Photochemistry and Photobiology, 2012, 88: 840–843

Nucleophilic Addition-Triggered Lanthanide Luminescence Allows Detection of Amines by Eu(thenoyltrifluoroacetone)$_3$

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Received 29 December 2011, accepted 21 March 2012, DOI: 10.1111/j.1751-1097.2012.01150.x

ABSTRACT

Herein, a novel fluorescent indicator for the real-time monitoring of amines is described. This probe contains a complex of europium-(thenoyltrifluoroacetone)$_3$ (Eu(TTA)$_3$) that efficiently reacts with primary and secondary amines. The electron-withdrawing trifluoroacetyl undergoes a nucleophilic addition with amines, and the complex was used to selectively detect $BuNH_2$ and Et_2NH (quenching concentration for $BuNH_2$: 10^{-4} M, for Et_2NH: 1.2×10^{-3} M) by monitoring emission; no changes were observed in the emission spectrum of Eu(TTA)$_3$ in the presence of Et_3N, $[Bu_4N]Cl$, or $PhNH_2$ in aqueous solution (THF/H_2O = 1:1). The ratio of emission intensity to amine concentration was linear by the least-squares fitting method.

INTRODUCTION

Convenient, precise and rapid amine sensing techniques are vital for solving the industrial and environmental problems that occur due the presence of fertilizers, waste water or surfactants (1,2). Numerous analytical methods, including chromatographic, electrochemical and optical approaches, have been applied to monitor amine-containing analytes (3–5). Recently, a broad class of organic fluorescent molecules has been used as probes for recognition amines (6–12).

Lanthanide luminescence compounds are of interest due to their unique photophysical properties (13,14). Lanthanide complexes have been used as the smart sensors for detection of anions, metal ions, pH, DNA, gas and temperature (15,16). Recently, Tsukube *et al*. designed a series of receptors specific for amino acids using combinatorial methods (17,18). Lanthanide tri(β-diketonates) are typical rare earth complexes that exhibit strongly red emissive signals through antenna effects (19). In this article, we report that the luminescence of Eu(thenoyltrifluoroacetone)$_3$ (Eu(TTA)$_3$) was completely quenched by $BuNH_2$ and Et_2NH even in the presence of Et_3N, $[Bu_4N]Cl$ or $PhNH_2$. The proposed mechanism of the nucleophilic addition is shown in Fig. 1. The nucleophilic addition reaction occurred between $BuNH_2$ (or Et_2NH) and the carbonyl moiety of trifluoroacetyl group, and the coordination bonds collapse during the quenching process (20). In contrast, Et_3N, $[Bu_4N]Cl$ and $PhNH_2$, which are less nucleophilic, were not reactive. To the best of our knowledge, this is the first report of changes in europium luminescence behavior in response to amines.

MATERIALS AND METHODS

Eu_2O_3 (99.9%) was purchased from Shanghai Yuelong Company. Europium acetate was obtained by dissolving Eu_2O_3 in concentrated acetic acid. 1-Butyl-3-methylimidazolium chloride (97%), microcrystalline cellulose (AR), thenoyltrifluoroacetone (99%), acetylacetone (99.6%) and all the amines (AR grade) were provided by Aladdin. Acetic acid (AR) and all the other reagents were purchased from Guangzhou Chemical Reagent Factory and were used without further purification. ^{13}C-NMR spectra were recorded in $CDCl_3$ at 293 K on a Varian 400 (100 MHz) with tetramethylsilane (TMS) as an internal standard. Fluorescence spectra were measured using a Hitachi-2500 (Hitachi Company, Tokyo, Japan) spectrophotometer with a 150 W xenon lamp as light source. The scan speed was fixed at 300 nm min^{-1}. Both excitation and emission slit widths were 5.0 nm. Infrared (IR) spectra were measured using a Fourier transform infrared method on a Prestige-21 (Shimadzu).

