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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(methylenenitrilo) tetrakis(acetate)-Eu^{3+} (BTTA-Eu^{3+}), has been designed and synthesized as a luminescence probe for hydrogen peroxide (H_2O_2). The complex is highly luminescent in aqueous buffers to display a typical Eu^{3+} emission pattern with a sharp emission peak at 610 nm and a long luminescence lifetime of 1.34 ms. Upon reaction with H_2O_2, the deboronation derivative of BTTA-Eu^{3+}, (4′-hydroxy-2,2′:6′,2″-terpyridine-6,6″-diyl) bis(methylenenitrilo) tetrakis(acetate)-Eu^{3+} (HTTA-Eu^{3+}), can be generated. It was found that the luminescence of BTTA-Eu^{3+} was pH-insensitive, whereas that of HTTA-Eu^{3+} was pH-dependent and could be remarkably weakened in neutral and basic buffers, which allowed BTTA-Eu^{3+} to be a luminescence probe for the time-gated luminescence detection of H_2O_2 in neutral and basic buffers. The H_2O_2–BTTA-Eu^{3+} system was applied to monitor the kinetics of the palladium-catalyzed Suzuki cross-coupling reaction between BTTA-Eu^{3+} and bromobenzene, which suggested a useful strategy for the application of time-gated luminescence technique in catalysis reaction researches.

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 H_2O_2 [8–13]. Upon reaction with H_2O_2, 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 H_2O_2, 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-H_2O_2 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 Eu^{3+} complex with a borono-substituted terpyridine polyacid ligand, (4′-borono-2,2′:6′,2″-terpyridine-6,6″-diyl) bis(methylenenitrilo) tetrakis(acetate)-Eu^{3+} (BTTA-Eu^{3+}), and its

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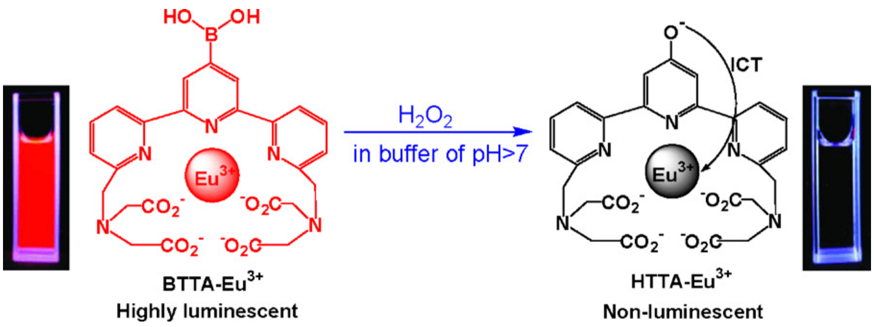


Scheme 1. Luminescence response reaction of BTTA-Eu^{3+} to H_2O_2 (the photos show the luminescence colors of the two complexes in 0.05 M Tris–HCl buffer of pH 7.4 under a 365 nm UV lamp).

application for the monitoring of the Suzuki cross-coupling reaction process between BTTA-Eu^{3+} and bromobenzene.

The new complex BTTA-Eu^{3+} is highly water-soluble with strong, pH-insensitive and long-lived luminescence, and can react with H_2O_2 to yield its deboronation derivative, (4′-hydroxy-2,2′:6′,2″-terpyridine-6,6″-diyl) bis(methylenenitrilo) tetrakis(acetate)-Eu^{3+} (HTTA-Eu^{3+}). Contrary to BTTA-Eu^{3+}, HTTA-Eu^{3+} 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-Eu^{3+}, since which forms a 4′-oxo anion in the ligand to quench the luminescence of the complex based on an intramelecular charge transfer (ICT) mechanism (Scheme 1). Because both the luminescence intensities of BTTA-Eu^{3+} and HTTA-Eu^{3+} can be measured by a time-gated mode, and by which the short-lived fluorescence from the coexisted substances cannot be collected due to the introduction of a delay time, the complex BTTA-Eu^{3+} can be used as a H_2O_2 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(methylenenitrilo) tetrakis(acetic acid) (PTTA). In the reaction process, the PTTA formation can be monitored by using the H_2O_2–BTTA-Eu^{3+} system, since the luminescence of BTTA-Eu^{3+} can be quenched by H_2O_2, while that of PTTA-Eu^{3+} is not affected by H_2O_2. Based on this strategy, a simple time-gated luminescence method for tracking the kinetics of the Suzuki cross-coupling reaction between BTTA-Eu^{3+} 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 (H_2O_2) 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 Eu^{3+} complexes were measured in a 0.05 M Tris–HCl buffer of pH 7.4, and calculated by using the equation $\phi_1 = I_1\varepsilon_2C_2\phi_2/I_2\varepsilon_1C_1$ with a standard luminescence quantum yield of $\phi_2 = 0.16$ for the PTTA-Eu^{3+} complex ($\varepsilon_{335\,nm} = 14300\,cm^{-1}\,M^{-1}$) [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

