



Easy assembly of visible light excited lanthanide containing edifices and structural origin



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ARTICLE INFO

Article history:

Received 24 November 2014

Received in revised form

16 March 2015

Accepted 26 March 2015

Available online 4 April 2015

Keywords:

Lanthanide

Emission

Visible light excitation

Quinolone

Complex

Morphology

ABSTRACT

Reaction of quinolone type antibiotics (enrofloxacin, ciprofloxacin, norfloxacin and ofloxacin) with lanthanide ions (Eu^{3+} and Tb^{3+}) afforded eight kinds of complexes that can be dissolved in water. These compounds possess not only the advantages of long excited state lifetimes, but also allow excitation in the visible light range depending on the concentration variation. Especially the excitation wavelength of the terbium complexes can be extended into 405 nm. Theoretical studies demonstrated that the calculated energy gaps between HOMO and LUMO+1 orbital could be reduced and a dimeric structure was formed during the concentration experiments. Moreover, uniform and long rod-like structures (diameter: 100 nm; length: 10 μm) were achieved and concentration dependence has been investigated. The strategy of combining lanthanide characteristic emission nature and longer wavelength excitations can be applicable to the development of luminescent devices with controllable shapes.

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1. Introduction

Rare earth complexes have played important roles in chemical sensing, optical devices, medical diagnosis and amplifiers field due to their intrinsically better photoluminescence features [1,2]. The light absorption by the ligands and energy transfer to the metal ions induce large Stokes shifts. Forbidden transitions lead to long lifetimes and a group of well-defined narrow peaks with high color purity [3–11]. But most of them require ultraviolet lights for the lanthanides sensitization which were the main limitations for the industrial or biological uses. These short wavelengths could be closely related to the bio-medium (through absorption) and triggered phototoxicity for the living organs or tissues. For this purpose, representative cases of novel lanthanide complexes and new equipments with longer excitations have been designed in recent years [12–14]. As far as the complex is concerned, all the work

focused on the molecular design and modifications. It needs several organic synthesis circles or cautious steps. The preparation processes will be time-consuming. The latter example requires the use of two photons excitations and the expensive confocal biphotonic microscope will be necessary. Therefore, the development of easily accessible visible light sensitized lanthanide compounds will be a key challenge in gaining a deeper understanding about the structure and properties of rare earth chemistry. Our idea, which we find in this report from a purely molecular assembly viewpoint, is that it is not only critical to simply extend the conjugation planes (such as π system), but also it is reasonable to take into consideration the molecular assembly. Our assumption relies on the point that the assembled complex in good order will lead to red shifts occurred in the excitation bands. In the current work, the synthesis and characterizations of eight complexes of $\text{Eu}(\text{III})$, $\text{Tb}(\text{III})$ with norfloxacin, ciprofloxacin, enrofloxacin and ofloxacin have been reported (Scheme S1). A comprehensive analysis of the spectral data from the achieved complexes is given. First of all, their high stabilities allow practical uses in aqueous media and all the spectroscopic studies were carried out in water. Secondly, extensive photoluminescence studies revealed that concentration dependence was the most effective way to move the excitation bands towards the

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longer wavelength. Typical red shift values could be more than 130 nm. Thirdly, it allows the use of visible light (405 nm) to sensitize terbium containing complexes. Phototoxicity for biological tissues could be minimized. Fourthly, careful calculations were performed and the results found that the dimer formation of this quinolone type molecule has led to the band shifts to the red side. Fifthly, morphological transformation of the different complexes has been clarified and it has never been systematically studied. Last but not the least, simple devices such as hydrogel rods, films and LED bulbs were fabricated and the potential application features have been summarized.

2. Experimental

2.1. Materials

Enrofloxacin, ciprofloxacin hydrochloride, norfloxacin, ofloxacin, Eu_2O_3 , Tb_4O_7 and Polyvinyl alcohol (PVA-1799, alcoholysis degree: 99.8%–100%) were purchased from Aladdin company. Europium chloride and terbium chloride were obtained by dissolving their oxides in concentrated hydrochloric acid. All the other reagents were provided by Guangzhou Chemical Reagent Factory and used without further purification.

2.2. Characterization

Fluorescence emission and excitation spectra were measured using an Edinburgh FLS920 spectrometer (Great Britain). FT-IR spectra was measured within the 4000–400/cm region on an infrared spectrophotometer, Prestingge-21, using the KBr pellet technique. Ultraviolet–visible absorption spectra were collected by a Shimadzu UV-2550 spectrophotometer. Elemental analysis was carried out in an Elementar Vario EL elemental analyzer. SEM was measured using a Zeiss Ultra 55 scanning electron microscope. Photostability experiments were studied under the exposure to daylight. All samples were recorded intermittently during a time period of 48 h and kept under the same conditions at room temperature.

