

PhD thesis

Helicenes in the design of magneto-optical molecular materials

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Kraków 2023

Abstract

The following doctoral dissertation considers the design and synthesis of new molecular compounds comprising lanthanides and helicenes. The combination of these two unique building blocks allows to obtain specific magnetic and optical properties of the final material by merging a different functionality of each component. Lanthanide ions provide strong magnetic anisotropy, depending on the selected ion. A properly designed ligand field can tune up this anisotropy and result in interesting magnetization dynamics of the final complex. On the other hand, helicenes bring a strong chirality to the system as organic ligands as they are characterized by extremely high values of specific rotation. Despite promising physical properties, such as the cross-effects of magnetism and chirality, compounds combining lanthanides and helicenes are relatively rare in the literature.

The results described in this doctoral thesis concern research carried out for a series of isostructural compounds based on lanthanide ions and the smallest helicene: 1,10-phenanthroline *N,N'*-dioxide (phendo). Despite only a single-step synthesis of phendo, these complexes are the first examples of using this organic molecule as a ligand in coordination chemistry. Most helicenes require multi-step, much more time-consuming synthetic procedures, which may be the main reason for their rarity as ligands.

The presented PhD thesis is based on three scientific papers. Two of them (**P1** and **P2**) describe detailed studies on the dynamic magnetization behavior of lanthanide ions in a series of structural analogs $[\text{Ln}(\text{phendo})_4](\text{NO}_3)_3 \cdot x\text{MeOH}$ ($\text{Ln} = \text{Gd}, \text{Er}, \text{Yb}$; $\text{MeOH} = \text{methanol}$) and in their diamagnetic dilutions in the isostructural yttrium matrix, obtained at the synthetic stage. The magnetic properties of these compounds were characterized using alternating current SQUID magnetometry and electron paramagnetic resonance techniques. The observation of an unusually slow magnetic relaxation for the analog based on the magnetically isotropic gadolinium(III) ion initiated an extensive analysis of the magnetization dynamics for several diamagnetic dilutions of this compound. The properties of this molecule as a potential molecular qubit (the quantum equivalent of a classical bit) were fully characterized. Similar units are already being used as components in prototype quantum computers. Contrary to the currently used entities, like superconducting electronic circuits, synthetic chemistry

allows obtaining many identical qubits in the form of molecules, which are free of structural defects and are easily modifiable.

All three described structural analogs show slow magnetic relaxation induced by an external DC magnetic field, a behavior characteristic for Single Molecule Magnets. These types of molecules are potential units for a very dense recording of magnetic information. Studies on structural factors affecting the relaxation mechanisms of quantum nanomagnets are currently being conducted by research teams in the field of molecular magnetism around the world. The main conclusion from the research presented in paper **P2** considers the reliable fitting of parameters of the Raman relaxation in the diamagnetic dilutions of a series of isostructural compounds. Avoiding excess parameters during the analysis of magnetization dynamics allows for better modeling of reality and, consequently, for developing more effective strategies in the design of new, improved materials.

The possibilities offered by the combination of helicenes and lanthanides in one material are discussed in the paper **P3**, which is a review of the current achievements in this field. The characterization of the magnetic properties of the series of compounds presented in the papers **P1** and **P2** provides a solid groundwork for exploring the cross-effects of magnetism and chirality, which is going to be investigated for enantiomerically pure compounds containing chiral cations Δ/Λ -[Ln(phendo)₄]³⁺. The preliminary results of this work are presented at the end of this thesis in the conclusions and perspectives section. Other complexes obtained during PhD studies, but not published yet, are also briefly presented at the end of this thesis. All of them are examples of the use of larger helicenes as ligands in the construction of molecular materials.