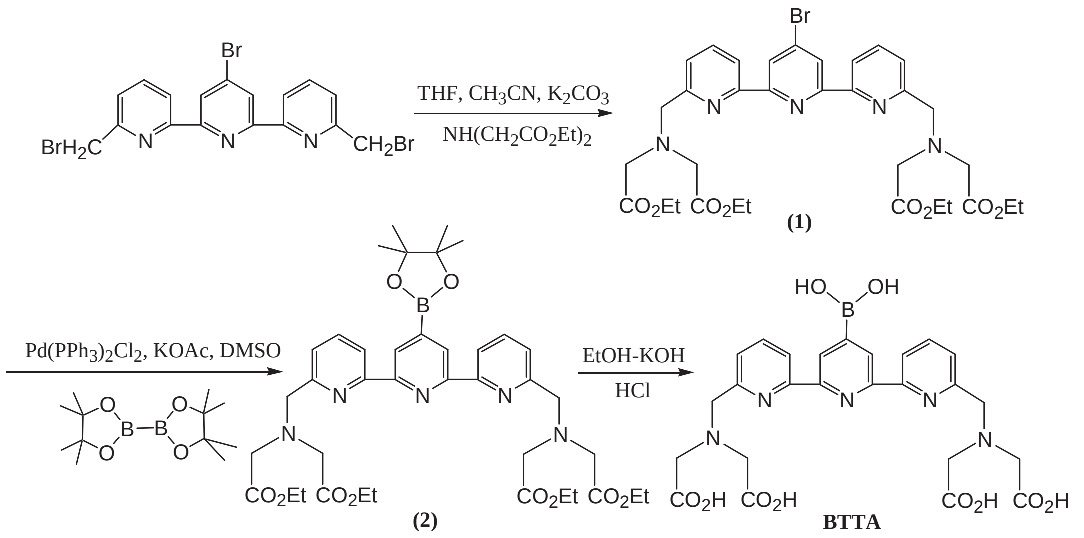
The new Eu^{3+} chelating ligand BTTA was synthesized following the three-step reactions as shown in Scheme 2. The details are described as follows.

2.2.1. Synthesis of tetraethyl (4′-bromo-2,2′:6′,2″-terpyridine-6,6″-diyl) bis(methylenenitrilo) 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 K_2CO_3 (0.81 g, 5.88 mmol) in 50 mL dry CH_3CN and 15 mL tetrahydrofuran (THF) was stirred at 50 °C overnight under an nitrogen atmosphere. After filtration, the filtrate was evaporated, and the residue was dissolved in 100 mL CH_2Cl_2. The solution was successively washed with 5% $NaHCO_3$, water and brine, and then dried with Na_2SO_4. After filtration and evaporation, the crude product was purified by silica gel column chromatography using CH_2Cl_2–CH_3OH (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 ($CDCl_3$): 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(methylenenitrilo) tetrakis (acetate) (compound *2*)

After a schlenk tube was charged with $Pd(PPh_3)_2Cl_2$ (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 N_2 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 $CHCl_3$. The solution was washed with 4 × 100 mL water, and then dried with Na_2SO_4. 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 ($CDCl_3$): 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 $[M+H]^+$.



Scheme 2. Synthesis procedure of BTTA.

