Spectroscopy and magnetic properties of Ln-$[Ag(CN)_2]_n$ coordination polymers

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The $[Ag(CN)_2]^-$ ions have a natural predisposition to form Ag···Ag bonds, generating diverse structures, including one-dimensional chains and two-dimensional layers. Meanwhile, tris(2-pyridylmethyl)amine (tpa) is a versatile ligand for lanthanide(III) complexes, enhancing their single-molecule magnet (SMM) properties and sensitizing their luminescence. Substituted tpa ligands can be easily synthesized, enabling functionalization. Despite the potential application of such complexes, including luminescence[1], SMM properties[2], and terahertz absorption[3], reports on lanthanides(III)-silver(I) complexes remain scarce, as do studies employing tpa as a coordinating ligand for lanthanides.

In this study, cyanometallate-bridged lanthanide complexes incorporating tris(2-pyridylmethyl)amine were synthesized using Tb(III), Dy(III), Ho(III), and Y(III) ions. Their spectroscopic and magnetic properties were studied (Figure 1), revealing distinct features such as lanthanide-centered luminescence in the Tb(III)-Ag(I) and Dy(III)-Ag(I) systems, lanthanide-centered absorption in the Ho(III)-Ag(I) system, and broad luminescence attributed to extensive Ag···Ag bonding in all systems. Notably, all emissions are temperature-dependent. In addition, the Dy(III)/Y(III)-Ag(I) compounds show field-induced single-molecule magnetism, with dilution by Y(III) reducing Dy(III) dipole interactions and increasing the energy barrier. These compounds hold potential for various applications, including lanthanide-centered luminescence thermometry.

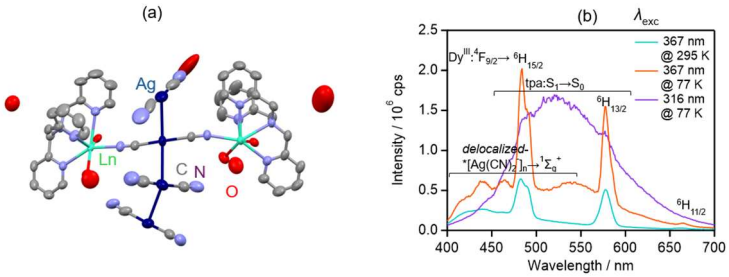

Figure 1. Structural unit of Ln-Ag systems (a) and emission spectrum of Dy-Ag system (b).

1) S. Ohkoshi et al., *Inorg. Chem.*, **2019**, 58, 5677-5687. 2) S. Ohkoshi et al., *J. Mater. Chem. C*, **2023**,11, 1008-1020. 3) S. Ohkoshi et al., *Inorg. Chem. Front.*, **2024**,11, 3906-3918.