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# Dual signaling of thallium(III) ions via oxidative cleavage of a sulfonhydrazide linkage

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ABSTRACT

The thallium is widely used in various research and industrial applications but is very toxic. In this work, we developed a novel reaction-based dual signaling probe for the selective and sensitive determination of $Tl^{3+}$ via the oxidative cleavage of a rhodamine–dansylhydrazide conjugate. The designed probe showed pronounced colorimetric and fluorescence signaling behavior toward $Tl^{3+}$ with a detection limit of $1.3 \times 10^{-7}$ M (0.027 ppm), as well as selectivity over other common metal ions, anions, and oxidants. The $Tl^{3+}$ signaling process required less than 2 min and was not influenced by the solution pH within the range of 4.0–5.5; however, the signal diminished significantly above pH 6.0. To demonstrate the practical applicability of the designed probe, a simple and convenient colorimetric assay for the determination of $Tl^{3+}$ in commercial reagents was established using an office scanner as a readily available signal capturing device.

## 1. Introduction

The development of selective and sensitive detection methods for toxic metal ions is crucial for the monitoring and remediation of hazardous species toward environmental protection [1]. Thallium is of particular relevance in this regard because it is used in various modern industrial activities [2], including the manufacture of various electrical and electronic components, optical lenses, semiconductor materials, gamma radiation detection equipment, infrared detectors, and low-temperature thermometers [3]. Thallium is also used in acid-resistant, corrosion-resistant, antifriction alloys and in medicines, health products, and pigments for cosmetics [4]. These applications and the subsequent release of thallium into the environment have led to an increase in thallium levels in our ecosystems [5–7].

Despite its widespread use, thallium is highly toxic to humans [8]. In fact, thallium is more toxic to mammals than mercury, lead, or cadmium [9], and chronic exposure leads to changes in cell-cycle progression and the nervous system [10]. Thallium exists in two oxidation states, thallous ($Tl^{+}$) and thallic ($Tl^{3+}$), with the latter being ~4 orders of magnitude more toxic than the former to human beings and domestic and wild animals [11,12]. Therefore, thallium is considered a priority pollutant by the United States Environmental Protection Agency. The maximum contaminant levels for thallium in drinking water and wastewater effluent have been set at 0.002 and 0.14 mg/L, respectively. The National Institute for Occupational Safety and Health has also recommended that thallium species at a concentration of 15 $mg/m^3$ be considered an immediate threat to life and health [13]. Therefore, convenient and sensitive thallium-selective analytical methods are urgently required.

Determination of $Tl^{3+}$ has been carried out using several instrumental methods, including atomic absorption spectroscopy [14,15], inductively coupled plasma-mass spectrometry [16,17], and X-ray fluorescence spectroscopy [18]. Electroanalytical methods [19–21] such as potentiometry using a tetrachlorothallate(III)-PVC membrane sensor [22], measurements using a solid-contact ion-selective electrode with an electropolymerized transducer [23], and square-wave voltammetric stripping analysis using a poly(4-vinylpyridine)/mercury film electrode [24] have also been used. However, optical methods that rely on colorimetric or fluorescence signaling are much more advantageous because of their selectivity, sensitivity, convenience, and potential for miniaturization to satisfy the requirements of on-site measurements [25,26].

For this purpose, several spectrophotometric methods that employ optical indicating materials, such as chloro-substituted hydroxamic acid extractants [27], a quinalizarin ion associate on a styrene–divinylbenzene anion-exchange resin [28], an optode membrane prepared from plasticized PVC using a complexing agent [29], and 3-methyl-2-benzothiazolinone hydrazone in an oxidative coupling reaction [30] have been reported. However, the selectivity and sensitivity of the techniques they were involved in were not satisfactorily elucidated

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the frequently encountered matrix effect in $Tl^{3+}$ analysis so that such methods could be applied in routine investigation of analytes originating from various sources (Table S1) [31–33].

In organic synthesis, thallium(III) salts have been widely employed as versatile oxidants for many practical applications [34–36] such as the oxidation of phenols, oxidative rearrangement of ketones to esters or acids and olefins to aldehydes or ketones, electrophilic cyclization of unsaturated substrates bearing an internal nucleophile, and phenolic oxidative coupling [37]. In particular, $Tl^{3+}$ has proven to be very effective for the deprotection of some commonly employed protecting groups. For instance, thallium(III) trifluoroacetate, a mild oxidant with soft acid characteristics, was found to cleave various *S*-protecting groups of cysteine with the spontaneous formation of cystine [38]. The regeneration of aldehydes or ketones from their oximes [39,40], dithioacetals [41], toluene-*p*-sulfonylhydrazones [42], and semicarbazones [40] has also been successfully accomplished.