2.2.3. *Synthesis of BTTA*

A mixture of compound **2** (200 mg, 0.263 mmol) and KOH (441 mg, 7.88 mmol) in 20 mL ethanol was stirred at room temperature for 24 h. After evaporation, the residue was dissolved in 15 mL water. The solution was added dropwise 1 M HCl to adjust the pH to ~3, and the suspension was stirred for 3 h at room temperature. The precipitate was filtered and washed with water. After drying, the solid was refluxed in 10 mL dry acetonitrile for 10 min. The product was filtered and dried to yield BTTA (120 mg, 80.5%) as a pale yellow solid. ^{1}H NMR (DMSO-d_6): δ 8.74 (s, 2H), 8.50 (d, J = 7.6 Hz, 2H), 8.01 (t, J = 7.6 Hz, 2H), 7.67 (d, J = 7.6 Hz, 2H), 4.15 (s, 4H), 3.60 (s, 8H). ESI-MS (*m/z*): 568.2 $[M+H]^+$. Elemental analysis calcd (%) for $C_{25}H_{26}N_5O_{10}B \cdot 2H_2O$ ($BTTA \cdot 2H_2O$): C 49.77, H 5.01, N 11.61; found (%): C 49.85, H 4.69, N 11.93.

2.3. *Luminescence response of BTTA-Eu^{3+} to H_2O_2*

The stock solution of BTTA-Eu^{3+} complex was prepared by *in-situ* mixing equivalent molar of BTTA (0.01 mmol) and $EuCl_3 \cdot 6H_2O$ (0.01 mmol) in 5.0 mL of 0.05 M Tris–HCl buffer of pH 7.4. The luminescence titration experiment of BTTA-Eu^{3+} with H_2O_2 was carried out by adding different concentrations of H_2O_2 (0.0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 mM) to 3.0 mL of 0.05 M Tris–HCl buffer of pH 7.4 containing 5.0 μM of BTTA-Eu^{3+}. After incubation for 30 min at 60 °C, the solutions were subjected to the time-gated luminescence measurement on the PerkinElmer LS 50B luminescence spectrometer.

2.4. *Luminescence monitoring of the Suzuki cross-coupling reaction*

To a mixture of $BTTA \cdot 2H_2O$ (3.0 mg, 0.005 mmol) in 7.4 mL acetone and 0.5 mL of 0.05 M $EuCl_3$ aqueous solution were added 1.7 mg of K_2CO_3 in 2.0 mL water, 3.0 mg of solid $Pd(OAc)_2$ and 0.1 mL of bromobenzene. After the solution was degassed and flushed with an argon gas, the solution was stirred at 40 °C under an argon atmosphere. At different reaction times, a portion of 30 μL reaction solution was added to 3.0 mL of 0.05 M Tris–HCl buffer of pH 7.4 containing 50 mM of H_2O_2. After incubating for 30 min at 60 °C, the time-gated excitation and emission spectra of the solutions were measured.

3. Results and discussion

3.1. *Design and synthesis of the probe*

It has been known that the oxidative deboronation of aryl boronic acids is chemically selective for H_2O_2 and involves the oxidative conversion of a C—B bond into a C—O bond [31]. In recent years, this reaction has been successfully used by Chang's group for the design of a series of organic dye-based fluorescent probes for H_2O_2 [8–13]. In this work, a novel Eu^{3+} complex, BTTA-Eu^{3+}, was designed as a H_2O_2 probe with several unique properties. At first, the 4′-borono group in the complex ligand allows the complex to be able to recognize H_2O_2 through the H_2O_2-mediated oxidative deboronation reaction, by which a new Eu^{3+} complex, HTTA-Eu^{3+}, that displays different luminescence behaviors from those of the probe itself can be yielded. In addition, the terpyridine polyacid structures of the ligands BTTA and HTTA not only enable their Eu^{3+} complexes to be highly stable and soluble in aqueous buffers, but also can provide an excellent antenna efficiency for sensitizing the Eu^{3+} emission with relatively long excitation wavelengths (>320 nm) by effectively shielding Eu^{3+} from the luminescence-quenching water molecules.

The new ligand BTTA was synthesized following the synthetic route as shown in Scheme 2. It can rapidly react with equivalent molar of Eu^{3+} to form a highly stable Eu^{3+} complex in aqueous buffers due to its nonadentate chelating property [28,29]. When BTTA-Eu^{3+} was challenged with a 5-fold excess of ethylenediamine tetraacetic acid (EDTA), a conditional stability constant was measured to be 8.2×10^{20} by Verhoeven's method [32]. Furthermore, no significant decay in luminescence intensity of BTTA-Eu^{3+} was found even after the solution was left at room temperature for a few weeks. These results indicate that the complex BTTA-Eu^{3+} has good kinetic and thermodynamic stabilities in aqueous buffers.

