Journal of Molecular Structure 1099 (2015) 204–208

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Detection of double analytes by employing new luminescent lanthanide probe

Qianmin Ma [b], Qianming Wang [a, b, c, *]

[a] Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry & Environment, South China Normal University, Guangzhou 510006, PR China
[b] School of Chemistry & Environment, South China Normal University, Guangzhou 510006, PR China
[c] Guangzhou Key Laboratory of Materials for Energy Conversion and Storage, 510006, PR China

ARTICLE INFO

Article history:
Received 17 April 2015
Received in revised form
17 June 2015
Accepted 18 June 2015
Available online 20 June 2015

Keywords:
Phenanthroline
Lanthanide
Luminescence
Sensor
Anion

ABSTRACT

The synthesis and spectroscopic features of 1,4-bis([1,10] phenanthroline-[5,6-d] imidazol-2-yl) benzene (BPIB) with its europium (III) complex have been described. Characteristic red emissions can be achieved upon the excitation at 369 nm. This compound exhibited ultraviolet absorption shifts as well as fluorescence emission quenching upon exposure to Cu^{2+} ions. Hence, it can be utilized as a responsive copper sensor in terms of double routes including naked-eye observation and fluorescent probing. In the case of anions, this sensor could be used for direct determination of F^- in DMSO through fluorescence signal changes with satisfied results.

1. Introduction

The development of novel chemo-sensors has been extensively investigated because they can be applied in biological and environmental detection [1,2]. It has been accepted that copper behaves as an ecological pollutant and could enter the living cells at elevated concentrations [3–5]. The search for effective methods in detecting copper ions will be a real challenge. On the other side, the synthesis of different chemical transducers to selectively recognize various anions also has been attracted great attention because they play important roles in health, food and biological processes [6–8]. Among those anions, fluoride has unique chemical properties and it has been frequently used in nerve gas and drinking water analysis [9–11]. Hence, many efforts have been explored to make new probe for its recognition.

In recent years, lanthanide complexes have been investigated owing to special electronic and optical characteristics such as long lifetime, sharp emission peaks and large Stokes shifts [12,13]. In particular, they emerged as luminescent sensors to detect various guest ions [14]. In this field, chemical sensing using fluorescence to signal a recognition event has been extensively discussed. However, color change study as another powerful transduction way was limited based on lanthanide edifices. It will contribute for the fast detection and the feasibility of naked-eye detection for analysts [15,16]. In this work, 1,4-bis([1,10] phenanthroline-[5,6-d] imidazol-2-yl) benzene was synthesized (abbreviated as BPIB) and its europium complex has been assembled (Fig. 1). The resultant compound provided strong and direct metal coordination capacity and showed interesting luminescence properties [17,18]. Furthermore, imidazole moiety can be used as building blocks for anion binding and sensing [19,20]. We demonstrate that the incorporation of the ligand in the form of europium complex leads to selective copper sensing as well as colorimetric responses which are visible to the naked eyes. In addition, fluoride anion induced quenching (*on to off*) has also been studied. It is the pioneer work concerning the use of single europium complex for the recognition and colorimetric sensing of both cation and anions.

2. Experimental

2.1. Materials and characterizations

1,10-phenanthroline, dibenzoyl methane and europium oxide

* Corresponding author. Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry & Environment, South China Normal University, Guangzhou 510006, PR China.
E-mail address: qmwang@scnu.edu.cn (Q. Wang).

http://dx.doi.org/10.1016/j.molstruc.2015.06.057
0022-2860/

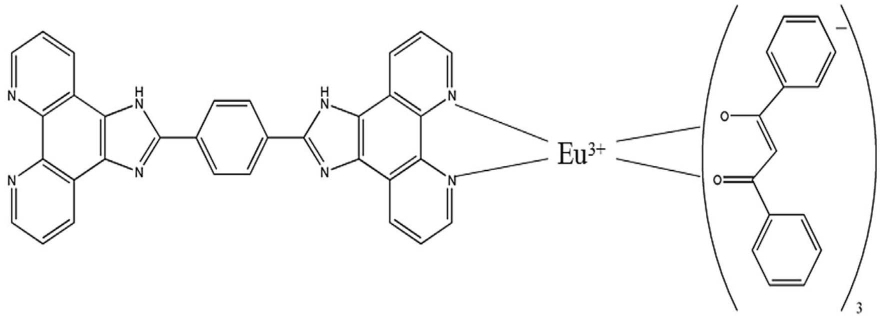

Fig. 1. Synthesis route of europium complexes.

were purchased from Aladdin Reagent Company. All the other organic solvents and reagents were provided by Guangzhou Chemical Reagent Factory and used without further purification. Europium (III) acetate hydrate was prepared according to the reference [8]. ^{1}H-NMR spectra were recorded at room temperature on a Varian 500 (500 MHz) using tetramethylsilane, TMS, as an internal standard. Fluorescence emission spectra were recorded with a computer controlled HITACHI F-2500 fluorescence spectrophotometer with a 150 W xenon lamp as the excitation source (excitation slit = 5 nm; emission slit = 5 nm; voltage 400 V). The measurements of UV–vis absorption spectra were carried out through a SHIMADZU UV-1700 Spectrophotometer equipped with a deuterium lamp and a tungsten lamp as light sources (resolution = 2 nm). Elemental analysis was carried out with an Elementar Vario EL elemental analyzer.