In this work, we developed a novel reaction-based probe for the selective colorimetric and fluorescence signaling of toxic, environmentally important $Tl^{3+}$ ions. We found that the sulfonhydrazide functionality, which has previously been used as a colorimetric and fluorescence switch in a hypochlorite signaling probe based on the rhodamine–dansyl dyad framework [43], is readily cleaved by oxidation using $Tl^{3+}$ ions under mild conditions at room temperature [42]. By exploiting this facile reaction, we designed an optical probe for the colorimetric and fluorescence sensing of $Tl^{3+}$ species. The probe consisted of conjugated rhodamine and dansyl dyes with an oxidatively cleavable sulfonhydrazide linkage as a signal trigger. The designed system showed pronounced colorimetric and fluorescence responses toward $Tl^{3+}$ with high selectivity over other metal ions, anions, and some representative oxidants. Furthermore, the signaling behavior could be evaluated with the aid of an easy-to-use office scanner.

## 2. Experimental section

### 2.1. General

Thallium(III) nitrate, rhodamine B base, dansyl chloride, phosphorus oxychloride, and hydrazine monohydrate were purchased from Aldrich Chemical Co. All other reagents and solvents were obtained from commercial sources and used as received. $^1$H NMR (300 and 600 MHz) and $^{13}$C NMR (150 MHz) spectra were recorded using a Varian Gemini 2000 or VNS NMR spectrometer and referenced against the residual solvent signal. UV–vis and fluorescence spectra were acquired using a Scinco S-3100 spectrophotometer and a FluoroMate FS-2 fluorescence spectrophotometer, respectively. Mass spectra were collected using a Micromass Autospec mass spectrometer. Dansylhydrazine was prepared by reacting dansyl chloride with hydrazine according to a previously reported procedure [44].

### 2.2. Preparation of rhodamine–dansylhydrazide 1

Rhodamine–dansylhydrazide **1** was prepared by reacting rhodamine B base with dansylhydrazine following a reported procedure [43]. A solution of rhodamine B base (0.44 g, 1.0 mmol) in 15 mL of $POCl_3$ was stirred under reflux for 6 h. After removing the volatiles under reduced pressure, the residue was dissolved in dichloromethane. The resulting solution was added dropwise to a mixture of dansylhydrazine (0.27 g, 1.0 mmol) and triethylamine (1 mL) in dichloromethane (20 mL), and the reaction mixture was stirred for 12 h. Then, the reaction mixture was washed with distilled water three times. The organic phase was separated and evaporated under reduced pressure, and the residue was purified by column chromatography (silica gel, $CH_2Cl_2/CH_3OH$ = 29:1, *v/v*) to yield rhodamine–dansylhydrazide **1** (0.32 g, 46%) as a pale white powder. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, $J$ = 8.4 Hz, 1 H), 7.99–7.84 (m, 2 H), 7.67–7.60 (m, 1 H), 7.45–7.41 (m, 2 H), 7.31 (t, $J$ = 8.0 Hz, 1 H), 7.11 (t, $J$ = 7.9 Hz, 2 H), 6.94 (dd, $J$ = 6.2, 2.1 Hz, 1 H), 6.70 (s, 1 H), 6.42–6.27 (m, 2 H), 6.18 (dd, $J$ = 9.1, 2.6 Hz, 2 H), 5.73 (s, 2 H), 3.30 (q, $J$ = 7.2 Hz, 8 H), 2.90 (s, 6 H), 1.17 (t, $J$ = 7.1 Hz, 12 H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 168.3, 153.0, 152.3, 151.4, 148.6, 134.2, 133.7, 130.0, 129.5, 129.4, 129.3, 128.6, 128.3, 128.0, 127.4, 124.4, 123.5, 122.9, 119.7, 114.6, 107.7, 104.4, 97.6, 66.6, 45.6, 44.3, 12.8. HRMS: ($FAB^+$); *m/z* calcd. for $C_{40}H_{44}N_5O_4S^+$ $[M+H]^+$: 690.3114, found: 690.3109.

### 2.3. Preparation of stock solutions

A stock solution of probe **1** ($5.0 \times 10^{-4}$ M) was prepared in spectroscopic-grade DMSO. A thallium(III) nitrate stock solution ($1.0 \times 10^{-2}$ M) was prepared in a 0.1 N HCl solution. Stock solutions ($1.0 \times 10^{-2}$ M) of other metal ions and anions were prepared by dissolving the appropriate metal perchlorate salts or sodium salts of anions in distilled water.