3.2. *Luminescence response of BTTA-Eu^{3+} to H_2O_2*

At first, to reveal the reaction course of the H_2O_2–BTTA-Eu^{3+} system, the room temperature UV absorption spectrum changes during the reaction of BTTA-Eu^{3+} (25 μM) with H_2O_2 (25 mM) in 0.05 M Tris–HCl buffer of pH 7.4 were recorded for 150 min at 15 min intervals. As shown in Fig. 1, accompanied by the gradually decrease of the absorption band of BTTA-Eu^{3+} at ~340 nm, the absorption band of BTTA-Eu^{3+} at 294 nm was gradually increased

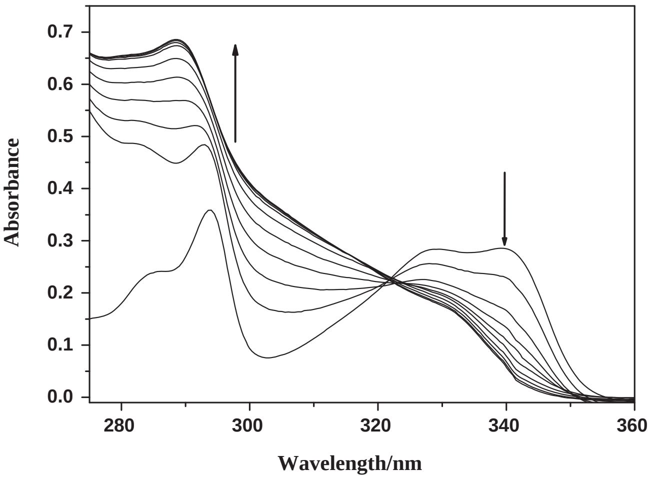


Fig. 1. UV absorption spectrum changes during the reaction of BTTA-Eu^{3+} (25 μM) with H_2O_2 (25 mM) at room temperature in 0.05 M Tris–HCl buffer of pH 7.4 for 150 min at 15 min intervals.

and blue-shifted to 288 nm with the increase of the reaction time from 0 to 90 min. After reaction for 90 min, the spectrum was kept at a stable pattern. These results indicate that the H_2O_2-mediated oxidative deboronation reaction of BTTA-Eu^{3+} is not rapid at room temperature, and also demonstrate that the $\pi \rightarrow \pi^*$ transition absorption of BTTA at 330–340 nm can be significantly weakened after the oxidative deboronation.

The temperature-dependent luminescence response kinetic curves of BTTA-Eu^{3+} (5.0 μM) to H_2O_2 (50 mM) were determined in 0.05 M Tris–HCl buffer of pH 7.4 to investigate the effect of temperature on the reaction between BTTA-Eu^{3+} and H_2O_2 (Fig. 2). Notably, the increase of reaction temperature was significantly beneficial to the increase of the reaction rate. In contrary to the slow reaction at temperature below 30 °C, the reaction could be remarkably quickened when the reaction was carried out at 60 °C. With this temperature, the reaction could be fully completed within 30 min.

Based on the above results, the time-gated excitation and emission spectra of BTTA-Eu^{3+} reacted with different concentrations of H_2O_2 were measured according to the conditions shown in Table 1. As shown in Fig. 3A, BTTA-Eu^{3+} showed the maximum excitation wavelength at 333 nm, and a typical Eu^{3+} emission spectrum ($\varepsilon_{333\,\mathrm{nm}} = 1.39 \times 10^4\ \mathrm{cm^{-1}\,M^{-1}}$, $\phi = 12.1\%$, $\tau = 1.34$ ms) with a main emission peak at 610 nm and several side peaks centred at 583, 593, 646, and 692 nm, corresponding to the ${}^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions of Eu^{3+} ion, respectively. Upon reaction with different concentrations of H_2O_2, due to the formation of HTTA-Eu^{3+}, the luminescence intensity of BTTA-Eu^{3+} was gradually decreased with an exponential correlation against the H_2O_2 concentration (Fig. 3B). By plotting the luminescence intensity (610 nm) changes ($\log(F_0 - F)/F$) against the H_2O_2 concentrations ($\log[H_2O_2]$) (Stern–Volmer equation) [33] in a range of 0.1–10 mM, a good linear relationship that can be express as $\log(F_0 - F/F) = 3.362 + 1.173\ \log[H_2O_2]$ ($r = 0.998$) was obtained (the inset in Fig. 3B). The product of BTTA-Eu^{3+} reacted with H_2O_2 was confirmed by ESI-MS spectrum, in which the base peak at m/z 538.2 $[M-H]^-$ could be assigned to be the molecular ion peak of HTTA-Eu^{3+}.

