



## An efficient Eu-based anion-selective chemosensor: Synthesis, sensing properties, and its use for the fabrication of fluorescent hydrogel probe

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### ARTICLE INFO

#### Article history:

Received 9 October 2012  
Received in revised form  
19 November 2012  
Accepted 19 November 2012  
Available online 29 November 2012

#### Keywords:

Eu-complex  
Anion sensor  
Optical sensor  
Hydrogen bonding interaction  
Hydrogel probe  
Molecular oxygen

### ABSTRACT

A novel Eu-complex Eu(TTA)<sub>2</sub>vinyl-phen has been designed and synthesized via simple reaction as an efficient fluorescent sensor for F<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. The anion-sensitivity of Eu-complex was evaluated using a series of anion in DMSO solution. On binding with F<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, or H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, fluorescence quenching of Eu-complex was easily observed, while no obvious fluorescence change could be observed in the presence of other anions. More importantly, the Eu-complex exhibited excellent selectivity and sensitivity for F<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> in water/DMSO (5/5) solution. The titration results of UV-vis, fluorescence, and <sup>1</sup>H NMR spectra indicated that the fluorescence quenching can be attributed to the strong hydrogen bonding interaction between anions and imidazole group of Eu-complex. To meet application requirements for biological and environmental detection in water, we successfully prepared a Eu-based fluorescent hydrogel probe using Eu(TTA)<sub>2</sub>vinyl-phen and *N*-isopropyl acrylamide (NIPAAm) as monomers through free radical copolymerization in DMF. Emission spectra titration experiments indicated that this hydrogel probe can effectively recognize H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (detection limit 10<sup>-5</sup> M), but cannot recognize F<sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup> in pure water. To the best of our knowledge, this is first report that Eu-based fluorescent hydrogel probe for H<sub>2</sub>PO<sub>4</sub><sup>-</sup> detection in pure water. In addition, the emission of Eu-complex is also found to be sensitive to molecular oxygen through energy back-transfer mechanism.

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### 1. Introduction

In the last decade, the development of synthetic sensors for anions has attracted considerable attention within the field of supramolecular chemistry due to the fact that a large number of biological processes involve the recognition of anionic species [1]. Among these anions, fluoride plays a critical role in nerve gas, drinking water analysis, and refinement of uranium [2]. In addition, the important role of carboxylates in many ligand-binding interactions with proteins motivates fundamental studies of carboxylate recognition and sensing, ranging from the simple acetate anion to more biologically relevant amino acids and di- and tricarboxylates [3]. Also, metabolic pathways driven by the hydrolysis of adenosine triphosphate involves the release of orthophosphate and pyrophosphate, and synthetic receptors selective for these anions have also been the objective of numerous studies [4]. Hence, the development of molecular systems combining both anion

recognition components and signaling units for the use as anion sensors is of high interest for probing biological systems.

In past decades, considerable work has been devoted to the design of fluorescent probes and sensors because they provide the basis of analytic methods useful in environmental, biological, and metabolic fields. Unfortunately, the lifetime of the emission from the excited states of these common synthetic molecules is quite short (usually range of nano-seconds or sub-microseconds), and their emission were easily affected by auto-fluorescence and light scattering from surrounding biological environments [5]. To overcome these problems, the lanthanide complex (such as Eu-, and Tb-complex), with long emission lifetime has appeared as a new and active area of research for anion recognition [6]. Lanthanide fluorescence-based sensors have been developed based on their unique photophysical properties such as long lifetimes, sharp emission peaks, and large Stokes shifts. Wang et al. [7] found that the phenanthroline-based imidazole Eu- or Tb-complexes can efficiently detect different anions (F<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, and HSO<sub>4</sub><sup>-</sup>) through hydrogen bonding interaction by the virtue of rare earth f-f forbidden emission changes. Santos and Gunnlaugsson [8] synthesized some cyclen based Tb-complexes luminescent sensors; they can efficiently recognize CH<sub>3</sub>COO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> through

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hydrogen bonding interaction and potential metal ion coordination to  $\text{Tb}^{3+}$  ion. Gulgas and Reineke [9] have obtained a series of Eu-complexes containing macrocycles, which exhibited unique luminescent responses in the presence of strong hydrogen bond accepting anions ( $\text{F}^-$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{H}_2\text{PO}_4^-$ ) in DMSO solution. Recently, our group prepared a series of Eu-complexes based on phenanthroline derivatives as second ligands, the primary results of anions sensing indicated that these Eu-complexes can effectively recognize  $\text{CH}_3\text{COO}^-$  through hydrogen bonding interaction in DMSO solution [10]. However, many fluorescence anions sensor have been reported in the past decades of years, but the long fluorescence lifetime anions, which can efficiently sense and recognize  $\text{F}^-$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{H}_2\text{PO}_4^-$  in the presence of mixed anions ( $\text{HSO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) were limited. Most importantly, though amounts of anion sensors worked in organic solvents have been reported, the sensors can be used in pure water are very limited. As well-known, organic solvents are very destructive to the environment and life entity, so the sensors worked in organic solvents largely limited their application scope. Generally speaking, emissions of lanthanide complexes are very easy to be quenched by high frequency vibrations such as hydroxyl groups in water, so it is very significant to prepare a series of lanthanide complexes-based anion sensors which can be worked in pure water.

