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Determination of thallium(III) ions by oxidative hydrolysis of rhodamine–hydroxamate†

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Thallium ions are widely used in chemical and industrial applications but are very toxic. Through this research, a novel dual signaling probe that is based on an oxidative cleavage reaction is examined. The probe showed selective and sensitive optical signaling behavior toward Tl^{3+} through the oxidative hydrolysis of rhodamine–hydroxamate. The probe designed for this study exhibited a distinct colorimetric and fluorescence signaling activity for thallium ions compared to the ions of common metals and oxidants. In particular, the hypochlorous acid response of the probe was successfully suppressed using DMSO as a scavenger. The detection limit for thallium determination was 2.9×10^{-7} M and signaling was concluded within 5 minutes. The exploitation of the probe for the rapid screening of elevated urinary thallium levels due to thallium poisoning using smartphone images was also conducted.

1. Introduction

Thallium is a highly hazardous metal, and its toxicity is well recognized in the environmental and medical science fields.[1] Thallium metal is most commonly found as thallous (Tl^{+}) and thallic (Tl^{3+}) ions and is more toxic than other heavy metal ions such as cadmium and mercury.[2] The United States Environmental Protection Agency (USEPA) lists thallium as a major pollutant owing to its hazardous nature.[3] However, there is an increasing demand for thallium in high-technology electronic, chemical, aerospace, pharmaceutical, and optical industries for applications such as high-temperature superconducting and high-energy physics materials.[4] Thallium is a potent oxidizing agent in synthetic chemistry. It has wide application in the oxidation and oxidative rearrangements of ketones, olefins, acetylenes, and compounds containing double bonds between carbon and nitrogen.[5] Owing to its widespread use, it is now estimated that 2000–5000 tons of thallium species per year are released by industrial processes such as mineral processing (including cement production and recycling of concrete) and as waste from the electric or electronic industries.[6] It is highly imperative to minimize the current environmental concerns regarding thallium by developing selective and sensitive monitoring methods to protect humans from this poisonous species.

Long-term exposure to thallium causes chronic poisoning. On the other hand, accidental or short exposure to high concentrations of thallium results in acute poisoning, which is principally diagnosed by gastrointestinal, neurological, and dermatological indications.[7] In cases of acute thallium poisoning, blood and urine thallium concentrations are significantly elevated. Reliable diagnosis of thallium poisoning occurs when thallium levels in the blood exceed 50 μg L^{-1} (2.45×10^{-7} M) or when the levels surpass 300 μg L^{-1} (1.47×10^{-6} M) in the urine.[8] In humans, the reference ranges for thallium in both blood and urine is 2.45×10^{-8} M.[9] Inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry are the routinely used methods to measure thallium levels in blood and urine samples that are suitable for diagnosis.[8,10] In fact, thallium has been traditionally determined by various instrumental methods, such as voltammetry/potentiometry,[11] atomic absorption spectrometry,[12,13] spectrophotometry,[14,15] fluorimetry,[16] and ICP-MS[17,18] which has become one of the most popular techniques in recent years. However, it is more advantageous to use colorimetric or fluorescence analysis methods than these procedurally complicated heavy instrument-based methods.

Several colorimetric assays based on the extraction using chloro-substituted hydroxamic acid and 2,6-bis(*N*-phenyl carbamoyl)pyridine have been reported.[14,19] Also, oxidation of trifluoperazine[20] and oxidative coupling reaction of 3-methyl-2-benzothiazolinone[21] have been used as a colorimetric Tl^{3+} determination method. On the other hand, only a few fluorescence assays exist for thallium speciation and determination. Representative examples are the catalytic kinetic method employing arsenoxylphenylazo rhodanine[22] and the native fluorescence of reduced Tl^{+}.[23] Alternatively, the sulfonhydrazide of a rhodamine–dansyl conjugate is used for the colorimetric and off–on type fluorescence signaling by cleaving the linkage through oxidation.[24] The analytical

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† Electronic supplementary information (ESI) available: UV-vis and fluorescence data, ^{1}H and ^{13}C NMR spectra of probes (**1–3**) were reported. See DOI: 10.1039/d0nj05002d

characteristics of the reported Tl^{3+} signaling methods including their applications are summarized in Table S1 (ESI†).