### 2.4. Investigation of $Tl^{3+}$ signaling behavior

All signaling experiments were conducted under optimized conditions using a mixture of pH 4.76 acetate buffer and DMSO (8:2, *v/v*). For thallium(III) signaling experiments, the probe **1** stock solution (30 μL, $5.0 \times 10^{-4}$ M), analyte stock solution ($Tl^{3+}$, oxidant, metal ion, or anion; 15 μL; $1.0 \times 10^{-2}$ M), and pH 4.76 acetate buffer (450 μL, 0.20 M) were added to a vial and subsequently diluting the mixture with distilled water and DMSO (3.0 mL, 8:2 (*v/v*) mixture of acetate buffer and DMSO). The final probe **1**, analyte, and buffer concentrations were $5.0 \times 10^{-6}$, $5.0 \times 10^{-5}$, and $3.0 \times 10^{-2}$ M, respectively.

### 2.5. Determination of detection limit for $Tl^{3+}$

The limit of detection (LOD) for $Tl^{3+}$ was estimated according to the IUPAC guidelines using the equation LOD = $3s_{bl}/m$, where $s_{bl}$ is the standard deviation of the responses of probe **1** alone (number of measurements = 10) and $m$ is the slope of the titration curve [45].

### 2.6. Confirmation of the $Tl^{3+}$ signaling process of probe 1

The $Tl^{3+}$-assisted conversion of probe **1** to rhodamine B base and dansyl acid was confirmed by $^1$H NMR spectral measurements. A signaling mixture of probe **1** and $Tl^{3+}$ was prepared by slowly adding thallium(III) nitrate trihydrate (8.9 mg, 0.02 mmol) to a solution of probe **1** (6.9 mg, 0.01 mmol) in 1.0 mL of DMSO-$d_6$, and the $^1$H NMR spectrum was obtained in situ. The $^1$H NMR spectra of probe **1** alone, rhodamine B base, and dansyl acid in DMSO-$d_6$ were also obtained.

### 2.7. Determination of $Tl^{3+}$ in commercial reagents using an office scanner

The concentration of $Tl^{3+}$ in commercial reagents was assayed using an office scanner as a readily available color determination device. All signaling measurements were carried out under the optimized conditions using a mixture of pH 4.76 acetate buffer and DMSO (8:2, *v/v*).

#### 2.7.1. Preparation of calibration curve for $Tl^{3+}$

Calibration was carried out using a $Tl^{3+}$ solution standardized by iodometry [46]. The solutions used to construct the $Tl^{3+}$ calibration curve were prepared by mixing probe **1** (120 μL, $5.0 \times 10^{-4}$ M), a standardized $Tl^{3+}$ solution (6.0, 12.0, 18.0, 24.0, or 30.0 μL, $1.0 \times 10^{-3}$ M), and pH 4.76 acetate buffer (450 μL, 0.20 M) in a vial and subsequently diluting the mixture with distilled water and DMSO (3.0 mL, 8:2 (*v/v*) mixture of acetate buffer and DMSO). The final probe **1**, $Tl^{3+}$, and acetate buffer concentrations were $2.0 \times 10^{-5}$, 2.0–10.0 $\times 10^{-6}$, and $3.0 \times 10^{-2}$ M, respectively. The green channel level of the solutions was obtained for the images captured by an Epson Perfection V550 office scanner in transmittance mode. The calibration curve for the

standardized $Tl^{3+}$ reagent was plotted using the **ΔGreen** value (255 – green channel level), and the slope of the plot was then determined.

### 2.7.2. $Tl^{3+}$ assay of commercial reagents

The $Tl^{3+}$ assay of commercial reagents was conducted using five samples containing different amounts of $Tl^{3+}$. The samples were prepared by adding probe **1** (120 μL, 5.0 × $10^{-4}$ M), the $Tl^{3+}$ solution under analysis (6.0, 12.0, 18.0, 24.0, and 30.0 μL; 1.0 × $10^{-3}$ M), and pH 4.76 acetate buffer (450 μL, 0.20 M) to a vial and diluting the mixture with distilled water and DMSO to obtain a 8:2 (*v/v*) mixture of the acetate buffer and DMSO (3.0 mL). A calibration curve for the $Tl^{3+}$ reagent was constructed by plotting the **ΔGreen** value as a function of [$Tl^{3+}$], and the slope of the plot was estimated. The $Tl^{3+}$ content of reagent was calculated using the equation given below.

