



Synthesis and time-gated fluorometric application of a europium(III) complex with a borono-substituted terpyridine polyacid ligand

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ABSTRACT

A new europium(III) complex with a borono-substituted terpyridine polyacid ligand, (4'-borono-2,2':6',2''-terpyridine-6,6''-diyl) bis(methylenitrilo) tetrakis(acetate)-Eu³⁺ (BTTA-Eu³⁺), has been designed and synthesized as a luminescence probe for hydrogen peroxide (H₂O₂). The complex is highly luminescent in aqueous buffers to display a typical Eu³⁺ emission pattern with a sharp emission peak at 610 nm and a long luminescence lifetime of 1.34 ms. Upon reaction with H₂O₂, the deboronation derivative of BTTA-Eu³⁺, (4'-hydroxy-2,2':6',2''-terpyridine-6,6''-diyl) bis(methylenitrilo) tetrakis(acetate)-Eu³⁺ (HTTA-Eu³⁺), can be generated. It was found that the luminescence of BTTA-Eu³⁺ was pH-insensitive, whereas that of HTTA-Eu³⁺ was pH-dependent and could be remarkably weakened in neutral and basic buffers, which allowed BTTA-Eu³⁺ to be a luminescence probe for the time-gated luminescence detection of H₂O₂ in neutral and basic buffers. The H₂O₂-BTTA-Eu³⁺ system was applied to monitor the kinetics of the palladium-catalyzed Suzuki cross-coupling reaction between BTTA-Eu³⁺ and bromobenzene, which suggested a useful strategy for the application of time-gated luminescence technique in catalysis reaction researches.

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1. Introduction

In the past thirty years, the Suzuki cross-coupling reaction has been used in widespread throughout the organic synthetic community for the syntheses of various organic compounds and natural products due to its accessibility and ease of handling [1–3]. In general, this reaction is accomplished by the palladium-catalyzed cross-coupling of an organic boronic acid with organic halides to form the carbon–carbon bonds, and has become the most versatile and useful synthetic reaction for the assembly of biaryl systems. Although new methodology continues to emerge and there are numerous examples involved to the development of the Suzuki cross-coupling reaction in the recent literatures, a simple and low-cost method that can be used for tracking the reaction process and optimizing the reaction conditions is still highly desirable [4–7].

For quantitatively detecting a trace analyte in complicated chemical systems, the fluorescence probe (or sensor/indicator)-based detection technique can be considered to be one of the most promising methods to replace other complex instrumental detection methods (GC, HPLC and others) due to its high sensitivity, simplicity in data collection, and experimental convenience. However, the application of fluorescence probe technique in catalysis

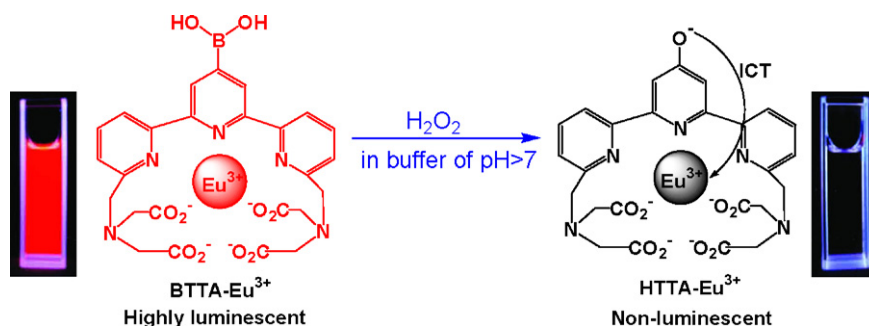
researches has rarely been reported. In recent several years, Chang and co-workers have developed a series of the fluorescent dye-boronate-based probes for H₂O₂ [8–13]. Upon reaction with H₂O₂, the hydrolytic deboronation of the probes can subsequently result in the increase in fluorescence intensity. Taking account of the selective response of the boronate group to H₂O₂, we are interested in the development of a boronic acid-containing luminescent probe for monitoring the kinetics of the Suzuki cross-coupling reaction by using the probe-H₂O₂ system to track the reaction process. One major challenge for this purpose is that the luminescence detection should be able to effectively eliminate the effect of the interfering background fluorescence from the coexisted compounds in the reaction.