2.3. Synthesis of the lanthanide complex

The preparation of antibiotic quinolone chelate of europium (III)/terbium (III) complex has been described as follows: quinolones (enrofloxacin, ciprofloxacin hydrochloride, norfloxacin, ofloxacin) (3 mmol) and $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) were dissolved in 10 ml deionized water with magnetic stirring. The pH value of the solution was adjusted to 9 upon the addition of ammonium hydroxide. The mixture was stirred for 2 h at room temperature. Then the resulting precipitate was collected and washed twice with water and ethanol to give the titled complex. The obtained complexes were confirmed by elemental analysis (EA). $\text{Eu}(\text{enrofloxacin})_3 \cdot 2\text{H}_2\text{O}$ EA found: C, 53.43; H, 5.21; N, 10.03%. Anal. Calcd for $\text{C}_{57}\text{H}_{67}\text{F}_3\text{N}_9\text{O}_{11}\text{Eu}$: C, 54.20; H, 5.35; N, 9.98%. $\text{Eu}(\text{norfloxacin})_3 \cdot 3\text{H}_2\text{O}$ EA found: C, 49.91; H, 4.79; N, 10.94%. Anal. Calcd for $\text{C}_{48}\text{H}_{57}\text{F}_3\text{N}_9\text{O}_{12}\text{Eu}$: C, 49.66; H, 4.95; N, 10.86%. $\text{Eu}(\text{ciprofloxacin})_3 \cdot 2\text{H}_2\text{O}$ EA found: C, 50.97; H, 4.82; N, 10.53%. Anal. Calcd for $\text{C}_{51}\text{H}_{55}\text{F}_3\text{N}_9\text{O}_{11}\text{Eu}$: C, 51.95; H, 4.70; N, 10.69%. $\text{Tb}(\text{enrofloxacin})_3 \cdot \text{H}_2\text{O}$ EA found: C, 54.45; H, 5.31; N, 9.85%. Anal. Calcd for $\text{C}_{57}\text{H}_{65}\text{F}_3\text{N}_9\text{O}_{10}\text{Tb}$: C, 54.68; H, 5.23; N, 10.07%. $\text{Tb}(\text{norfloxacin})_3 \cdot 2\text{H}_2\text{O}$ EA found: C, 49.87; H, 4.91; N, 10.85%. Anal. Calcd for $\text{C}_{48}\text{H}_{55}\text{F}_3\text{N}_9\text{O}_{11}\text{Tb}$: C, 50.13; H, 4.82; N, 10.96%. $\text{Tb}(\text{ciprofloxacin})_3 \cdot 2\text{H}_2\text{O}$ EA found: C, 51.42; H, 4.73; N, 10.58%. Anal. Calcd for $\text{C}_{51}\text{H}_{55}\text{F}_3\text{N}_9\text{O}_{11}\text{Tb}$: C, 51.65; H, 4.67; N, 10.63%. $\text{Tb}(\text{ofloxacin})_3 \cdot 2\text{H}_2\text{O}$ EA found: C, 50.72; H, 4.76; N, 9.73%. Anal. Calcd

for $\text{C}_{54}\text{H}_{61}\text{F}_3\text{N}_9\text{O}_{14}\text{Tb}$: C, 50.83; H, 4.82; N, 9.88%. EA data of $\text{Eu}(\text{ofloxacin})_3 \cdot 2\text{H}_2\text{O}$ has been reported in previous literature [15].

2.4. Synthesis of lanthanide complex containing luminescent hydrogels

Briefly, lanthanide complex was dissolved in 10 ml water (concentration 10^{-2} M), then acrylamide monomer (1 g), ammonium persulfate (APS) (5 mg) and N,N'-methylenebisacrylamide (MBA) (1 mg) were added into the solution. The mixture was protected under nitrogen in a 10 ml tube and put into water bath at 60 °C for 1 h. After the mixture turned into colloidal materials, we broke up the test tube and got the target hydrogel.

For the preparation of luminescent hydrogel films, PVA was used as the soft matrix. The lanthanide complex (concentration 10^{-2} M) and PVA (500 mg) were dissolved in 10 ml deionized water in a 25-ml round bottom flask as solution A. The mixture was stirred at 95 °C until PVA was totally dissolved. Subsequently, 37 mg boric acid was dissolved in 5 ml deionized water as solution B. The pH value of solution B was adjusted to 7 by sodium hydroxide. Then, solution B was slowly added to solution A and stirred. The mixture was smeared on a glass sheet and kept in a fume hood under air atmosphere for 8 h at room temperature. Then, the dry luminescent film was achieved.

2.5. Theoretical calculation methods

All single-point calculations and geometry optimizations were performed at the B3LYP/6-31+G(d,p) level using the Gaussian 03 software. None of these optimized geometries have negative frequencies indicating that they are true minima. The visible absorption spectrum had been obtained for each structure by a single-point time-dependent extension TD-DFT calculation. The conductor polarizable continuum model (CPCM) was also applied to account for solvent effects (water) in electronic transitions.

3. Results and discussion

Infrared spectra reflect the formation of coordination structures. In the free ligand, an intense band located at around 1735 cm^{-1} was assigned to the carboxylic group. After the complexation, the C=O vibrations in COOH vanished and was replaced by two individual peaks at 1571 and 1490 cm^{-1} (Fig. S1). They were derived from asymmetric ($\nu_a\text{ COO}^-$) and symmetric vibrations ($\nu_s\text{ COO}^-$). The formation of coordination bonds between the carboxylic moiety and lanthanide ions has been proved. Similar changes were also found in other complexes (Figs not given). We could observe two bands at 270 and 320 nm in the ultra-violet absorption spectra (Fig. S2). These curves were ascribed to the conjugated structures in the complexes.

It has attracted considerable interests for extending the sensitization wavelength to visible range and the modification of the chelating chromophore has been regarded as a real challenge. The excitation spectra of representative complexes were provided in Fig. 1. A tendency was immediately observed. At a lower concentration (10^{-5} M), the major band of the spectrum occurred at 275 nm and it was consistent with the absorbance curve of the previous results. The spectral features enormously changed when the complex concentration increased to 10^{-4} M. The peak wavelength has red shifted to 360 nm. An important advantage is that the conventional europium (III) complex, which will arise in solution by concentration variation, could be excited at this longer wavelength. Things continued to move towards the more favorable side when the concentration has been increased stepwise. The largest change occurred at 10^{-2} M and it has red-shifted to 410 nm.

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