.

Since 2003, the introduction of lanthanide rare earth ions has allowed SMMs to enter a new stage. Rare earth SMMs exhibit magnetic bistability at a higher blocking temperature (T_B) than $3d$ SMMs because lanthanide ions are f -orbital-based elemental ions with unparalleled single-ion anisotropy, T_B is a key performance parameter of an SMM, one description of which refers the maximum temperature at which it is possible to observe hysteresis in the field-dependence of the magnetization, subject to the field sweep rate. Meanwhile, phthalocyanines (Pcs) are large rings with 18π electron conjugation and have a wide range of applications in spintronics. Therefore, $LnPc_2$ SMMs have shown great potential for spintronics and device applications. The first example of the $[TbPc_2]^-$ effective energy barrier (U_{eff} , that is the potential energy required for molecular magnetization (or magnetic moment) reversal) of 331 cm^{-1} broke the record of U_{eff} for multinuclear $3d$ SMMs [11]. Subsequently, scientists have shown great interest in studying not only mononuclear rare earth SMMs but also binuclear rare earth SMMs and multinuclear rare earth SMMs [12][13].

2. Phthalocyanine Single-Molecule Magnets

SMMs are nanosized molecules with a stable magnetization intensity coming from within a single molecule and therefore can be used as independent magnetic functional units. In essence, a maximum value of the imaginary part of the magnetization related to the external field frequency occurs when Alternating Current magnetization rate tests are performed at low temperatures [1][14]. The development stages of monomolecular magnets are as follows. First, are transition metal monomolecular SMMs (Mn_{12} and Fe clusters); then are rare earth single-molecule magnets, mainly lanthanide-based metal SMMs. Therefore, the use of rare earth metal ions, especially Tb and Dy ions, to construct SMMs is still an effective method to improve the performance of SMMs [15].

The $4f$ orbitals of lanthanide ions are inner orbitals and thus have strong spin-orbit coupling, which allows the crystal field interaction to be regarded as perturbative. Therefore, Ln -SMMs ($Ln = Tb, Dy$) have become an important part of the field of SMMs, are widely favored by researchers and have been reported far more than other metallic SMMs, occupying half of the field of molecular magnets.

From **Figure 1**, it can be seen that the scanning tunneling microscopy (STM) images of $LnPc_2$ ($Ln = Tb, Dy$) molecules observed by the experiment have the shape of eight lobes. However, $DyPc_2$ is more regular than $TbPc_2$ [16][17].

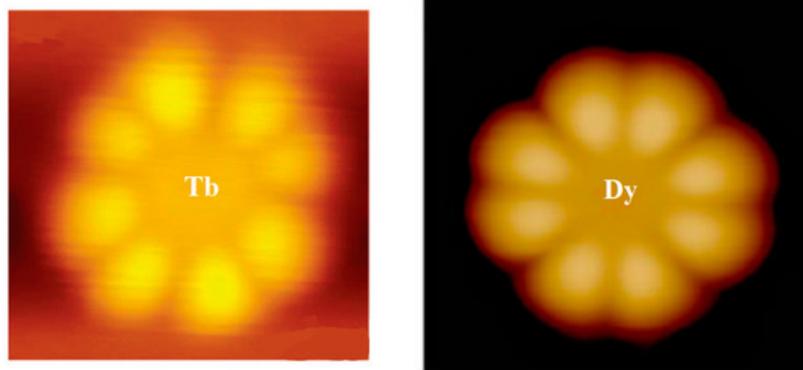


Figure 1. STM images in experiments. (Left): TbPc₂, bars indicate 1 nm; (Right): DyPc₂, image sizes: 3 × 3 nm² [16][17].

2.1. Structure and Category

Pc is an organic semiconductor with 18 π electrons, and it has been demonstrated that Ln-Pc double- and triple-decker complexes are capable of forming [18][19][20][21][22][23][24][25][26][27][28][29]. The structures are shown in **Figure 2** [30].

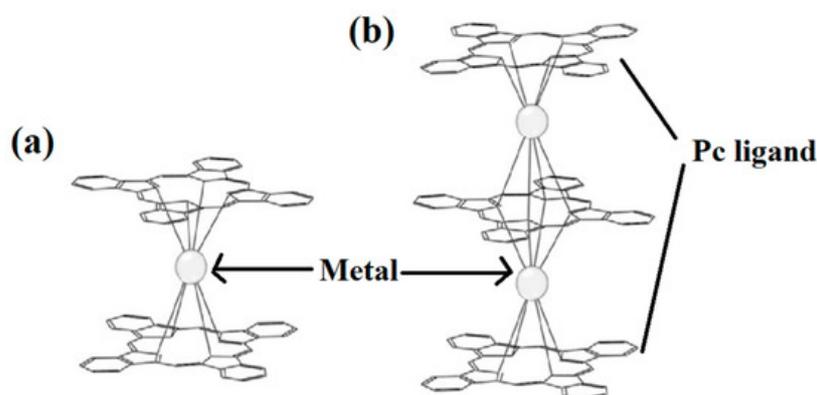


Figure 2. Structures of (a) double-decker metal Pcs, consisting of a metal ion sandwiched between two Pc ligands and (b) triple-decker metal Pcs, metal ions are stacked between sandwich-type Pc oligomers [30].