$$Tl^{3+}\ content\ of\ reagent\ (\%) = \frac{(Slope\ of\ calibration\ curve\ for\ reagent)}{(Slope\ of\ calibration\ curve\ for\ standard\ Tl^{3+})} \times 100\%$$

## 3. Results and discussion

Reaction-based $Tl^{3+}$-selective probe **1** was prepared in moderate yield (46%) by treating rhodamine B base with $POCl_3$ to obtain rhodamine acyl chloride, which was subsequently reacted with dansylhydrazine (triethylamine/$CH_2Cl_2$, rt) (Scheme 1) [43]. The probe was designed to include a sulfonhydrazide linkage between the rhodamine and dansyl fluorophores as an oxidatively cleavable group that can act as a signaling trigger for the analyte.

The signaling properties of the probe toward metal ions were investigated by UV–vis and fluorescence spectroscopy. The signaling conditions were optimized based on a systematic survey of the effects of pH and solvent composition. Probe **1** was nearly colorless and showed a broad absorption band of moderate intensity at 320 nm. Upon treatment with $Tl^{3+}$ ions, a new absorption band at 556 nm was evolved and the response was maximized in a mixture of acetate buffer (pH 4.76) and DMSO (8:2, *v/v*) (Fig. 1). The $Tl^{3+}$ signal of the probe was found to be strongly dependent on the pH of the medium, as shown in Fig. S1. Strong $Tl^{3+}$ signals were observed between pH 4.0 and 5.5, but the signal diminished significantly above pH 6.0. Furthermore, we confirmed that the pH-sensitive $Tl^{3+}$ ions [47] are stable in acetate-buffered solutions at pH 4.0–5.6 based on the turbidity profiles of the solution under illumination by laser light (Fig. S2). Therefore, the signaling experiments were carried out in an acetate buffer solution at pH 4.76.

In acetate buffered (pH 4.76) solution, further optimization of the organic solvent composition for the efficient $Tl^{3+}$ signaling was conducted. Among common organic solvents, DMSO acting as a scavenger for the hypochlorous acid was selected. Although 2% DMSO is sufficient for this scavenging purpose, 20% DMSO was employed to ensure satisfactory solubility of the probe. The response of the probe in aqueous DMSO became enhanced with the increases in water content up to 50% and then remained constant (Fig. S3).

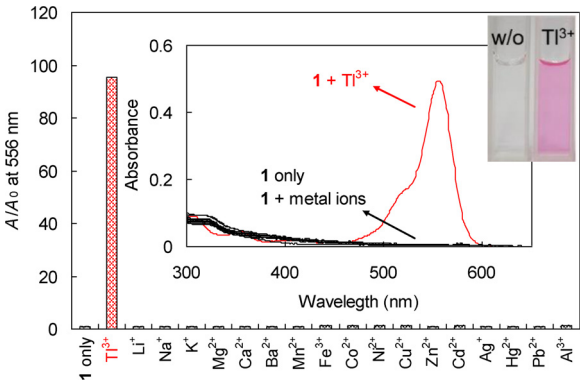
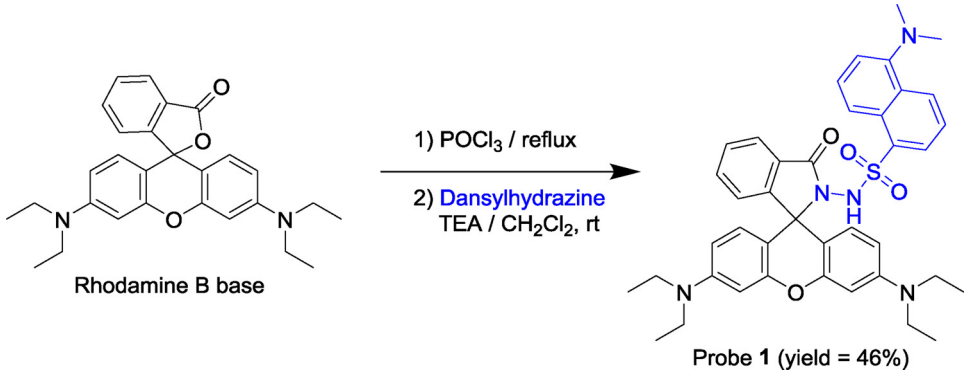


