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Responsive europium emission for paralytic shellfish saxitoxin detection in water

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ABSTRACT

A water-soluble europium complex (**EuL1**), with the chromophore conjugated with both the Eu^{3+} ion and the aza-18-crown-6 ether moiety (receptor), were synthesized and its photophysical properties were studied. Saxitoxin (STX) selectively binds to **EuL1** and induced a 4-fold enhancement in europium emission in the presence of a variety of metal ions. A mechanistic study indicated that the luminescence enhancement could be triggered by a two-interaction binding mechanism, in which the initial interaction between STX and the aza-18-crown-6 ether moiety of **EuL1** induces the secondary interactions between STX and the Eu^{3+} ion, which resulted in displacement of the coordinated water molecule on Eu^{3+} ion.

1. Introduction

Paralytic shellfish poisons (PSP) are a group of marine neurotoxins produced by a variety of marine dinoagellates and natural water cyanophytes (blue-green algae) [1]. Bioaccumulation of PSP in marine organisms has become an increasing wide public concern on local marine environment, aquaculture industry and human health [2]. The most representative PSPs are saxitoxin (STX) and its analogues, such as neosaxitoxin and decarbamoylsaxitoxin (Fig. 1). The toxicity of STX is a result of binding towards the voltage gated sodium channel, blocking the passage of nerve impulses and leading to death *via* respiratory paralysis [3]. It is undoubtedly important and necessary to develop accurate and reliable tools for PSP toxins detection. There are several common methods for detection of STX, such as cells and mouse bioassays [4–6], immunoassays [7–19] and high-performance liquid chromatography (HPLC) coupled with chemical derivatization or mass spectrometric (MS) detection [20–24]. Although immune analysis technology is highly sensitive, convenient and rapid, it is not easy to obtain pure antibodies, cross-reaction of the toxin is low, and does not fully reflect the toxicity of the source of the sample. The post column fluorescent derivatization HPLC method is the most widely adopted analytical protocol for PSP determination. However, the current analytical process is tedious, and the results obtained are not always reproducible.

Compared to the existing analysis methods, molecular chemosensors could be a promising alternative for detection of PSP toxins. This strategy usually involves a reversible binding of the analyte with an appropriate receptor, follows by a cascade transduction of the binding event into the generation of physically measurable signals. Recently, the group of Gawley reported a number of organic chemosensors containing a diaza-18-crown-6 moiety for STX detection [25–27]. Our group is particularly interested in developing lanthanide-based luminescence sensors for biologically important molecules [28–31] due to their long-lived luminescence lifetimes and finger-print emission bands [32,33]. We have previously reported a europium-based fluorescent indicator for paralytic shellfish saxitoxin with the europium-crown-chromophore motif [28], in which the energy transfer efficiency of the chromophore to the Eu^{3+} ion was weakened since they were separated by the crown ether moiety (STX receptor). To improve the antenna effect, we herein report a new europium-based fluorescent STX sensor (**EuL1**) with the chromophore is conjugated with the both Eu^{3+} ion and the crown ether moiety (Fig. 1). This molecular architecture could provide a good environment for the chromophore-to-europium energy transfer efficiency and the fluorescence signal change upon binding with STX. Moreover, the positive charge of **EuL1** should improve the solubility of the complex for the detection of STX in water/food samples.