Preparation of Eu(thenoyltrifluoroacetone)$_3$ and Eu(acetylacetone)$_3$. Eu(TTA)$_3$·2H$_2$O was prepared according to the method described previously (21). Briefly, thenoyltrifluoroacetone (TTA-H, 66.5 mg, 0.3 mmol) was dissolved in 10 mL of ethanol. An ethanol solution of Eu(CH$_3$COO)$_3$·4H$_2$O (44 mg, 0.1 mmol) was added. The solution was stirred for 2 h, and then the solvent was evaporated. The collected solid was washed with distilled water three times to give the target complex (85.4 mg, 92%) as a yellow powder. Eu(acetylacetone)$_3$·2H$_2$O was prepared in an analogous fashion except that the ligand TTA-H was replaced by acetylacetone. Anal. Calcd for $C_{24}H_{16}EuF_9O_8S_3$ (Eu(TTA)$_3$·2H$_2$O): C, 33.85; H, 1.89%. Found: C, 33.88; H, 1.77%. Anal. Calcd for $C_{15}H_{25}EuO_8$ (Eu(acetylacetone)$_3$·2H$_2$O): C, 37.12; H, 5.19%. Found: C, 37.11; H, 5.10%.

Preparation of thick cellulose films doped with Eu(TTA)$_3$. 1-Butyl-3-methylimidazolium chloride (10 g) was added to a 25 mL round bottom flask in an oil bath at 80°C. After 1-butyl-3-methylimidazolium chloride was melted, microcrystalline cellulose (2 g) was added with magnetic stirring. Eu(TTA)$_3$ (5 mg) was added into this mixture. The mixture was stirred at 80°C for 0.5 h. After the cellulose was completely dissolved in the ionic liquid, the hot solution was quickly cast onto a glass substrate. It was cooled to room temperature and washed with deionized water three times to obtain the transparent cellulose film. The luminescence sensing experiment was performed in THF/H$_2$O (1:1, vol/vol) with different amines at 10^{-3} M.

RESULTS AND DISCUSSION

The excitation spectrum of the complex, achieved by monitoring the emission wavelength at 615 nm, is shown in Fig. S1. In the excitation spectra, sharp peaks at 265 and 280 nm and a

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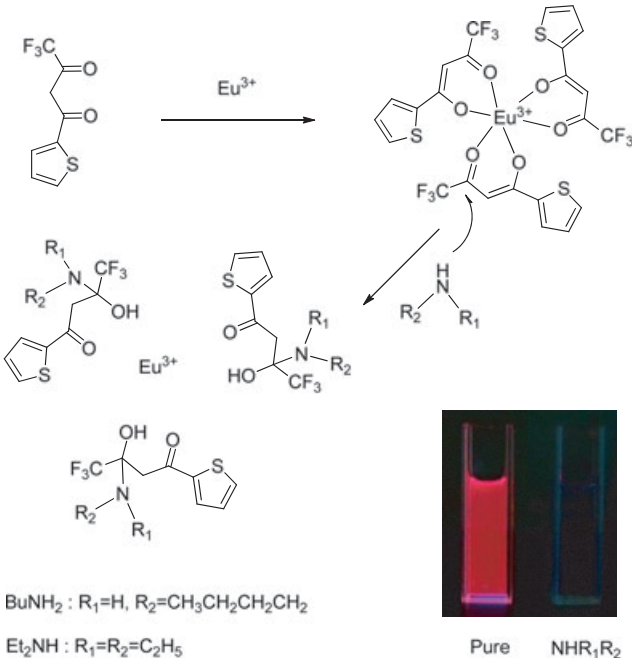

Figure 1. Schematic representation of $Eu(TTA)_3$ and the mechanism of luminescence quenching by $BuNH_2$ and Et_2NH. Photo: $Eu(TTA)_3$ in THF/H_2O (1:1, vol/vol) excited by UV light at 365 nm with and without amine ($BuNH_2$: 10^{-4} M, Et_2NH: 1.2×10^{-3} M).

broad band covering the range from 300 to 400 nm was observed. When the excitation wavelength was fixed at 327 nm, a series of narrow-width emission bands with maxima at 580, 593, 615, 654 and 705 nm were recorded. These bands are ascribed to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+}, respectively.

$Eu(TTA)_3$ dissolved in THF/H_2O (1:1, vol/vol) at concentrations as low as 10^{-6} M displayed the characteristic metal-centered emission. The overall europium luminescence changes upon addition of $BuNH_2$ are shown in Fig. 2 (left). In the excitation spectra, two broad bands were observed (from 250 to 300 nm and from 290 to 400 nm, respectively, Fig. S2). When the excitation wavelength was fixed at 345 nm, the excited $^5D_0 \rightarrow {}^7F_J$ transitions had five main components, assigned as $J = 0, 1, 2, 3$ and 4, respectively. Upon addition of $BuNH_2$ at concentrations ranging from 1×10^{-6} to 1×10^{-4} mol L^{-1}, the luminescence of $Eu(TTA)_3$ decreased gradually until it was completely quenched. The correlation of luminescence intensity at 615 nm *versus* $BuNH_2$ concentration fit a simple linear function ($y = -10.81x + 1195.5$) as determined by the least-squares fitting method with a correlation coefficient (R^2) of >0.99 (Fig. S3).