In the present work, we designed and synthesized a novel phenanthroline derivative 2-(4-(4-vinylbenzyloxy)phenyl)imidazo[4,5-f][1,10]phenanthroline (vinyl-phen), and use it as second ligand for preparing a long fluorescence lifetime and highly fluorescent property Eu-complex  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$ . Due to containing one N–H group in this system, we hope that the interaction between the hydrogen donor NH group in vinyl-phen and the hydrogen acceptor anions could change the structure of  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$ , and consequently affected its spectral property. To meet application requirements for biological and environmental detection, we successfully fabricated a fluorescent hydrogel probe using  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$  and NIPAAm as copolymer monomers through free radical copolymerization in DMF. Emission spectra titration results indicated that this hydrogel probe can effectively recognize  $\text{H}_2\text{PO}_4^-$  (detection limit  $10^{-5}$  M) in pure water. To the best of our knowledge, this is the first example of Eu-based fluorescent hydrogel probe for  $\text{H}_2\text{PO}_4^-$  detection in pure water.

## 2. Results and discussion

### 2.1. Design, synthesis, and characterization

With the aim of developing long fluorescence lifetime anions sensor, we chose the long emission lifetime Eu-complex  $\text{Eu}(\text{TTA})_2$  as a starting reagent to coordinate with vinyl-phen. Due to the neutral ligand vinyl-phen possess the imidazole group; it can form the strong hydrogen bonding interaction between N–H group and anions, so we predicted the long fluorescence lifetime Eu-complex had the excellent recognition ability for anions. The synthesis procedures of vinyl-phen and  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$  were outlined in Scheme S1. In the first step, 4-(4-vinylbenzyloxy)benzaldehyde was obtained from 1-(chloromethyl)-4-vinylbenzene and 4-hydroxybenzaldehyde reaction in DMF in the presence of KOH at room temperature in a high yield (85%). 2-(4-(4-Vinylbenzyloxy)phenyl)imidazo[4,5-f][1,10]phenanthroline (vinyl-phen) was formed by the condensation of 1,10-phenanthroline-5,6-dione and 4-(4-vinylbenzyloxy)benzaldehyde, according to a slightly modified imidazole ring preparation method [12]. The chromophore  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$  was synthesized according to the well-established procedure with a yield of 83% as a light-yellow powder. To overcome the high

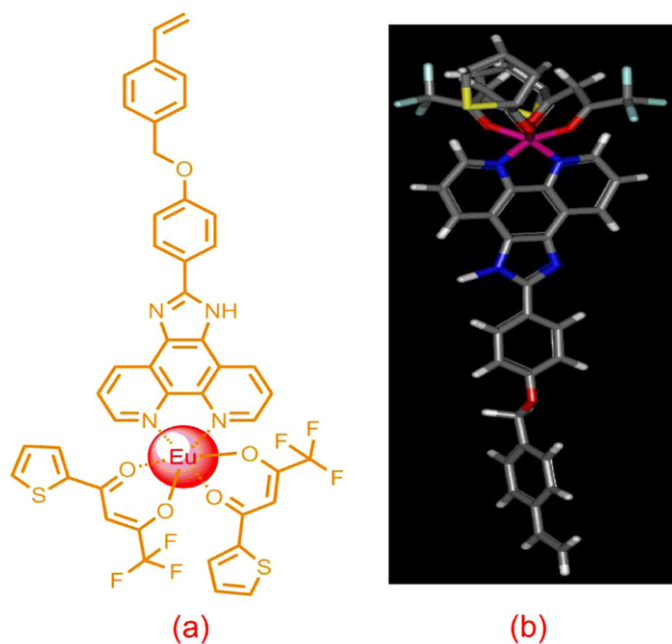


Fig. 1. The structure of title compound  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$  (a); the ground state geometry of  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$  calculated using the Sparkle/PM3 model (b).

frequency vibration of water molecules effect for the emission of europium ions, and developed a high sensitive and selective anions sensors in pure water, we first successfully fabricated a novel fluorescent hydrogel probe using NIPAAm and  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$  as monomers, and found this hydrogel can effectively detected  $\text{H}_2\text{PO}_4^-$  anion in pure water. The detailed synthesis procedure of Eu-based hydrogel was shown in Scheme 1.

The formation of vinyl-phen-based Eu-complex was reasonably proved by FTIR spectra of  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$ , in which not only the vibration absorptions at  $1624$  and  $1540\text{ cm}^{-1}$  attributed to  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$  in TTA were recognized but the characteristic absorption peaks at  $582$  and  $459\text{ cm}^{-1}$  originating from  $\text{Eu}\rightarrow\text{N}$  and  $\text{Eu}\rightarrow\text{O}$  in  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$  were recognized (Fig. S1). We tried our best to obtain single crystal of Eu-complex in our experiment, unfortunately, we failed. To deeply understand the complex structure, we optimized the molecular structure of the Eu-complex using Sparkle/PM3 model [13], and were displayed in Fig. 1. The polyhedron in  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$  is formed by four oxygen atoms of the TTA and two nitrogen atoms of the vinyl-phen molecule. The site symmetry of the complex is  $\text{C}_1$ , consistent with the luminescence spectrum. In addition, the ESI-MS spectrum result (ESI-MS:  $m/z$  1022.9 ( $\text{M}+\text{H}^+$ )) also indicated that the structure we obtained is  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$ . The HOMO and LUMO energy levels of  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$  was calculated according to the CV (Fig. S2) and UV-vis result, they were  $-6.29$  and  $-3.1$  eV, respectively. The thermograms showed that the Eu-complex exhibited good thermal stability with a weight loss 5% above  $260^\circ\text{C}$ , shown in Fig. S3.

In addition, the absorption and fluorescence properties of  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$  in solid and in THF solution were carried out, and the quantum yield ( $\Phi$ ) of  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$  in solid and in THF solution were calculated according to the typical Refs. [14,15], respectively. The detailed discussion was shown in Electronic Supporting Information (please see the section of absorption and fluorescence properties of  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$ ).

### 2.2. Anions sensing properties

In order to examine the sensing behavior of the  $\text{Eu}(\text{TTA})_2\text{vinyl-phen}$ , the absorption spectral change of Eu-complex upon the

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