

Synthesis, characterization and properties of 1,2,4-triazolo[3,4-b][1,3,4]thiadiazole derivatives and their europium complexes



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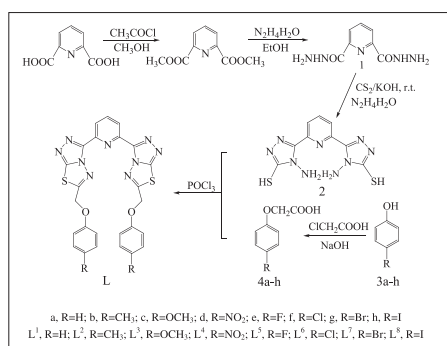
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HIGHLIGHTS

- Eight novel europium complexes have been prepared and characterized.
- All the target europium complexes emit characteristic fluorescence of europium ions.
- The relationship between the structure of ligands and luminescence intensity of the europium complexes have been discussed.
- The electrochemical properties of the title complexes have been estimated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 April 2014

Received in revised form 27 May 2014

Accepted 9 June 2014

Available online 19 June 2014

Keywords:

Triazolo

Complexes

Rare earth

Synthesis

Electrochemical properties

Luminescence

ABSTRACT

Eight novel 1,2,4-triazolo[3,4-b][1,3,4]thiadiazole derivatives and their corresponding Eu(III) complexes were synthesized and characterized. From the spectral studies it has been concluded that the title Eu(III) complexes display six coordination. The investigation of the luminescence properties of the title complexes showed that the ligands favor energy transfers to the emitting energy level of europium ions. The title Eu(III) complexes exhibited characteristic emissions of europium ions, and possessed strong luminescence intensities, good fluorescence quantum yields, and the highest fluorescence quantum yield is up to 0.522. Furthermore, the luminescence intensity of the complex with chlorine-substituted group is the strongest than that of other complexes. The exploration of the electrochemical properties of the title complexes shows that the introduction of electron-donating groups can increase the HOMO energy levels, LUMO energy levels and the oxidation potential of the complexes, however, the result of introduction of electron-withdrawing groups was just opposite.

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Introduction

Rare earth complexes have quickly become the focus of research in academia on the basis of their specific physical and chemical properties. Rare earth organic complexes often show good optical properties, mainly due to their large Stokes shifts,

Abbreviations: NMR, nuclear magnetic resonance; UV–Vis, ultraviolet visible; EDTA, ethylenediaminetetraacetic acid; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

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narrow emission bandwidths and long luminescence lifetimes [1,2], and they have been widely used in biomedical and functional materials [3], such as lasers materials [4], analytical and structure probe [5,6], and light emitting diodes [7,8]. The efficiency of ligand absorption in the UV region, ligand-to-metal energy transfer and rare earth luminescence play an important role in determining luminescence intensity [9]. Therefore, it is significant to design and synthesize the ligand, whose triplet energy level matches better to the emitting level of the rare earth ions. The 1,2,4-triazolo[3,4-b][1,3,4]thiadiazole ring systems have been extensively studied due to their properties with respect to versatile biological activities including antibacterial, antifungal, anticancer, antitubercular and analgesic activities and other potential applications [10,11]. However, 1,2,4-triazolo-[3,4-b][1,3,4]thiadiazoles have been seldom reported in literature with their corresponding rare earth ions complexes due to their poor solubility, not to mention the luminescence properties of their rare earth complexes. On the other hand, the triazole-thiadiazole compounds possess good conjugated plane, rigid structure and various coordination sites, are theoretically suitably used as the organic ligand of the rare earth luminescent complexes.

In this paper, we tried to design and synthesize a series of novel triazolo-thiadiazole systems and their Eu(III) complexes, investigated the luminescent and electrochemical properties of the complexes and explored the relationship between the structure of the ligand and the performance of complexes. This work might provide a reference for the development of the luminescent materials. The synthetic route of the 2,6-bis(4-(4-substituted phenoxy)methyl)-1,2,4-triazolo[3,4-b][1,3,4]thiadiazole-pyridine derivatives is depicted in Scheme 1.

Experimental

Materials

Pyridine-2,6-dicarboxylate and $\text{Eu}(\text{NO}_3)_3$ were prepared according to literature methods [12,13]. Chloroacetic acid and ethyl acetate were of CP grade, phenol derivatives and other reagents were of AR grade, and used without further purification.