Compared to conventional magnetic particles composed of metals, metal alloys, or metal oxides at the nanoscale, SMMs have many important advantages: (1) SMMs consist of relatively independent molecular units, so they have a single size and a fixed structure [31]. (2) SMMs are generally soluble in organic solvents, which makes it possible to obtain magnetic materials that were previously available only under special conditions in chemical solutions under ordinary conditions. (3) The magnetic characteristics of SMMs can be refined through metal ions and Pcs and by improving the synthesis methods [32].

SMMs generally consist of an intrinsic metal nucleus surrounded by an organic ligand shell. Lanthanide elemental metal ions with a high spin ground state are good choices for the preparation of molecular materials with SMMs. However, designing the SMMs of such ions requires care to optimize the spatial distribution of ligand electrons with respect to the ion.

2.2. Double-Decker Pc of Tb/Dy

To date, more than one hundred Ln-SMMs have been discovered and studied. Owing to their excellent physical properties, Ln-Pcs (Ln = Tb, Dy) are widely favored by researchers [33][34][35][36][37]. The model of Ln-Pcs is shown in **Figure 3a,b**, the Ln³⁺ (Ln = Tb, Dy) ion is located in the center of the molecule with two parallel Pc rings to form a sandwich structure molecule. The double-decker Ln-Pcs (Ln = Tb, Dy) has D_{4d} symmetry [33][34][38]. DyPc₂ is similar in properties to TbPc₂, which possesses an anisotropic U_{eff} of 410 cm⁻¹ and a spin-orbit coupling quantum number of J = 6 [39].

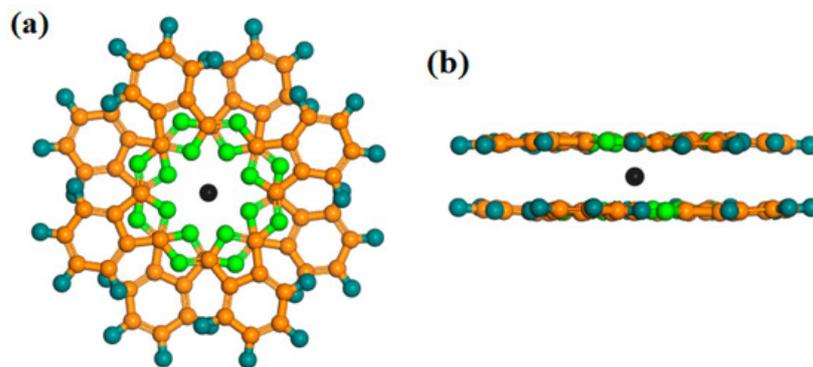


Figure 3. Diagrammatic sketch of $[\text{LnPc}_2]^-$ ($\text{Ln} = \text{Tb}, \text{Dy}$), the angle between Pc ligands is 45° . (a) Top view; (b) side view. Colors: ($\text{Ln} = \text{Tb}, \text{Dy}$), black; N, green; C, orange; H, navy blue.

Rare earth Pcs were discovered by Kirin and Moskalev. Notably, double-decker Ln-Pcs could also be achieved at that time ^{[40][41]}. The crystal structure data of LnPc_2 ($\text{Ln} = \text{Tb}, \text{Dy}$) are shown in **Table 1** ^[16]. TbPc_2 belongs to the same $\text{P2}_1\text{2}_1\text{2}_1$ space group as DyPc_2 , and the crystal parameters are close in size.

Table 1. Crystal structure data of LnPc_2 ($\text{Ln} = \text{Tb}, \text{Dy}$) ^[16].

	TbPc_2	DyPc_2
Formula	$\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{Tb}$	$\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{Dy}$
Formula weight	1183.99	1113.97
Crystal system	Orthorhombic	Orthorhombic
Space group	$\text{P2}_1\text{2}_1\text{2}_1(\#19)$	$\text{P2}_1\text{2}_1\text{2}_1(\#19)$
a (nm)	0.88	0.89
b (nm)	1.06	1.06
c (nm)	5.08	5.08
V (nm^3)	4.76	4.76
Z	4.00	4.00
F(000)	2372.00	2268.00

Dy ion-containing materials (such as magnetic resonance imaging, magnetostriction, and SMMs) have a wide range of promising applications in the magnetic field ^{[42][43][44][45]}. In SMMs, magnetic exchange interactions are important factors affecting the performance of SMMs, and early studies have shown that even very weak intermolecular magnetic exchange interactions can effectively suppress quantum tunneling effects and enhance the performance of SMMs ^{[46][47]}. Although the $4f$ electrons of rare earth ions are subject to the shielding effect of the outer electrons and the magnetic exchange between metal ions is relatively weak, this effect still has a significant impact on the properties of their SMMs.