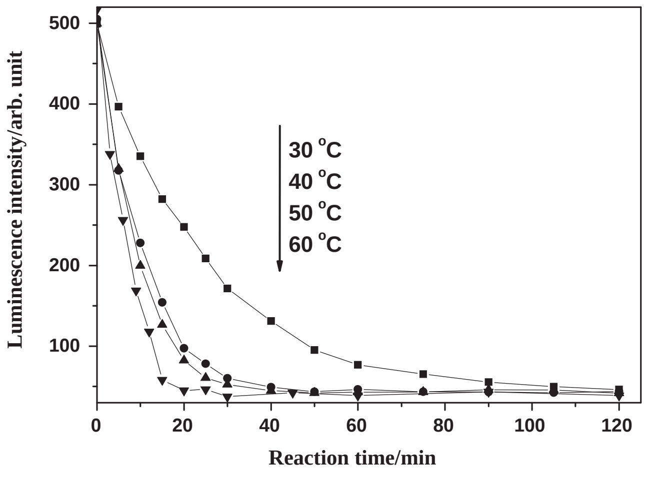


Fig. 2. Effect of temperature on the reaction of BTTA-Eu^{3+} (5.0 μM) with H_2O_2 (50.0 mM).

Table 1
Optimization conditions of BTTA-Eu^{3+} reacted with different concentrations of H_2O_2.

$C_{\mathrm{BTTA\text{-}Eu^{3+}}}$	Temperature	Reaction time	Buffer	pH
5.0 μM	60 °C	30 min	0.05 M Tris–HCl	7.4

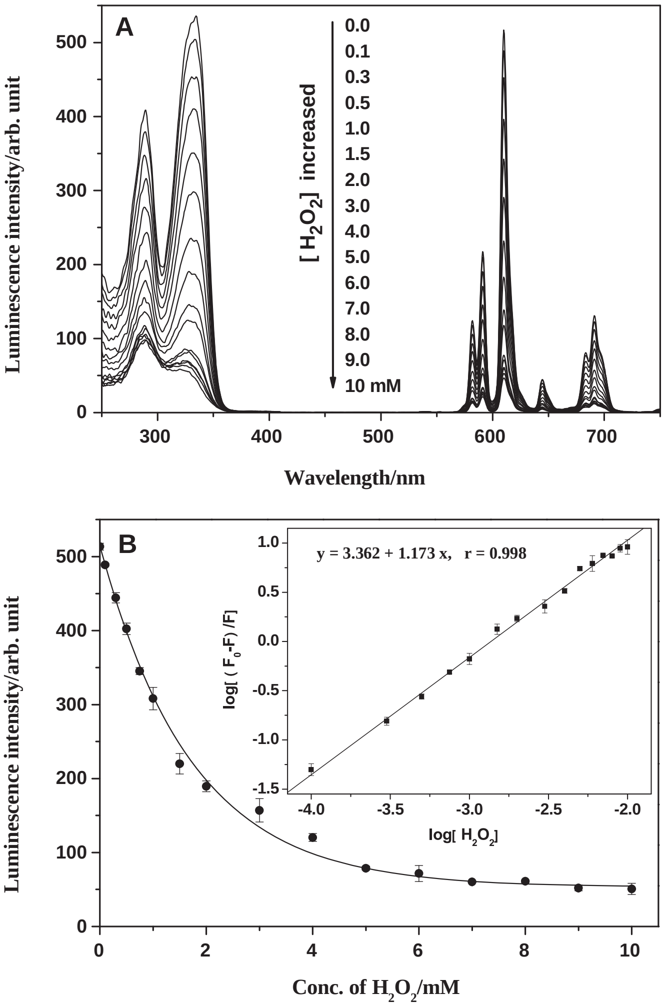
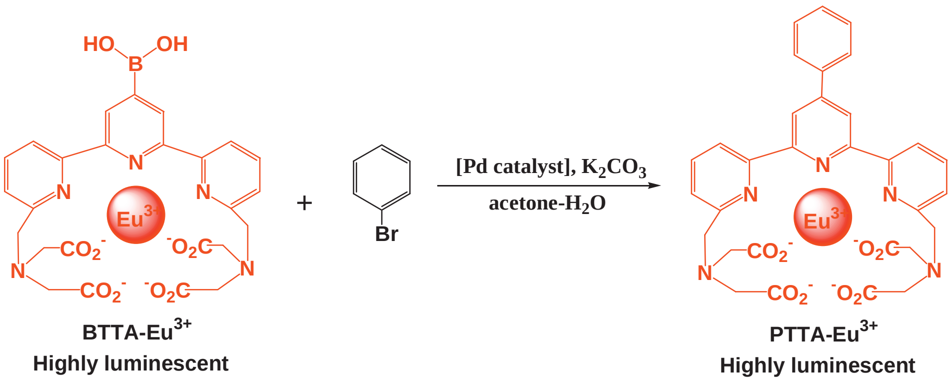