Similarly, the luminescence of $Eu(TTA)_3$ declined rapidly as the concentration of Et_2NH increased from 1×10^{-5} to 1×10^{-3} (Fig. 2, right). The correlation between concentration of Et_2NH and the intensity of emission at 615 nm can be fitted as a linear function ($y = -10.61x + 1189.6$, with an $R^2 > 0.99$, see Fig. S4). We calculated the association constant based on the Stern–Volmer equation during the quenching process (22,23). The correlation between I_0/I *versus* the amine concentration was linear, and the binding constants were 8.2×10^3 L mol^{-1} for $BuNH_2$ and 1.04×10^3 L mol^{-1} for Et_2NH. Changes could be observed with the naked eye under the excitation of the ultraviolet light (Fig. 1). Similar experiments were performed by titration of Et_3N, $[Bu_4N]Cl$, or $PhNH_2$ (10^{-2} mol L^{-1}) with $Eu(TTA)_3$. No obvious reduction was observed in the fluorescence spectra of $Eu(TTA)_3$ in the presence of these compounds (Fig. S5).

In general, nucleophiles such as amines have the ability to attack the carbon of the carbonyl moiety in the trifluoroacetyl group (24). Accordingly, we propose a possible mechanism for the selective recognition of primary and secondary amines by $Eu(TTA)_3$. Due to the strong electron-withdrawing power of CF_3, the polarity of C = O and the partial positive charge on the carbonyl carbon increase dramatically (Fig. S6). In the presence of $BuNH_2$ or Et_2NH, nucleophilic addition occurs between the amine and trifluoroacetyl group, and fluorescence was quenched (Fig. 1). We noted that the quenching concentration ($BuNH_2$: 10^{-4} M, Et_2NH: 1.2×10^{-3} M) were related to the nucleophilic ability of amines. Compared with $BuNH_2$ or Et_2NH, the nucleophilicity of both Et_3N and $[Bu_4N]Cl$ are weak, so no obvious changes in emission spectra were detected (Fig. S5). $PhNH_2$ is also a poor nucleophile that does not react with trifluoroacetyl group due to the steric hindrance effect.

To more clearly understand the role of trifluoroacetyl group in the recognition process, we prepared another europium complex using a similar ligand, acetylacetone (ACAC-H). The excitation and emission spectra of $Eu(ACAC)_3$ powder are shown in Fig. S7. When $Eu(ACAC)_3$ was dissolved in THF/H_2O (1:1, vol/vol) at a concentration as low as 10^{-5} M, the characteristic europium(III) emission was observed (Fig. S8). The luminescence of $Eu(ACAC)_3$ was relatively stable

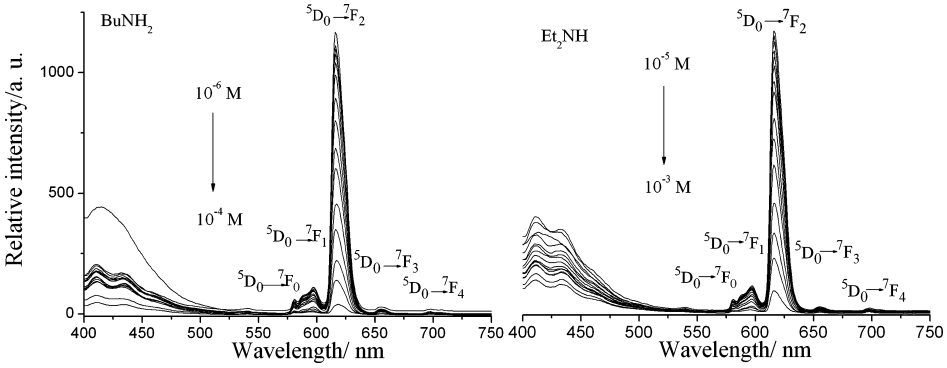

Figure 2. Emission spectra of $Eu(TTA)_3$ at 10^{-6} M excited at 345 nm upon addition of 5×10^{-5} to 10×10^{-5} M $BuNH_2$ (left) or 2×10^{-4} to 12×10^{-4} M Et_2NH (right) in THF aqueous solution.

