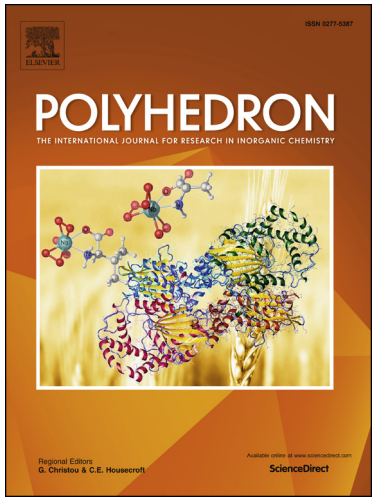

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Two new lanthanide-nitronyl nitroxide complexes: magnetic and fluorescence properties

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ABSTRACT

Two new lanthanide complexes of nitronyl nitroxide radical have been synthesized and characterized on the structure, magnetism and fluorescence: $[Ln(hfac)_3(NITPh\text{-}(OCH_3)_2)_2]$(Ln=(Tb(**1**),Dy(**2**)), (NITPh-$(OCH_3)_2$=2-(3′,4′-dimethoxy-phenyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide); hfac=hexafluoroacetylacetonate). Two complexes crystallize in monoclinic space group C2/c, which have similar mononuclear structures. The central metal ion is eight coordinated by six oxygen atoms from three hfac molecules and two oxygen atoms from two nitronyl nitroxide radicals. The varying temperature magnetic susceptibility indicates that there are weak antiferromagnetic interaction between metal ions and nitronyl nitroxide radicals in complexes **1** (zJ' = -0.145 cm^{-1}) and **2** (zJ' = -0.140 cm^{-1}). Ac magnetic susceptibility studies exhibit no single-molecule magnet behavior in complexes **1** and **2**. In addition, the fluorescence properties of **1** show that it is an excellent fluorescent probe of recognizing $Cr_2O_7^{2-}$ anion. Because of the linear relationship at low concentration and detection limit reached 1×10^{-7} M, it can be used as a luminescence-based sensor for quantitative analysis.

Keywords: Nitronyl nitroxide; Lanthanides; Magnetic properties; Luminescence properties

1. Introduction

In recent years, the unique structure and properties of nitronyl nitroxide radical have attracted many researchers due to their advantages such as good chemical stability, versatility, easy to modify[1-2]. The metal-radical method has been proved to be one of the most effective methods for synthesizing molecular-based magnetic materials[3-4]. Based on the electronic arrangement rule, the 4f electron orbit of lanthanide ions is effective shielded by the outer-shell electrons. Furthermore, lanthanide ions have large anisotropic magnetic moments, the energy barrier value increase obviously, therefore magnetic characteristics of lanthanide ions are difficult to be analyzed[5]. To explore the magnetic properties of lanthanide-radical complexes, different types of lanthanide complexes with nitronyl nitroxide radicals were synthesized[6]. Tb(III) and Dy(III) ions have large magnetic anisotropies and become an ideal choice for constructing SMMs and SCMs[7-8], especially since the first 4f–2p SMM $[Dy(hfac)_3NITpPy]$ was reported[9]. Hence, we decided to use Tb and Dy ions combined with new nitronyl nitroxide radicals to obtain single-molecule magnets.

Lanthanide metal with light physical characteristics of photochemical stability, long fluorescence lifetime, emission wavelength and large Stokes shift, can avoid the

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