It has been known that luminescent lanthanide complexes have several very unique luminescence properties, including long luminescence lifetime, large Stokes shift and sharp emission profile, which have enabled them to be used as luminescence probes, components of optoelectronic devices, or key sensor materials [14–21] for time-gated luminescence measurement to eliminate fast decaying background noises from the sample and scattering lights. Recently, we have demonstrated that some lanthanide complexes can act as useful time-gated luminescence probes for metal ions and reactive oxygen/nitrogen species [22–27]. Herein we describe the synthesis and characterization of a novel luminescent Eu³⁺ complex with a borono-substituted terpyridine polyacid ligand, (4'-borono-2,2':6',2''-terpyridine-6,6''-diyl) bis(methylenitrilo) tetrakis(acetate)-Eu³⁺ (BTTA-Eu³⁺), and its

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Scheme 1. Luminescence response reaction of BTTA-Eu³⁺ to H₂O₂ (the photos show the luminescence colors of the two complexes in 0.05 M Tris–HCl buffer of pH 7.4 under a 365 nm UV lamp).

application for the monitoring of the Suzuki cross-coupling reaction process between BTTA-Eu³⁺ and bromobenzene.

The new complex BTTA-Eu³⁺ is highly water-soluble with strong, pH-insensitive and long-lived luminescence, and can react with H₂O₂ to yield its deboronation derivative, (4'-hydroxy-2,2':6',2''-terpyridine-6,6''-diyl) bis(methylenitrilo) tetrakis(acetate)-Eu³⁺ (HTTA-Eu³⁺). Contrary to BTTA-Eu³⁺, HTTA-Eu³⁺ shows a pH-dependent luminescence behavior, and its luminescence intensity can be remarkably decreased with the pH increase from weakly acidic to basic solutions. This phenomenon is caused by the deprotonation (dissociation of proton) of the 4'-hydroxyl group in HTTA-Eu³⁺, since which forms a 4'-oxo anion in the ligand to quench the luminescence of the complex based on an intramolecular charge transfer (ICT) mechanism (Scheme 1). Because both the luminescence intensities of BTTA-Eu³⁺ and HTTA-Eu³⁺ can be measured by a time-gated mode, and by which the short-lived fluorescence from the coexisting substances cannot be collected due to the introduction of a delay time, the complex BTTA-Eu³⁺ can be used as a H₂O₂ probe capable of eliminating the effect of the interfering background fluorescence. In addition, the pyridine-4-boronic acid structure of BTTA allows it to be also a useful reagent for the Suzuki cross-coupling reaction with bromobenzene to synthesize (4'-phenyl-2,2':6',2''-terpyridine-6,6''-diyl) bis(methylenitrilo) tetrakis(acetic acid) (PTTA). In the reaction process, the PTTA formation can be monitored by using the H₂O₂–BTTA-Eu³⁺ system, since the luminescence of BTTA-Eu³⁺ can be quenched by H₂O₂, while that of PTTA-Eu³⁺ is not affected by H₂O₂. Based on this strategy, a simple time-gated luminescence method for tracking the kinetics of the Suzuki cross-coupling reaction between BTTA-Eu³⁺ and bromobenzene was developed.

2. Experimental

2.1. Materials and physical measurements

4'-Bromo-2,2':6',2''-terpyridine-6,6''-dibromomethyl [28] and PTTA [29] were synthesized according to the literature methods. Hydrogen peroxide (H₂O₂) was diluted immediately from a stabilized 30% solution, and was assayed by using its molar absorption coefficient of 43.6 M⁻¹ cm⁻¹ at 240 nm [30] before use. Unless otherwise stated, all chemical materials were purchased from commercial sources and used without further purification.

