



Novel lanthanide pH fluorescent probes based on multiple emissions and its visible-light-sensitized feature



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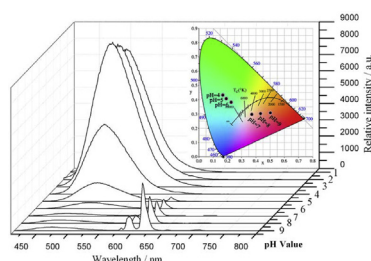
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HIGHLIGHTS

- The pH probe offers a very wide working range in water (pH 1–14).
- The emission changes have multiple colors.
- Long-lived excited state lifetimes of Eu(III) has been used.
- Two types of pH sensitive hydrogels were fabricated.

GRAPHICAL ABSTRACT

A new type of Eu(III) ofloxacin complex as the fluorescent pH indicator has been reported. Compared to pure ligand, the complex offers more distinguished color changes (green–red–blue) derived from both lanthanide line emissions and the secondary ionization steps of ofloxacin.



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ABSTRACT

A new type of Eu(III) ofloxacin complex as the fluorescent pH indicator has been presented. Compared to pure ligand, the complex offers more distinguished color changes (green–red–blue) derived from both lanthanide line emissions and the secondary ionization steps of ofloxacin. During the concentration dependence experiments, the photoluminescence studies on the complex showed that the excitation of this pH probe can occur at a very long wavelength which extends to visible range (Ex = 427 nm). Furthermore, the functional complex was successfully incorporated into soft networks and two novel luminescent hydrogels (rod and film) were fabricated. The soft materials also exhibited specific responses towards the pH variation. Finally, the onion cell-stain experiments were carried out to further confirm the validity of pH dependence and the results support the idea that the material will be suitable for monitoring biological samples in the future.

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1. Introduction

The determination of pH has been widely studied in a wide range of fields such as medical, environmental and life science [1,2]. Although it is well accepted that electrochemical pH sensing methods have been established and developed, the influence of electromagnetic radiations, special analytes (the presence of fluorides) and mechanical destruction would severely restrict its

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applications. Therefore, a number of fluorescent pH sensors have been designed as promising alternatives due to convenience, non-invasive and high-sensitivity [3–10]. However, the current techniques are still subject to several limitations. For example, the luminescent sensors usually have limited responsive ranges compared with electrochemical method. The ambient noise lights, auto-fluorescence and scattering signals will interfere with the detection processes. Last but not the least, the stabilities of the synthetic organic chromophores are relatively weak.

In order to circumvent the above drawbacks, lanthanide complexes as new luminescent species have been applied in biological sensing systems due to their predominant photophysical properties such as long-lived excited state lifetimes, sharp emission peaks and large Stokes shifts [11–13]. It has been reported that lanthanide complexes are highly sensitive to specific environmental factors or substances. They have been widely used for the detection of anions, cations, singlet oxygen, temperature, pH and DNA [14–21]. Here we provided a new type of ofloxacin chelated europium(III) complex which can be fully dissolved in water. It was found that the photophysical properties of the complex were highly pH-dependent, which could have a reversible and multiple emission color changes (green–red–blue) within the pH range from pH 1 to 14. More interestingly, the striking tunable color variation can be observed directly by naked eyes under 365 nm UV-light. It is known that most lanthanide complexes were very easy to be quenched by high frequency hydroxyl groups. Therefore, the exploration of highly stable host materials in aqueous media is also rather important. In addition, the retrieved powder materials (lanthanide complex) would be difficult in collection and reusability. For the sake of improving its limited long-term stabilities, new classes of soft matters have been incorporated. Polymeric hydrogels are well known for their tunable chemical and physical structure, good mechanical properties, high water content, and biocompatibility [22,23]. Moreover, they could accommodate various guest species and possess numerous possible applications including sensing devices and drug releases [24–26]. Thus, it would be interesting to assemble recyclable novel sensor materials by using hydrogels as new carriers.

In this work, we encapsulated the functional europium(III) complex into the polyvinyl alcohol (PVA) matrix and developed two novel lanthanide luminescent hydrogels (including rod-shape

and film), which were both very sensitive to pH values. These lanthanide-based soft-materials gained the advantage of broad pH response range and tri-color emissions that would be displayed task-specific usages in sensor devices.