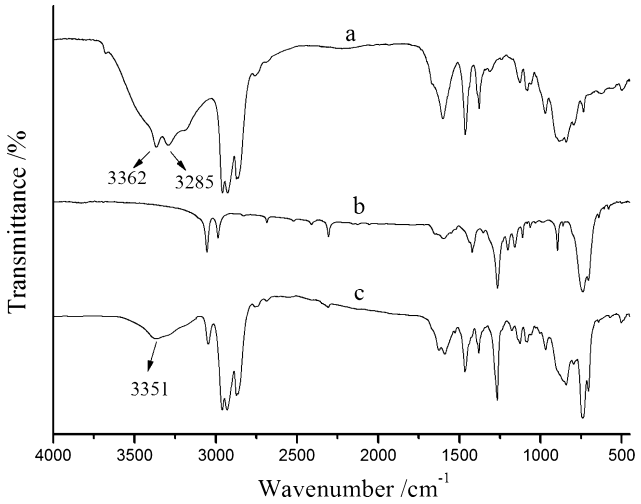

Figure 3. IR spectra of (a) $BuNH_2$, (b)TTA and (c) $BuNH_2$ with 1 equivalent of TTA.

in the presence of all tested amines, $BuNH_2$, Et_2NH, Et_3N, $[Bu_4N]Cl$ and $PhNH_2$ (Fig. S9). Therefore, the trifluoroacetyl group plays an important role in the recognition process.

To identify the mechanism of the reaction, IR and ^{13}C NMR spectroscopy were employed to investigate the reaction between TTA and amines. Figure 3 shows the FTIR absorbance spectra of solutions of $BuNH_2$, TTA and the solution of both TTA and $BuNH_2$. Doublet bands located at 3362 and 3285 cm^{-1} were attributed to -NH_2 stretching vibrations of $BuNH_2$. When an equivalent of TTA was added into the $BuNH_2$ solution, one of the two bands disappeared (Fig. 3c), indicating that the primary amine was transformed into secondary amine. This is due to the nucleophilic addition between $BuNH_2$ and the trifluoroacetyl group. In the ^{13}C-NMR spectra (Fig. 4, top), the quadruplet peaks located at 171.61, 171.24, 170.88 and 170.52 ppm are attributed to the signal of the carbonyl carbon adjacent to trifluoroacetyl group. After the addition of 1 equivalent of butyl amine, the C-2 signal shifted to higher field (from 171 to 77.92 ppm), and the quadruplet peak was changed into the single peak (Fig. 4, bottom and Fig. S10), indicating reaction between $BuNH_2$ and TTA.

A transparent film of $Eu(TTA)_3$ in cellulose hydrogel was formed on a glass substrate. The obtained composite was clear and robust. It bent under external forces with high flexibility as pure cellulose. The luminescence properties of the polymer gel containing $Eu(TTA)_3$ were investigated in detail. The red emission bands, including five main components attributed to the excited $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0, 1, 2, 3 and 4, respectively) were observed. The luminescence of the film was altered in the presence of $BuNH_2$ and Et_2NH (10^{-3} M in THF/H_2O [1:1, vol/vol]), but not any of the other tested amines. Distinct changes were observed by the naked eye under the excitation of a UV light (Fig. 5, inset photo).

CONCLUSIONS

In summary, we report that $Eu(TTA)_3$, a common luminescent lanthanide complex, can be used as a fluorescence probe for the recognition of primary and secondary amines. The emission of this complex in THF/H_2O (1:1, vol/vol) was

