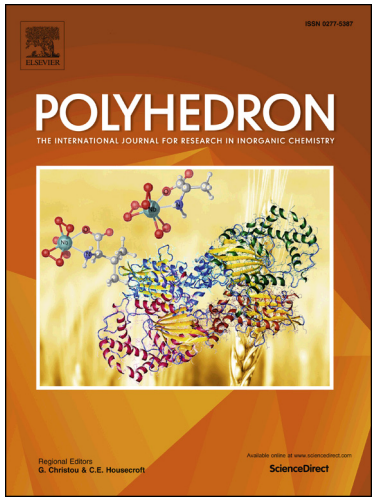

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Four new rare-earth nitronyl nitroxide radical complexes: magnetic and luminescent properties

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ABSTRACT

Four new rare-earth nitronyl nitroxide radical complexes, $[Ln(hfac)_3(NITPh\text{-}Pa)_2][0.5CH_3(CH_2)_5CH_3]$ (Ln = Gd(**1**), Tb(**2**), Dy(**3**), Ho(**4**), hfac = hexafluoroacetylacetonate, NITPh-Pa = 2-(3',4'-dioxylmethylene-phenyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide), have been synthesized. The X-ray crystal structure analysis revealed that four compounds have similar mononuclear tri-spin structures, in which the Ln(III) ions are eight-coordinated by two nitronyl nitroxide radicals and three hexafluoroacetylacetonate ligands to form a slightly distorted dodecahedron. In complexes **1-4**, isolated mononuclear molecules connect each other through intermolecular hydrogen bonds to form 3D supermolecular framework. Magnetic investigation indicates there are ferromagnetic interactions between Gd(III) ions and radicals in complex **1**. Alternating current(ac) magnetic susceptibilities of complexes **2** and **3** show that there are no non-zero out-of-phase signal, which indicates the inexistence of slow magnetic relaxation. The luminescence properties of complex **2** exhibit the characteristic emission peaks of Tb^{3+} ions and the potential for recognition of $Cr_2O_7^{2-}$ and Cr^{3+} ions. Furthermore, nearly linear at low concentration and the low detection limit (0.01uM) indicate that complex **2** may potentially be acted as luminescence-based sensor for quantitative and highly sensitive detection of $Cr_2O_7^{2-}$ ion.

Keywords: Rare-earth complexes; Nitronyl nitroxide; Supermolecular framework; Magnetic properties; Luminescence properties

1. Introduction

In recent years, much attention has been paid to the molecular magnetic materials [1-4] owing to their potential applications in molecular spin-based quantum computers, high-density magnetic memories and molecular spintronics [5,6]. A large amount of organic radicals were synthesized as organic magnetic species, such as nitronyl nitroxide, semiquinone, verdazyl, thiazyl, and so on [7-9]. Thereinto, nitronyl nitroxide has been

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