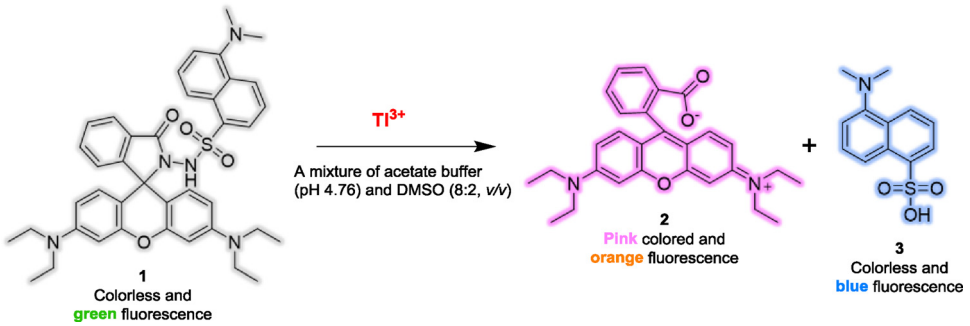

**Fig. 1.** $Tl^{3+}$-selective signaling behavior of probe **1** as expressed by the absorbance change ($A/A_0$) at 556 nm. Inset: UV–vis spectra of probe **1** in the absence and presence of various metal ions. [**1**] = 5.0 × $10^{-6}$ M, [$Tl^{3+}$] = [$M^{n+}$] = 5.0 × $10^{-5}$ M, [buffer] = 3.0 × $10^{-2}$ M in a mixture of acetate buffer (pH = 4.76) and DMSO (8:2, *v/v*).

Under these conditions (acetate buffer solution (pH 4.76) containing 20% DMSO), the probe solution exhibited weak light-blue fluorescence, with a weak emission band centered at 498 nm. The colorimetric responses of the probe toward common metal ions and anions were assessed by UV–vis spectroscopy. Upon treatment with 10 equiv of representative metal ions, a strong absorption band at 556 nm was observed exclusively in the presence of $Tl^{3+}$ ions (Fig. 1 and Fig. S4), and the solution color changed from nearly colorless to pink. The absorbance enhancement induced by $Tl^{3+}$ at 556 nm ($A/A_0$) was greater than 95-fold, whereas the other tested metal ions and anions caused no measurable response.

The observed signal is due to the oxidative cleavage of the sulfonhydrazide linkage in the probe by $Tl^{3+}$. Upon reaction with $Tl^{3+}$, probe **1** is converted to its two constituent dyes: pink-colored rhodamine **2**, which exhibits orange fluorescence, and colorless dansyl acid **3**, which exhibits blue fluorescence (Scheme 2). The postulated transformation was confirmed by the $^1$H NMR and mass spectra of the signaling products. As shown in Fig. 2, the $^1$H NMR spectrum of the signaling product (**1** + $Tl^{3+}$) was similar to the sum of the spectra of the expected signaling products rhodamine B base and dansyl acid. In addition, the TLC behavior of the **1** + $Tl^{3+}$ signaling system (Fig. S5) confirmed that rhodamine B base and dansyl acid were produced from probe **1** during the $Tl^{3+}$ signaling process. Furthermore, the mass spectrum of the signaling product obtained from probe **1** in the presence of $Tl^{3+}$ ions showed a diagnostic peak at *m/z* 442.3, in agreement with the expected signaling product, rhodamine B base (calcd. for $[C_{28}H_{30}N_2O_3]^+$, *m/z* 442.2) (Fig. S6).




**Scheme 1.** Preparation of $Tl^{3+}$-signaling probe **1**, which functions via oxidative cleavage of the sulfonhydrazide linkage.




**Scheme 2.** $Tl^{3+}$ signaling via oxidative cleavage of sulfonhydrazide-based probe **1**.

As the $Tl^{3+}$ sensing mechanism is based on the oxidative cleavage of the probe, we investigated potential interference from other common oxidants. As shown in Fig. S7, no measurable responses were observed in the presence of the tested oxidants, including $H_2O_2$, peracetic acid (PAA), hypochlorous acid (HOCl), and ammonium persulfate (APS). Note that the same molecule, rhodamine–dansyl conjugate **1**, has been reported to show a significant response toward HOCl [43]. However, as described earlier, the HOCl signal was suppressed under the present measurement conditions by the introduction of DMSO, which acts as a scavenger for HOCl, into the signaling medium [48].

Next, the competitive signaling behavior of probe **1** toward $Tl^{3+}$ in the presence of other common metal ions and anions was elucidated. As shown in Figs. 3 and S8, the $Tl^{3+}$ signaling response of probe **1** was not substantially influenced by the presence of most of the surveyed metal ions and anions. A competitive experiment with iodide ions was not conducted because $Tl^{3+}$ is routinely standardized by iodometric titration using the reaction with iodide ions.