Fig. 3. (A) Time-gated excitation and emission spectra of BTTA-Eu^{3+} (5.0 μM) reacted with different concentrations of H_2O_2 at 60 °C for 30 min in 0.05 M Tris–HCl buffer of pH 7.4. (B) Correlation of the luminescence intensity and H_2O_2 concentration ($n = 3$, the inset shows the Stern–Volmer plot of the luminescence intensity changes ($\log(F_0 - F)/F$) against the H_2O_2 concentration ($\log[H_2O_2]$)).



Scheme 3. The Suzuki cross-coupling reaction between BTTA-Eu^{3+} and bromobenzene.

3.3. Luminescence monitoring of the Suzuki cross-coupling reaction between BTTA and bromobenzene

The terpyridine-4′-bronic acid structure of BTTA allows it to be a useful material for the syntheses of various aryl-substituted terpyridine polyacid derivatives by reacting it with suitable aryl halides using the Suzuki cross-coupling reaction. In general, to track the reaction process of this kind of reaction, some tedious instrumental analysis methods, such as HPLC, LC–MS and others are necessary.

In this work, a simple time-gated luminescence method was successfully developed for the monitoring of the Suzuki cross-coupling reaction between BTTA-Eu^{3+} and bromobenzene in basic media. As shown in Scheme 3, the reaction between BTTA-Eu^{3+} and bromobenzene in the presence of palladium catalyst can yield a highly luminescent Eu^{3+} complex, PTTA-Eu^{3+}. Apparently, if the luminescence intensity of PTTA-Eu^{3+} is not affected by H_2O_2, the real-time formation amount of PTTA-Eu^{3+} can be lumineously monitored by adding H_2O_2 into the solution to quench the luminescence of the unreacted BTTA-Eu^{3+}. The effects of H_2O_2 on the luminescence intensities of BTTA-Eu^{3+} (5.0 μM) and PTTA-Eu^{3+} (5.0 μM) were investigated in 0.05 M Tris–HCl buffers with different pHs ranging from 5.0 to 11.0. As shown in Fig. 4, almost no change in the luminescence intensity of PTTA-Eu^{3+} was observed upon the addition of H_2O_2 in the pH range of 5.0–11.0, indicating that the luminescence of PTTA-Eu^{3+} is insensitive to H_2O_2. At the same time, the luminescence intensity of BTTA-Eu^{3+} was also unchanged with the pH changes from 5.0 to 11.0. However, after BTTA-Eu^{3+} was reacted with H_2O_2 to generate HTTA-Eu^{3+}, the luminescence intensity was remarkably decreased with the increase of pH from 5.0 to 11.0 due to the proton dissociation of the 4′-hydroxyl group in HTTA to result in the occurrence of ICT from the 4′-oxo anion to the excited state of the terpyridine-Eu^{3+} moiety. The effects of different H_2O_2 concentrations and pHs on the luminescence lifetime of BTTA-Eu^{3+} were also investigated. It was found that the luminescence lifetime of BTTA-Eu^{3+} was unchanged in the presence of different concentrations of H_2O_2 with different pHs.

The cross-coupling reaction between BTTA-Eu^{3+} and bromobenzene was carried out in an acetone–water solution. At different reaction times, a small portion of the reaction solution was added into a 0.05 M Tris–HCl buffer of pH 7.4 containing excessive H_2O_2 to stop the reaction. After incubation at 60 °C for 30 min, the solution was subjected to the time-gated luminescence measurement. Since the luminescence of unreacted BTTA-Eu^{3+} has been quenched by H_2O_2, the luminescence of the solution is derived from the product, PTTA-Eu^{3+}. Thus, the formation of PTTA-Eu^{3+} can be monitored in real time by the time-gated luminescence measurement. As shown in Fig. 5, the luminescence intensity of the reaction solution was gradually increased from 0 to 40 min, and then reached the maximum value, which indicates that the cross-coupling reaction between BTTA-Eu^{3+} and bromobenzene can be accomplished within 40 min under our experimental conditions. In addition,