2. Experimental

2.1. Materials

Ofloxacin (99%), Eu_2O_3 (99%), Polyving alkohol (PVA-1799, alcoholysis degree: 99.8–100%) were purchased from Aladdin company. Europium chloride was obtained by dissolving Eu_2O_3 in concentrated hydrochloric acid. All the other reagents were purchased from Guangzhou Chemical Reagent Factory and used without further purification.

2.2. Characterization

^1H NMR spectra were recorded at 293 K using a Bruker AVANCE III 500 (500 MHz) with tetramethylsilane, $\text{Si}(\text{CH}_3)_4$, as an internal standard; all chemical shifts were recorded in the standard notation of parts per million. ESI Mass spectra (MS) were obtained on a Thermo Finnigan LCQ Deca XP Max. Fluorescence spectra, emission lifetime and absolute quantum yields were measured using an Edinburgh FLS920 spectrometer (Great Britain), equipped with a 450 W lamp source. Absolute quantum yields (Φ) were determined at ambient temperature using an integrating sphere method. The deviations in the quantum yields were estimated to be 25% [27,28]. The errors for the lifetime measurements were within 10%. FT-IR spectra was measured within the $4000\text{--}400\text{ cm}^{-1}$ region on an infrared spectrophotometer, Prestingge-21, using the KBr pellet technique. UV-vis absorption spectra were obtained with a Shimadzu UV-2550 spectrophotometer. The fluorescence images were collected using a Nikon Eclipse TS100 inverted fluorescence microscope system (Japan), equipped with a 50 W mercury lamp source. The pH value data was acquired by a DDS-307 conductivity meter (INESA, Shanghai, China) under room temperature ($\sim 25^\circ\text{C}$). Elemental analysis was carried out in an Elementar Vario EL elemental analyzer. The molecular structure has been given in Fig. 1. Scanning electronic microscope (SEM) was measured with JSM-6360LV.

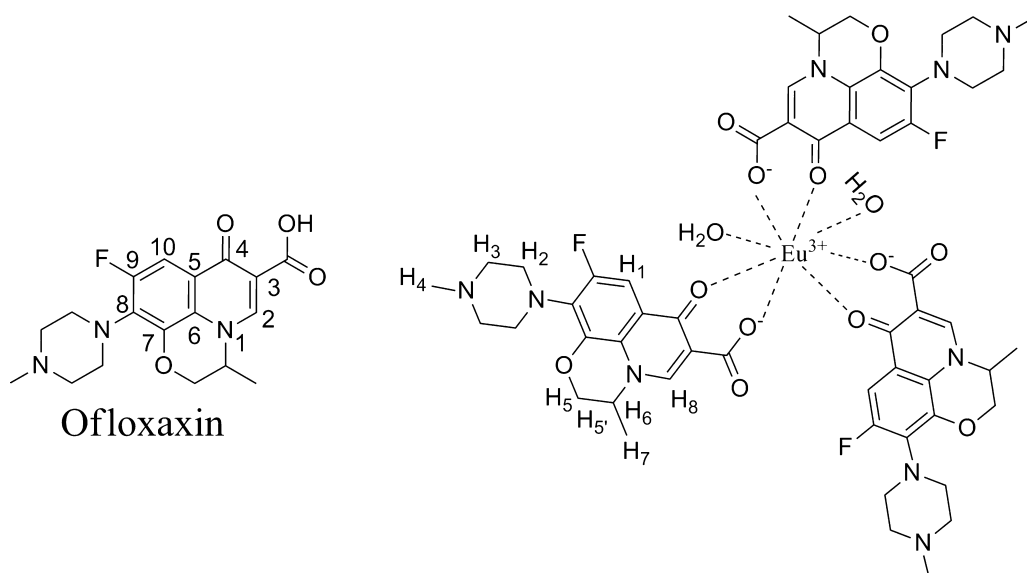


Fig. 1. Possible coordination structure of $\text{Eu}(\text{ofloxacin})_3 \cdot 2\text{H}_2\text{O}$ complex.

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