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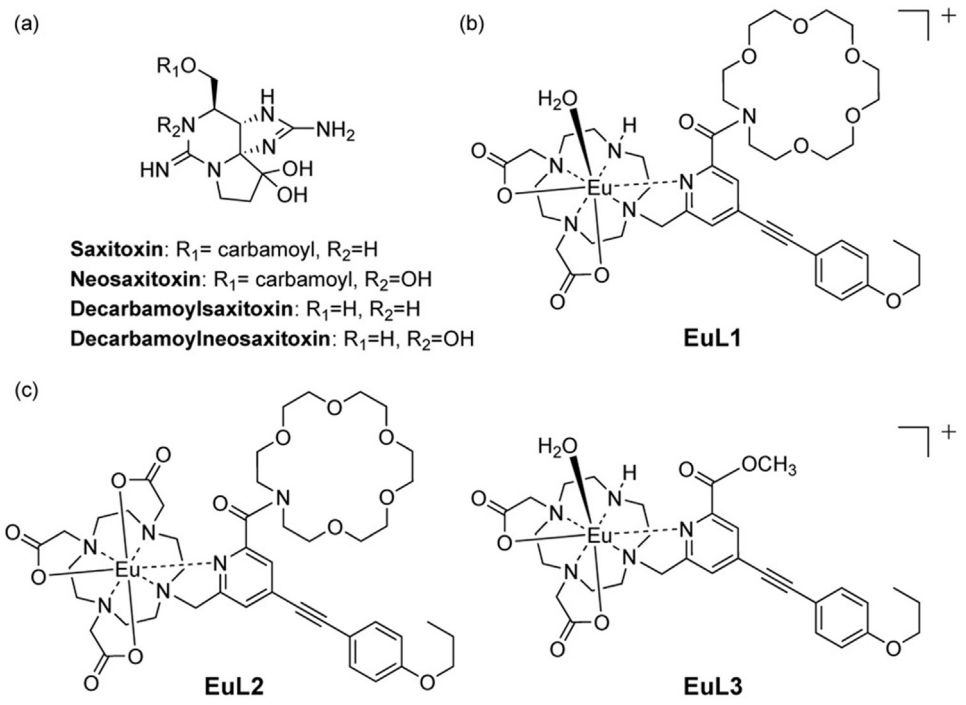
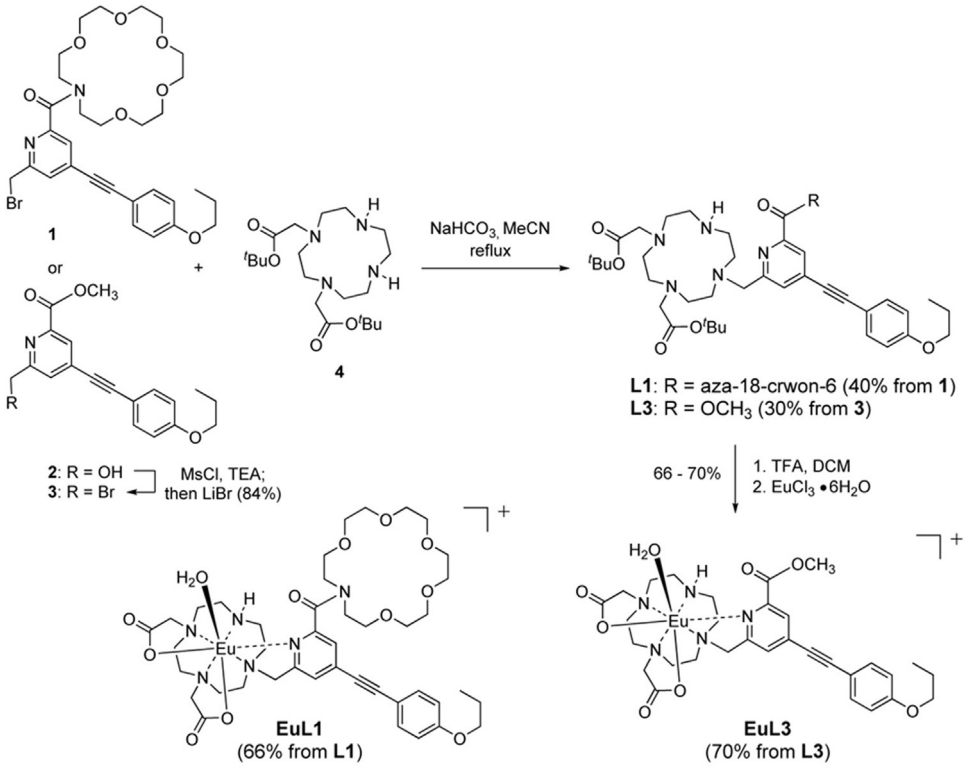


Fig. 1. (a) Structures of paralytic shellfish poisons (PSP), (b) Europium complex receptor **EuL1** and (c) control compounds **EuL2** and **EuL3**.



Scheme 1. Synthesis of Eu complexes **EuL1** and **EuL3**.

2. Experimental section

2.1. Materials and methods

All air and water sensitive reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially and used without further purification. NMR spectra were recorded on either a 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz), or 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz). High-resolution mass spectra were obtained from a MALDI-TOF Mass Spectrometer. UV–Visible absorption spectra in the spectral range 200–1100 nm were recorded by an HP UV-8453 spectrophotometer. Single-photon luminescence spectra were recorded using an Edinburgh Instrument FLS920 Combined Fluorescence Lifetime and