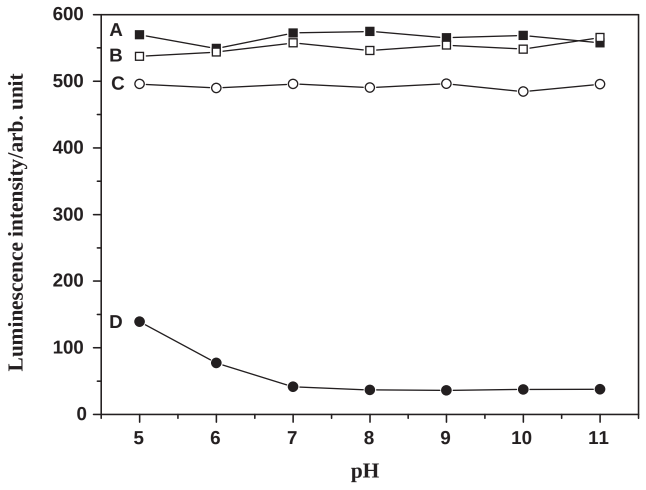


Fig. 4. Effects of pH on the luminescence intensities of PTTA-Eu^{3+} (A), PTTA-Eu^{3+} + 50.0 mM H_2O_2 (B), BTTA-Eu^{3+} (C), and BTTA-Eu^{3+} + 50.0 mM H_2O_2 (D) in 0.05 M Tris–HCl buffers with different pHs. The concentrations of all the Eu^{3+} complexes were 5.0 μM.

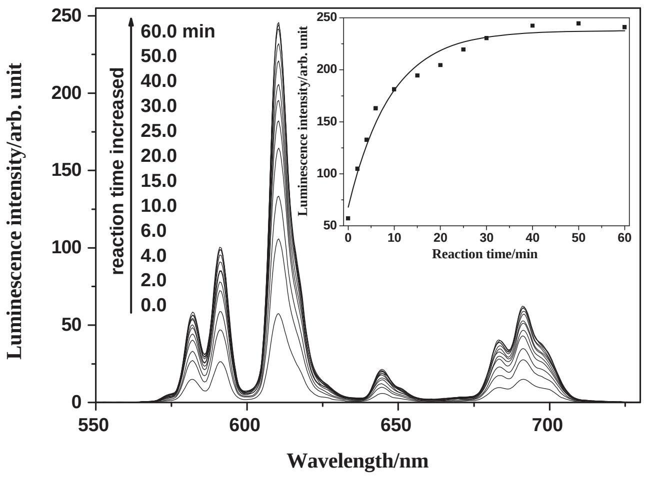


Fig. 5. Time-gated emission spectra of the solutions of the Suzuki cross-coupling reaction between BTTA-Eu^{3+} and bromobenzene at different reaction times (the solutions were treated at 60 °C for 30 min in 0.05 M Tris–HCl buffer of pH 7.4 containing 50 mM H_2O_2 before the measurements). The inset shows the correlation of the luminescence intensity and the reaction time.

according to the luminescence intensity of pure PTTA-Eu^{3+}, the formation yield of PTTA-Eu^{3+} in the cross-coupling reaction was calculated to be ~40%. These results indicate that the kinetics of the Suzuki cross-coupling reaction between BTTA-Eu^{3+} and an aryl halide can be easily monitored by our time-gated luminescence detection method.

4. Conclusions

In summary, we described here the design and synthesis of a novel Eu^{3+} complex-based luminescence probe, BTTA-Eu^{3+}, for the recognition and luminescence detection of H_2O_2. The new probe possesses several desirable properties such as excellent water solubility, high kinetic and thermodynamic stabilities, large stokes shift, and long luminescence lifetime, which enables the probe to be used for the time-gated luminescence detection of H_2O_2 in complicated systems to eliminate the effect of the interfering background noises. The successful application of the probe to monitor the reaction process of the Suzuki cross-coupling reaction provides a useful strategy of the time-gated luminescence technique for catalysis reaction researches. Indeed, this strategy could be also a useful tool for the optimization of the catalysis reaction conditions, such as solvent, catalyst, temperature, and others.