To quantify the analytical behavior of the probe for $Tl^{3+}$ determination, the absorbance at 556 nm was measured as a function of [$Tl^{3+}$] (Fig. 4). The calibration plot was linear up to a $Tl^{3+}$ concentration of $7.0 \times 10^{-6}$ M. From the linear part of the plot, the LOD of the probe for $Tl^{3+}$ was estimated to be $1.9 \times 10^{-7}$ M (0.039 ppm) according to the IUPAC guidelines ($3s_{bl}/m$) [45]. In addition, the UV–vis and fluorescence spectra of **1** + $Tl^{3+}$ ($1.0 \times 10^{-5}$ M) and rhodamine B base alone (Figs. S9 and S10) indicated that the absorbance and fluorescence intensities reach saturation when the concentration is further increased to $1.0 \times 10^{-5}$ M. The colorimetric signaling of $Tl^{3+}$ was fast, and a saturated response was achieved within 2 min of sample preparation. Furthermore, the probe was stable under the measurement conditions, and there was no detectable deterioration of the response over several hours (Fig. S11).

We also investigated the possibility of applying probe **1** for

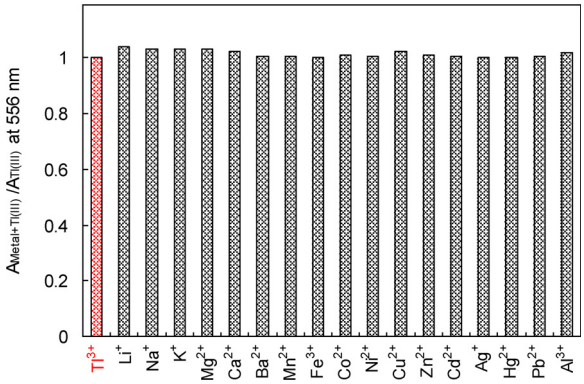



**Fig. 3.** $Tl^{3+}$-selective signaling of probe **1** in the presence of background metal ions as expressed by the absorbance ratio $A_{Metal+Tl(III)}/A_{Tl(III)}$ at 556 nm. [**1**] = $5.0 \times 10^{-6}$ M, [$Tl^{3+}$] = [$M^{n+}$] = $5.0 \times 10^{-5}$ M, [buffer] = $3.0 \times 10^{-2}$ M in a mixture of acetate buffer (pH = 4.76) and DMSO (8:2, *v/v*).

fluorescence signaling of $Tl^{3+}$. In the aqueous acetate buffer solution (pH = 4.76) containing 20% DMSO, probe **1** exhibited a broad emission band of moderate intensity centered at 498 nm. Upon treatment with $Tl^{3+}$, a strong emission band appeared at 583 nm, resulting in a change in the fluorescence color from green to orange. No measurable responses were discernible for other tested metal ions (Fig. 5) and anions (Fig. S12). Furthermore, the $Tl^{3+}$ fluorescence signaling behavior of probe **1** did not seem to be affected by the presence of common metal ions and anions in the background (Fig. S13). However, the signaling selectivity determined by ratiometry using the fluorescence intensities at 583 and 498 nm was not satisfactory owing to the relatively weak fluorescence of the dansyl moiety at 498 nm (Fig. S14). For this reason, we analyzed the fluorescence signaling behavior of probe **1** using the