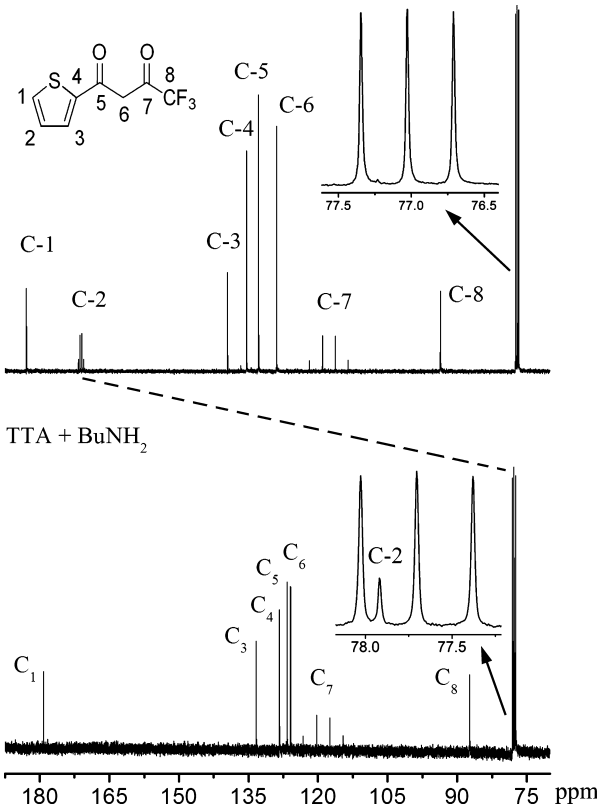

Figure 4. ^{13}C-NMR spectra measured by titration of a $CDCl_3$ solution of 1 M $Eu(TTA)_3$ with 1 equivalent of $BuNH_2$ recorded at 293 K.

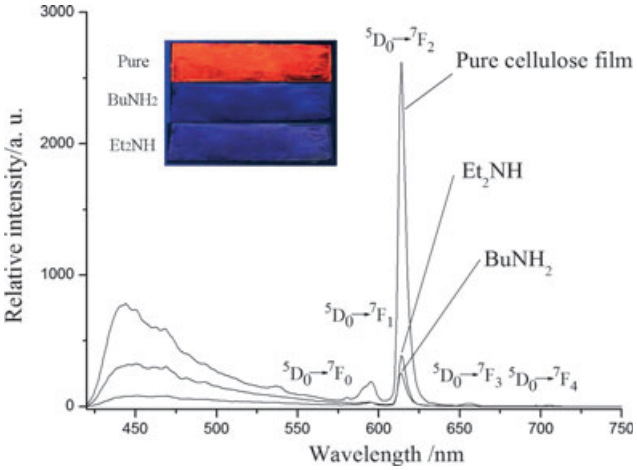

Figure 5. Emission spectra of the cellulose film doped with $Eu(TTA)_3$ and immersed in THF/H_2O (1:1, vol/vol; excited at 360 nm) containing $BuNH_2$ or Et_2NH (10^{-3} M).

selectively quenched by $BuNH_2$ and Et_2NH, but excess amounts of Et_3N, $[Bu_4N]Cl$, or $PhNH_2$ caused no significant changes in the emission bands of $Eu(TTA)_3$. Thus, $Eu(TTA)_3$ holds potential for use in amine-detecting applications as a simple optical europium complex sensor.

Acknowledgements—Q. M. acknowledges support from the National Natural Science Foundation of China (21002035) and start up funding from Guangdong Talents (C10208).

SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Figure S1. Excitation and emission spectra of $Eu(TTA)_3$ powder.

Figure S2. Excitation spectra of $Eu(TTA)_3$ (10^{-6} M in THF/H_2O, 1:1, vol/vol); emission at 615 nm.

Figure S3. Ratio of $BuNH_2$ concentration to 615 nm emission of $Eu(TTA)_3$ excited at 345 nm.

Figure S4. Ratio of Et_2NH concentration to the 615 nm emission of $Eu(TTA)_3$ excited at 345 nm.

Figure S5. Emission spectra of $Eu(TTA)_3$ (10^{-6} M in THF/H_2O, 1:1, vol/vol) excited at 350 nm upon addition of 0.01 M Et_3N, $[Bu_4N]Cl$ or $PhNH_2$.

Figure S6. The mechanism for the nucleophilic addition reaction between $BuNH_2$ (or Et_2NH) and the carbonyl moiety of trifluoroacetyl group.

Figure S7. Excitation and emission spectra of $Eu(ACAC)_3$ powder.

Figure S8. Excitation and emission spectra of $Eu(ACAC)_3$ (10^{-5} M in THF/H_2O, 1:1, vol/vol).

Figure S9. Fluorescence intensity of $Eu(ACAC)_3$ (10^{-5} M in THF/H_2O, 1:1, vol/vol) upon addition of 10^{-2} M $BuNH_2$, Et_2NH, Et_3N, $[Bu_4N]Cl$ or $PhNH_2$ (monitored at the maximum fluorescence intensity).

Figure S10. ^{13}C-NMR spectra measured by titration of a $CDCl_3$ solution of 1 M $Eu(TTA)_3$ with 1 equivalent of $BuNH_2$ recorded at 293 K.

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