The ¹H NMR spectra were recorded on a Bruker Avance spectrometer (400 MHz). ESI-MS spectra were measured on a HP1100LC/MSD MS spectrometer. Absorption spectra were measured on a PerkinElmer Lambda 35 UV–vis spectrometer. Elemental analysis was carried out on a Vario-EL analyser. Time-gated luminescence spectra were measured on a PerkinElmer LS 50B luminescence spectrometer with the conditions of delay time, 0.2 ms; gate time, 0.4 ms; cycle time, 20 ms; excitation slit, 10 nm,

and emission slit, 5 nm. The luminescence quantum yields (ϕ_1) of the new Eu³⁺ complexes were measured in a 0.05 M Tris–HCl buffer of pH 7.4, and calculated by using the equation $\phi_1 = I_1 \varepsilon_2 C_2 \phi_2 / I_2 \varepsilon_1 C_1$ with a standard luminescence quantum yield of $\phi_2 = 0.16$ for the PTTA-Eu³⁺ complex ($\varepsilon_{335 \text{ nm}} = 14300 \text{ cm}^{-1} \text{ M}^{-1}$) [29]. In the equation, I_1 and I_2 , ε_1 and ε_2 , C_1 and C_2 are the luminescence intensities, molar extinction coefficients, and concentrations for the measured complex and the standard complex, respectively.

2.2. Synthesis of the ligand BTTA

The new Eu³⁺ chelating ligand BTTA was synthesized following the three-step reactions as shown in Scheme 2. The details are described as follows.

2.2.1. Synthesis of tetraethyl (4'-bromo-2,2':6',2''-terpyridine-6,6''-diyl) bis(methylenitrilo) tetrakis (acetate) (compound 1)

A mixture of 4'-bromo-2,2':6',2''-terpyridine-6,6''-dibromomethyl (0.49 g, 0.98 mmol), diethyl iminodiacetate (0.76 g, 3.92 mmol) and K₂CO₃ (0.81 g, 5.88 mmol) in 50 mL dry CH₃CN and 15 mL tetrahydrofuran (THF) was stirred at 50 °C overnight under a nitrogen atmosphere. After filtration, the filtrate was evaporated, and the residue was dissolved in 100 mL CH₂Cl₂. The solution was successively washed with 5% NaHCO₃, water and brine, and then dried with Na₂SO₄. After filtration and evaporation, the crude product was purified by silica gel column chromatography using CH₂Cl₂–CH₃OH (gradient from 100:00 to 97:3) as eluent, and then recrystallized from *n*-hexane to yield compound **1** (0.27 g, 38%) as a white solid. ¹H NMR (CDCl₃): δ 8.62 (s, 2H), 8.47 (d, $J = 7.6$ Hz, 2H), 7.85 (t, $J = 7.6$ Hz, 2H), 7.66 (d, $J = 7.2$ Hz, 2H), 4.23–4.17 (m, 12H), 3.69 (s, 8H), 1.3–1.24 (m, 12H). ESI-MS (m/z): 714.3 [M+H]⁺.

2.2.2. Synthesis of tetraethyl [4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)-2,2':6',2''-terpyridine-6,6''-diyl] bis(methylenitrilo) tetrakis (acetate) (compound 2)

After a schlenk tube was charged with Pd(PPh₃)₂Cl₂ (5.90 mg, 0.0084 mmol), KOAc (82.5 mg, 0.84 mmol) and bis(pinacolato)diboron (285 mg, 1.13 mmol), and flushed with an argon atmosphere, 10 mL dimethyl sulfoxide (DMSO, dried over molecular sieves and degassed with N₂ before use) and compound **1** (200 mg, 0.28 mmol) were added. The mixture was stirred at 80 °C for 24 h under an argon atmosphere, and then diluted with 100 mL CHCl₃. The solution was washed with 4 × 100 mL water, and then dried with Na₂SO₄. After filtration and evaporation, the crude product was recrystallized from *n*-hexane to yield compound **2** (100 mg, 46.9%) as a pale yellow solid. ¹H NMR (CDCl₃): δ 8.75 (s, 2H), 8.47 (d, $J = 8.0$ Hz, 2H), 7.84 (t, $J = 7.6$ Hz, 2H), 7.66 (d, $J = 7.6$ Hz, 2H), 4.23–4.17 (m, 12H), 3.68 (s, 8H), 1.40 (s, 12H), 1.29–1.26 (m, 12H). ESI-MS (m/z): 762.5 [M+H]⁺.

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