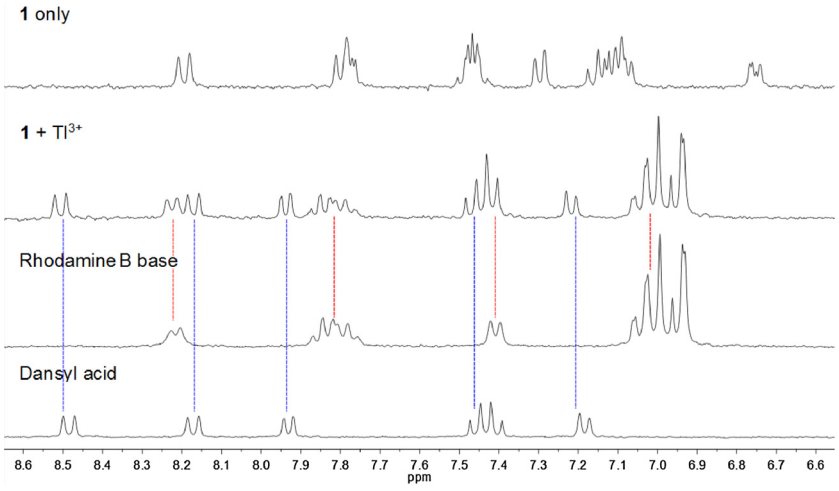



**Fig. 2.** Partial $^1$H NMR spectra of probe **1**, probe **1** treated with $Tl^{3+}$ (**1** + $Tl^{3+}$), rhodamine B base, and dansyl acid. [**1**] = [rhodamine B base] = [dansyl acid] = $1.0 \times 10^{-2}$ M in DMSO-$d_6$. The spectrum of **1** + $Tl^{3+}$ was recorded in situ using the signaling solution obtained by mixing probe **1** ($1.0 \times 10^{-2}$ M) and $Tl^{3+}$ ($2.0 \times 10^{-2}$ M).

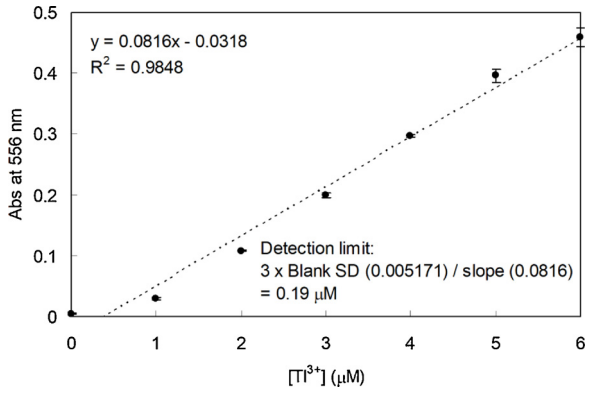



**Fig. 4.** Concentration-dependent absorbance changes at 556 nm for the $Tl^{3+}$ signaling behavior of probe **1**. [**1**] = 5.0 × $10^{-6}$ M, [$Tl^{3+}$] = 0–6.0 × $10^{-6}$ M, [buffer] = 3.0 × $10^{-2}$ M in a mixture of acetate buffer (pH = 4.76) and DMSO (8:2, *v/v*).

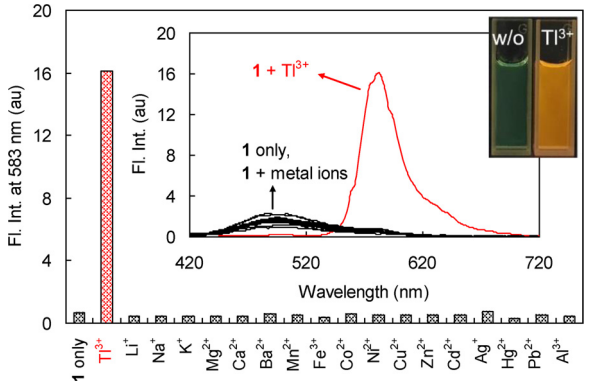



**Fig. 5.** $Tl^{3+}$-selective fluorescence signaling of probe **1** over other common metal ions as expressed by the fluorescence intensity at 583 nm. Inset: fluorescence spectra of probe **1** in the presence and absence of various metal ions. [**1**] = 5.0 × $10^{-6}$ M, [$Tl^{3+}$] = [$M^{n+}$] = 5.0 × $10^{-5}$ M, [buffer] = 3.0 × $10^{-2}$ M in a mixture of acetate buffer (pH = 4.76) and DMSO (8:2, *v/v*). $\lambda_{ex}$ = 400 nm.

fluorescence intensity at 583 nm alone, which originated from the rhodamine fluorophore. As shown in Fig. S15, the $Tl^{3+}$ fluorescence signaling behavior was unaffected by the presence of common metal ions and anions. These observations suggest that probe **1** can be used for the selective and sensitive determination of $Tl^{3+}$ by both colorimetric and fluorescence measurements.

Subsequently, probe **1** was applied for the colorimetric determination of $Tl^{3+}$ using a readily available office scanner. Several reports have described the use of a scanner as a portable device for the convenient chemical analysis of biologically and environmentally important chemical species [49–52]. We believe that the present system is particularly suited to this approach because the pronounced colorimetric and fluorescent responses of the probe to $Tl^{3+}$ is discernible to the naked eye. To develop this method, we chose colorimetric signaling rather than fluorescence signaling owing to the simplicity for routine applications and superior $Tl^{3+}$ selectivity under competitive conditions of the former approach. Solutions with different concentrations of $Tl^{3+}$ were prepared under the same signaling conditions and transferred to a microwell. The microwell was imaged using a scanner in transmission mode, and the obtained images were analyzed by a color analysis program (Photoshop CS6, Adobe Systems). As can be seen in Fig. 6, the colorimetric response of the probe toward $Tl^{3+}$ is readily perceived by the naked eye. The plots of the red, green, and blue channel values as a function of [$Tl^{3+}$] demonstrated that the most pronounced change was observed using the green channel value (Fig. S16). The calibration plot