Martínez-Flores et al. studied the geometries and electronic properties of LnPc_2 , as shown in **Figure 4**. They reported that unpaired electrons are transferred to Pc ligands ^[48], and the strong π - π interaction between intramolecular Pc rings becomes important for organic field effect transistors as intrinsic semiconductors compared to their monolayer analogs.

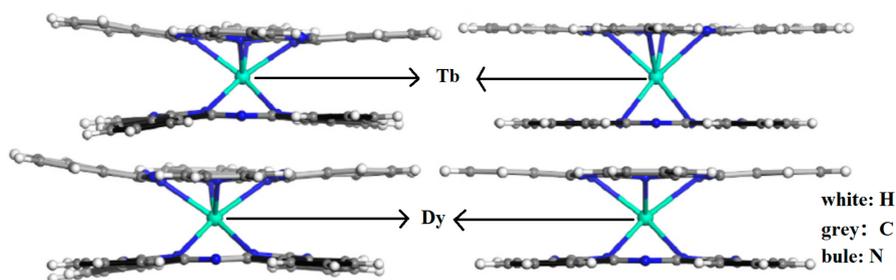


Figure 4. The structures of LnPc_2 ($\text{Ln} = \text{Tb}, \text{Dy}$) compounds from X-ray diffraction (XRD) measurement (left) and density functional theory (DFT) calculation (right). In the DFT calculation, the PBE GGA correlation functional by Perdew-Burke-

Ernzerhof (PBE) was the functional of choice, complemented by the empirical dispersion correction developed by Grimme [48].

The magnetic coupling of TbPc₂ molecules was reported by Corradini and coworkers. They placed TbPc₂, single-layer graphene, and an Au single-layer on top of a Ni(111) magnetic substrate. They found that the superexchange coupling leads to a change in the antiferromagnetic signal [49].

2.3. Multi-Decker Pc of Tb/Dy

Ln₂-SMMs are SMMs containing two lanthanide element ions forming a large collection, and double-nuclear Pcs SMMs containing Dy and Tb are more common. The radially contracted nature of the 4*f* orbitals of rare earth ions tends to lead to extraordinarily weak intramolecular exchange coupling in multinuclear lanthanide complexes. Therefore, for most multinuclear Ln₂-SMMs, the magnetic origin is mainly a single-ion effect.

There is another class of double nuclear Ln₂-SMMs that are trilayer structured Pc SMMs, and the chemical general formula of these molecules is [PcLn(μ-Pc₂)Ln(Pc₃)] when the ligand Pc can be heterocyclic. The spacing between the Ln ions in the molecule is approximately 0.36 nm, which makes it possible to study the effect of intramolecular *f-f* interactions on the dynamic magnetic properties, and the lanthanide ions have a significant role in the physical properties of triple-decker Pc compounds [50].

Hellerstedt et al. reported a method to form Tb₂Pc₃ from TbPc₂. The structures are shown in **Figure 5a,b**. The different colors (yellow and blue) of the densities represent the charge redistribution. The formation of Tb₂Pc₃ provides a novel way to investigate and control magnetic interactions [34].

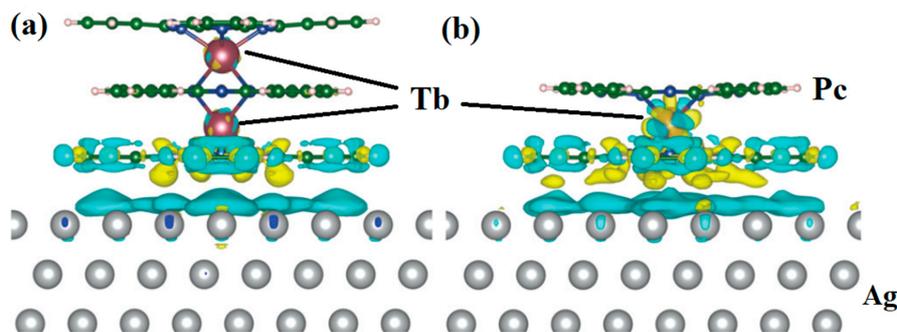


Figure 5. Calculated charge transfer between (a) Tb₂Pc₃ and (b) TbPc₂ molecules and the Ag(111) surface obtained from DFT calculations. It used exchange correlation functional PBE + U with U = 5 eV for *f*-electrons of Tb and van der Waals interaction was approximated by the Tkatchenko-Scheffler dispersion correction method. The yellow and blue colors represent the accumulation and loss of density, respectively. The presence of blue density on the upper surface layer indicates substantial charge transfer from the metallic surface toward the molecule [34].

Ln₃-SMMs can be divided into two main categories according to the structural arrangement of the metal ions: triangular and chain-like metal ion arrangements. Multinuclear Ln-SMMs are relatively rare in most rare earth elements because they are not easily synthesized due to their high nucleus numbers. Of course, Dy is the exception; the vast majority of rare earth SMMs with high nucleation numbers contain Dy, and the number of nuclei in Dy-SMMs can be as high as 50. However, in general, ligands for multinuclear Dy systems are not limited to Pcs.

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