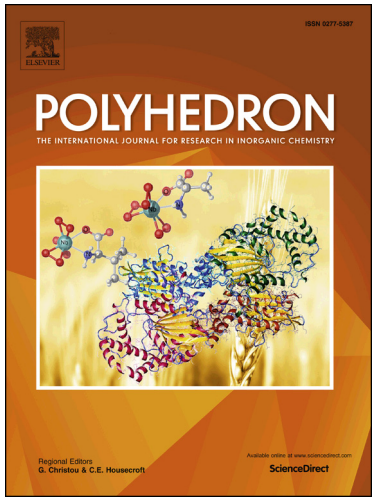

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Self-assembly of Luminescent Polynuclear Cd-Ln Complexes with a Flexible Long-chain Schiff Base Ligand

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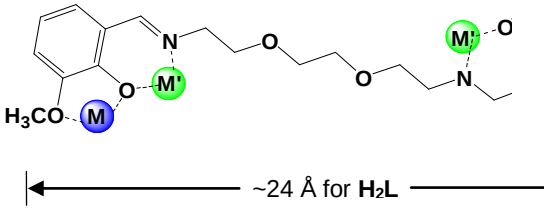
Abstract: Three multinuclear Cd-Ln complexes $[Er_2Cd_2L_2(OAc)_2(OH)_2(OCH_3)_2]$ (**1**) and $[Ln_2CdL_2(NO_3)_4]$ (Ln = Er (**2**) and Sm (**3**)) were prepared using a flexible long-chain Schiff base ligand. Interestingly, **1**-**3** show nano-rectangular-like structures (i.e. 8 × 12 × 12 Å for **1** and 7 × 10 × 15 Å for **2** and **3**). **1** has a tetranuclear structure with two lanthanide ions and two Cd^{2+} enclosed by two flexible Schiff base ligands (H_2L), while **2** and **3** show trinuclear structures with the Cd(II) ion located in the center. Upon excitation of the ligand-centered absorption bands, **1**-**2** and **3** show typical emission spectra for Er^{3+} and Sm^{3+} ions, respectively. Luminescence studies exhibit that **1** shows higher emission quantum yield than **2**.

Keywords: Self-assembly; Lanthanide nanoclusters; Schiff base ligands; Crystal structures; Visible and NIR luminescence properties

1. Introduction

Luminescent polynuclear d-f nanoclusters are currently of interest for potential applications in optoelectronics, magnetism and biology [1, 2]. For example, complexes of Nd(III), Er(III) and Yb(III) show near-infrared (NIR) emissions in the range of 900-1600 nm, where the absorption of the biological systems and fibre media is low. Consequently, these lanthanide complexes have potential applications in bioassays and luminescent probes [3-9]. One efficient way to construct polynuclear d-f clusters is self-assembly by metal-ligand coordination that organizes individual molecular components into frameworks.

In our previous studies, some polynuclear d-f complexes (i.e. d = Zn(II), Cd(II), Cu(II), Ni(II)) have been constructed by the use of salen-type Schiff base ligands [10-15]. Cadmium(II) complexes have excellent luminescent properties in the blue or green region [16,17], and may be used to sensitize the luminescence of the Ln(III) ions efficiently in Cd-Ln complexes. Thus, we report here three Cd-Ln clusters with a long-chain Schiff base ligand N,N'-bis(3-methoxysalicylidene)(1,2-bis(ethoxy)ethane)-1,6-diamine (H_2L), which has a flexible $(CH_2)_2O(CH_2)_2O(CH_2)_2$ backbone (Scheme 1). They are $[Er_2Cd_2L_2(OAc)_2(OH)_2(OCH_3)_2]$ (**1**) and $[Ln_2CdL_2(NO_3)_4]$ (Ln = Er (**2**) and Sm (**3**)). Interestingly, **1-3** show nano-rectangular-like structures, with sizes of approximately 8 × 12 × 12 Å and 7 × 10 × 15 Å for **1** and **2**-**3**, respectively. All of these clusters display the typical emission spectra of lanthanide ions. For the Cd-Er complexes, with the Ln(III) centers enclosed within the rectangular-like structure, **1** shows better **NIR** luminescence properties than **2**.



Scheme 1. Flexible long-chain Schiff base ligand H_2L.

2. Experimental

2.1. Materials and General Methods

Metal salts and solvents were purchased from Meryer and used directly without