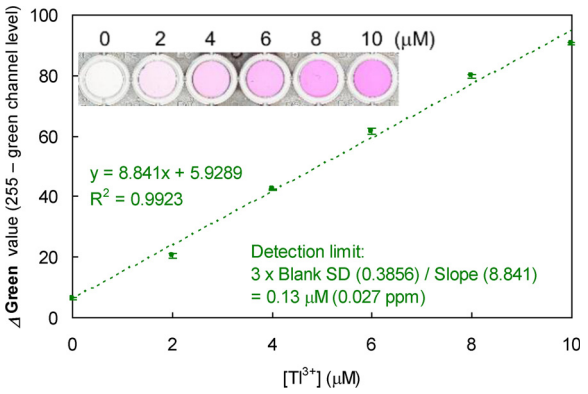



**Fig. 6.** Colorimetric signaling behavior of probe **1** as expressed by the change in the **ΔGreen** value (255 – green channel level) as a function of [$Tl^{3+}$]. [**1**] = 2.0 × $10^{-5}$ M, [$Tl^{3+}$] = 0 – 1.0 × $10^{-5}$ M, [buffer] = 3.0 × $10^{-2}$ M in a mixture of acetate buffer (pH = 4.76) and DMSO (8:2, *v/v*). The inset images were obtained with a scanner and analyzed using the Photoshop CS6 software.

obtained using the green channel was linear up to a $Tl^{3+}$ concentration of 10 μM ($R^2$ = 0.9923). Thus, this approach is suitable for the straightforward determination of $Tl^{3+}$ levels in various practical applications. From the concentration-dependent signaling response, the LOD of probe **1** for $Tl^{3+}$ using the scanner-based method was estimated as 1.3 × $10^{-7}$ M (0.027 ppm) according to the IUPAC guidelines [45].

Finally, this scanner-based method was applied to assay commercial thallium(III) reagents (thallium(III) nitrate trihydrate) (Table 1). The results of the colorimetric signaling-based assay of $Tl^{3+}$ ions performed using probe **1** were in good agreement with those of the standard iodometric titration method [46] (relative error = –0.8% to 0.2%).

## 4. Conclusion

A novel colorimetric and fluorescence reaction-based probe showed excellent selectivity for $Tl^{3+}$ over other relevant oxidants, metal ions, and anions. Signaling was realized by the $Tl^{3+}$-assisted oxidative cleavage of the sulfonhydrazide linkage in the probe to yield the constituent dyes, rhodamine B base and dansyl acid. The $Tl^{3+}$ signaling process was not considerably affected by pH in the range of 4.0–5.5. To demonstrate the practical applicability of the designed probe, we developed a method involving the use of an office scanner for the convenient and sensitive analysis of $Tl^{3+}$ with a detection limit of 0.13 μM (0.027 ppm). Our method was successfully applied to assay the $Tl^{3+}$ contents of laboratory reagents.

## CRediT authorship contribution statement

**Yu Jeong Lee:** Investigation, Writing - original draft, Formal analysis. **Myung Gil Choi:** Investigation, Writing - review & editing, Visualization. **Jae Hoon Yoo:** Investigation, Formal analysis. **Tae Jung Park:** Investigation, Writing - review & editing, Funding acquisition. **Sangdoo Ahn:** Writing - review & editing, Supervision. **Suk-Kyu Chang:** Conceptualization, Writing - review & editing, Supervision, Funding acquisition.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Table 1**
Assay of $Tl(NO_3)_3$ reagents using the scanner-based method with probe **1** and iodometric titration.

| Sample | $Tl^{3+}$ content determined using probe **1**[a] | $Tl^{3+}$ content determined by iodometric titration[a] | Relative error |
|---|---|---|---|
| $Tl^{3+}$ reagent #1[b] | 96.6% ± 0.6% | 96.8% ± 0.3% | 0.2% |
| $Tl^{3+}$ reagent #2[b] | 97.2% ± 0.3% | 96.4% ± 0.3% | –0.8% |

[a] Reported values are given as mean ± standard deviation (n = 3).
[b] $Tl^{3+}$ reagents #1 and #2 were obtained from Aldrich Chemical Co. as thallium(III) nitrate trihydrate.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2020.112471.

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