2.2. Synthesis of 1,10-phenanthroline-5,6-dione

Concentrated H_2SO_4 (35 ml) was added in a 250 ml three-necked flask at 0 °C. 1,10-phenanthroline (2.5 g, 28 mmol) was slowly added in this three-necked flask. Then KBr (5 g, 42 mmol) and HNO_3 (17.5 ml) were added at 5 °C. After stirring at room temperature for 20 min, the temperature was increased at 130 °C for 2 h. The hot yellow solution was poured over 150 g of ice and water and neutralized carefully with Na_2CO_3 until the pH of 6 ~ 7. The reaction mixture was extracted with $CHCl_3$. The resultant solution was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The precipitate was purified further by crystallization from absolute ethanol to give 2.4 g (96%) of 1,10-phenanthroline-5,6-dione.

2.3. Synthesis of BPIB

A mixture of 1,10-phenanthroline-5,6-dione (0.21 g, 9 mmol), ammonium acetate (1.54 g, 180 mmol), terephthalaldehyde (22.3 mg, 4.5 mmol) and glacial acetic acid (10 mL) was added in a three-necked flask and refluxed for 4 h at 95 °C, and then cooled to room temperature. The precipitate was collected, washed with H_2O for three times, and dried in vacuo at 50 °C, and a greenish yellow powder was obtained with a yield of 96.0 mg ^{1}H NMR (DMSO-*d6*, ppm), characterization results are as follows: 14.01 (2H, s, H–N), 9.09 (4H, d, J = 4.5 Hz, H-Py), 9.04 (4H, d, J = 5.0 Hz, H-Py), 8.53 (4H, H-Py), 7.94 (4H, H-Ph).

2.4. Synthesis of europium (III) complex

A mixture of BPIB (250 umol), europium(III) acetate hydrate (258 umol), dibenzoylmethane (750 umol) was dissolved in ethanol (50 ml) within a 100 ml round-bottom flask. The whole mixture was refluxed for 3 h when pH value was adjusted to 7. Then the resulting precipitate was collected and washed twice with water and ethanol to give the titled complex. Finally, the obtained complexes were confirmed by elemental analysis (EA). Eu(dibenzoylmethane)$_3$BPIB·H_2O EA has found: C, 68.37; H, 3.81; N, 8.18%, Anal. Calcd for $C_{77}H_{53}N_8O_7Eu$: C, 68.29; H, 3.94; N, 8.27%.

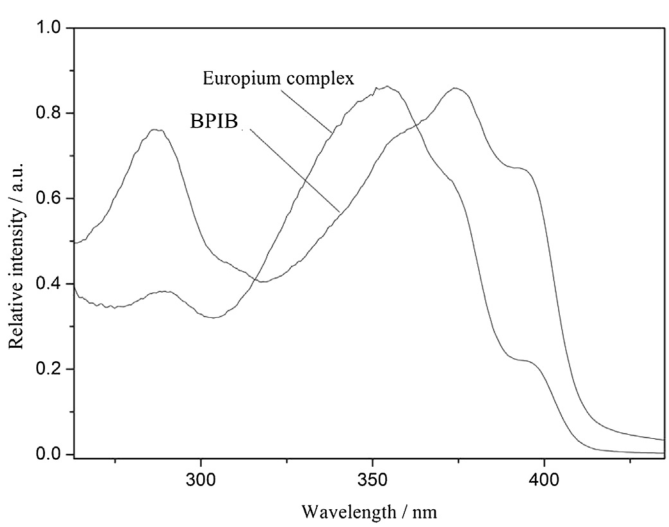

Fig. 2. UV–vis absorption spectra of pure BPIB and europium complexes in DMSO (10^{-6} M).

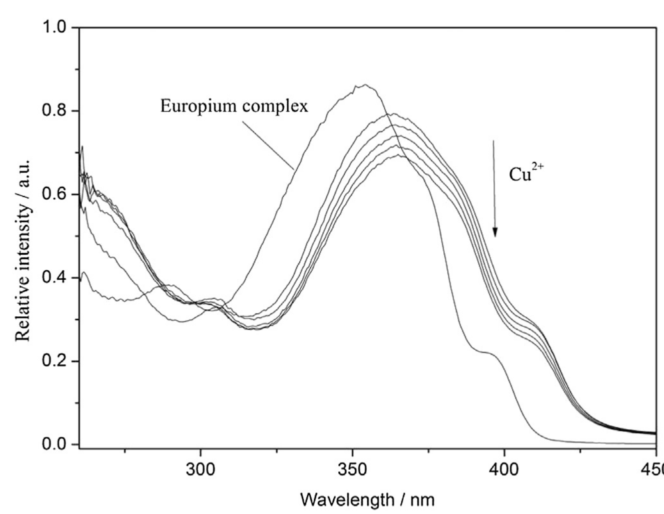

Fig. 3. UV–vis absorption spectra of the europium complex in DMSO (10^{-6} M) with the addition of Cu^{2+} from 10^{-6} M to 10^{-5} M (Cu^{2+} concentration increases along the arrow).