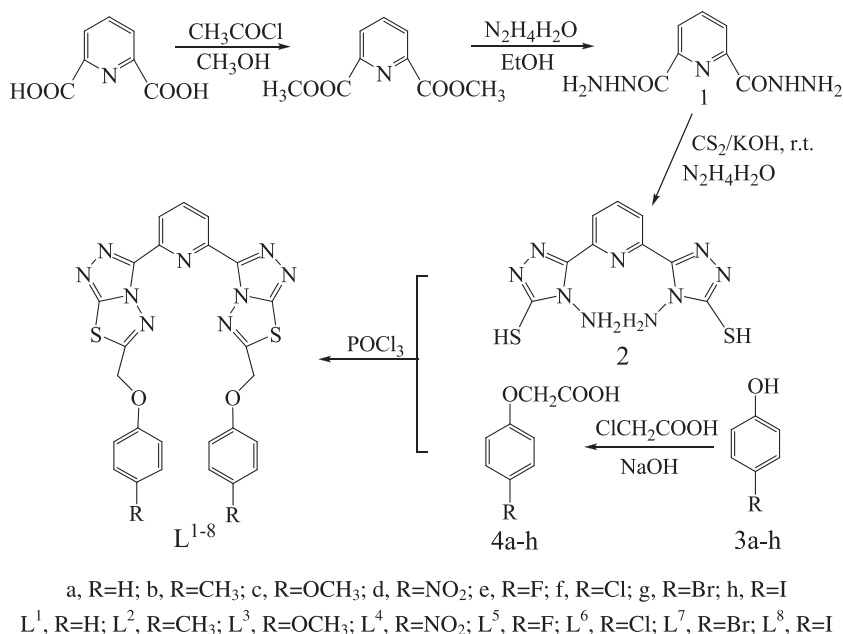
Methods

The melting points were determined on a TECH XT-4 binocular microscopic melting point apparatus (made in Beijing, China) and uncorrected. The europium ion was determined by ethylenediaminetetraacetic acid (EDTA) titration using xylenol orange as an indicator. The carbon, hydrogen, and nitrogen analyses were carried out using an Elementar Vario EL-III elemental analyzer, ^1H NMR spectra were measured on a Varian-400 NMR (400 MHz) spectrometer (both from Agilent Technologies Co., Ltd., Beijing, China), spectra were taken in CDCl_3 or DMSO-d_6 solution using tetramethylsilane (TMS) as an internal reference. IR spectra in the $4000\text{--}400\text{ cm}^{-1}$ region were measured using KBr pellets on a PerkinElmer spectrometer (PerkinElmer Chengdu, Chengdu, China). UV spectra were recorded on a LabTech UV-2100 (Columbia MO, USA) spectrophotometer using DMSO to dissolve the samples. Fluorescence measurements were made with a Hitachi F-2700 fluorescence spectrophotometer at room temperature. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was performed by NETZSCH STA 409PC simultaneous thermal analyzer with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Cyclic voltammetry (CV) measurements were performed using a CHI 660d electrochemical workstation under nitrogen. A three-electrode cell is equipped which consist of a glass carbon working electrode, Pt wire as auxiliary electrode, standard calomel electrode as reference electrode and using ferrocene ($E_{\text{ox}} = 0.3\text{ eV}$) as an external standard, sodium nitrite solution (0.1 M) as electrolyte, DMSO as solvent. The cyclic voltammogram was recorded at a scan speed of 100 mV s^{-1} at a sensitivity of 1 mA.

General procedure for the synthesis of the intermediates

Synthesis of pyridine-2,6-dihydrazide (1)

Pyridine-2,6-dimethyl ester (53 mmol, 10.34 g) and anhydrous ethanol (200 mL) were added into a 500 mL three-necked flask, the mixture was heated to $85\text{ }^\circ\text{C}$. Next, hydrazine (30 mL, 85%) was added to the mixture and refluxed for 6 h. Then the reaction mixture was distilled under reduced pressure in order to remove most of the solvent, and diluted with some distilled water, and then a large



Scheme 1. Synthetic route of the ligands L¹⁻⁸.

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