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References

[1] A. Suzuki, Acc. Chem. Res. 15 (1982) 178.
[2] N. Miyaura, K. Yamada, H. Suginome, A. Suzuki, J. Am. Chem. Soc. 107 (1985) 972.
[3] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
[4] T. Ishiyama, K. Nishijima, N. Miyaura, A. Suzuki, J. Am. Chem. Soc. 115 (1993) 7219.
[5] A. Suzuki, J. Organomet. Chem. 576 (1999) 147.
[6] A. Suzuki, Pure Appl. Chem. 63 (1991) 419.
[7] C.J. Aspley, J.A.G. Williams, New J. Chem. 25 (2001) 1136.
[8] M.C.Y. Chang, A. Palle, E.Y. Isacoff, C.J. Chang, J. Am. Chem. Soc. 126 (2004) 15392.
[9] E.W. Miller, A.E. Albers, A. Pralle, E.Y. Isacoff, C.J. Chang, J. Am. Chem. Soc. 127 (2005) 16652.
[10] A.E. Albers, V.S. Okreglak, C.J. Chang, J. Am. Chem. Soc. 128 (2006) 9640.
[11] E.W. Miller, O. Tulyathan, E.Y. Isacoff, C.J. Chang, Nat. Chem. Biol. 3 (2007) 263.
[12] B.C. Dichinson, C.J. Chang, J. Am. Chem. Soc. 130 (2008) 9638.
[13] B.C. Dickinson, C. Huynh, C.J. Chang, J. Am. Chem. Soc. 132 (2010) 5906.
[14] I. Hemmilä, V.M. Mukkala, Crit. Rev. Clin. Lab. Sci. 38 (2001) 441.
[15] J.L. Yuan, G.L. Wang, Trends Anal. Chem. 25 (2006) 490.
[16] A. Thibon, V.C. Pierre, Anal. Bioanal. Chem. 394 (2009) 107.
[17] W.H. Guo, Z.Q. Ye, G.L. Wang, X.M. Zhao, J.L. Yuan, Y.G. Du, Talanta 78 (2009) 977.
[18] C.P. Montgomery, B.S. Murray, E.J. New, R. Pal, D. Parker, Acc. Chem. Res. 42 (2009) 925.
[19] S.V. Eliseeva, J.C.G. Bünzli, Chem. Soc. Rev. 39 (2010) 189.
[20] J.C.G. Bünzli, Chem. Rev. 110 (2010) 2729.
[21] A.K. Hagan, T. Zuchner, Anal. Bioanal. Chem. 400 (2011) 2847.
[22] B. Song, G.L. Wang, M.Q. Tan, J.L. Yuan, J. Am. Chem. Soc. 128 (2006) 13442.
[23] C.H. Song, Z.Q. Ye, G.L. Wang, J.L. Yuan, Y.F. Guan, Chem. Eur. J. 16 (2010) 6464.
[24] Z.Q. Ye, G.L. Wang, J.X. Chen, X.Y. Fu, W.Z. Zhang, J.L. Yuan, Biosens. Bioelectron. 26 (2010) 1043.
[25] G.F. Cui, Z.Q. Ye, J.X. Chen, G.L. Wang, J.L. Yuan, Talanta 94 (2011) 971.
[26] Z.Q. Ye, J.X. Chen, G.L. Wang, J.L. Yuan, Anal. Chem. 83 (2011) 4163.
[27] Y.G. Chen, W.H. Guo, Z.Q. Ye, G.L. Wang, J.L. Yuan, Chem. Commun. 47 (2011) 6266.
[28] P. Kadjane, C. Platas-Iglesias, R. Ziessel, L.J. Charbonnière, Dalton Trans. (2009) 5688.
[29] M. Latvam, H. Takalo, V.M. Mukkala, C. Matachescu, J.C. Rodriguez-Ubis, J. Kankare, J. Lumin. 75 (1997) 149.
[30] B. Lei, N. Adachi, T. Arai, Brain Res. Protoc. 3 (1998) 33.
[31] M.E. Germain, M.J. Knapp, Inorg. Chem. 47 (2008) 9748.
[32] M.H.V. Werts, J.W. Verhoeven, J.W. Hofstraat, J. Chem. Soc. Perkin Trans. 2 (2000) 433.
[33] X.B. Zhang, C.C. Guo, Z.Z. Li, J.L. Shen, R.Q. Yu, Anal. Chem. 74 (2002) 821.