We attempted to create a new Tl^{3+} probe that is based on selective reactions and shows distinct colorimetric and fluorescence signals through the exploitation of the complex forming and oxidative hydrolytic characteristics of hydroxamic acid. Many hydroxamic acid-functionalized compounds have been employed as the basis of analytical methods based on their complex formation capability with a range of metal ions, such as Cu^{2+}/Ni^{2+},[25] UO_2^{2+}/Al^{3+},[26] and Fe^{3+}/Ga^{3+}.[27] In particular, applications in chelation therapy are noteworthy. The best known chelation therapy application is the formation of hydroxamate complexes with Fe^{3+} ions, such as desferrioxamine B, for the treatment of toxic side effects of iron-overloaded thalassemia patients.[28–31] Interestingly, a chelating agent containing a hydroxamic acid ligating group has also been used for the detoxification of Tl^{3+} by enhanced excretion through urine and feces in rats.[32]

Notably, several hydroxamate-based colorimetric and fluorogenic probes derived from rhodamine dyes have been designed for the sensing of hypochlorous acid,[33] hypervalent iodine reagent 2-iodoxybenzoic acid (IBX),[34] and nerve gas agents using Lossen rearrangement.[35] Further modification of the basic framework of rhodamine–hydroxamate has led to the selective sensing of many metal ions, for instance, Fe^{3+} by introducing a methyl group on the hydroxy function,[36] Hg^{2+} by thio-functionalization of the hydroxamate moiety,[37] Pd^{2+} by appending a cyclen ligand,[38] and Pt^{2+} by conjugating a triazole ligand.[39] These and other interesting rhodamine hydroxamate-based signaling systems for many important chemical species have recently been comprehensively reviewed.[40]

Here, we report a new Tl^{3+}-selective reaction-based optical probe that works through hydroxamate-to-carboxylic acid oxidative hydrolysis. The Tl^{3+}-assisted conversion of rhodamine–hydroxamate into ring-opened parent rhodamine dye induced substantial changes in the optical properties of the probe. The practical applicability of the probe for early screening of elevated urinary thallium levels in acute poisoning cases employing a ubiquitous smartphone with simulated urine was also carried out.

2. Experimental

2.1 General

Thallium(III) nitrate trihydrate, rhodamine 6G, rhodamine B base, and hydroxylamine hydrochloride were purchased from Merck KGaA. Other reagents, solvents, and metal perchlorates were obtained from commercial sources. Thallium(III) nitrate trihydrate was used after standardization *via* iodometry.[41] A Varian VNS NMR spectrometer was used to record ^{1}H and ^{13}C NMR spectra (600 MHz and 150 MHz, respectively). Scinco S-3100 and FS-2 spectrophotometers were used to measure UV-vis and fluorescence spectra, respectively. A Micromass Autospec mass spectrometer with electron ionization (EI) was used to extract mass data that had a low resolution. Mass outcomes of high resolution were acquired using Bruker Compact mass spectrometer with a fast-atom bombardment (FAB) ionization. Silica gel (240 mesh, Merck) was used to perform column chromatography. Probes **1** and **2** were prepared by following the reported procedures.[33,34]

2.2 Preparation of compound 3

Dichloromethane (40 mL) was used to dissolve rhodamine hydroxamic acid **1** (0.86 g, 2.0 mmol) and trimethylamine (0.546 mL, 4.0 mmol). Acetyl chloride (0.284 mL, 4.0 mmol) was added gradually to the mixture. Afterwards, the mixture was stirred at 25 °C for 12 h. Brine and distilled water were used to wash the reaction mixture multiple times and reduced pressure was used to evaporate the solvent. Compound **3** (0.36 g, 38%), a light brown solid, was obtained by the purification of the precipitate using a column chromatogram with silica gel and dichloromethane. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.95 (d, J = 6.6 Hz, 1H), 7.54–7.43 (m, 2H), 7.05 (d, J = 5.2 Hz, 1H), 6.48 (s, 2H), 6.34 (s, 2H), 3.20 (q, J = 7.3 Hz, 4H), 1.98 (s, 3H), 1.93 (s, 6H), 1.31 (t, J = 6.9 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.80, 162.95, 152.03, 150.89, 147.55, 133.25, 128.89, 128.33, 127.79, 123.82, 123.30, 117.60, 104.55, 96.38, 65.81, 38.33, 18.06, 16.71, 14.74; HRMS (ESI^+, m/z): calculated for $C_{28}H_{30}N_3O_4^+$ $[M + H]^+$: 472.2231, found 472.2234.

2.3 Preparation of stock solutions

A spectroscopy-level DMSO was used to prepare stock solutions of probes (5.0×10^{-4} M). HCl (0.05 M) was used to prepare a stock solution of thallium(III) ions (1.0×10^{-2} M). The stock solutions of metal ions (1.0×10^{-2} M) were prepared in distilled water. A method from previous reports was used to prepare synthetic urine.[42,43]

2.4 Measurement of signaling behavior

The conditions for thallium(III) ion signaling experiments were adjusted using a mixture of acetate buffer solution with a pH of 4.2 and 30% (v/v) DMSO. Probe **1** (30 μL, 5.0×10^{-4} M) and analyte (Tl^{3+}, metal ion, oxidant, or anion; 45 μL; 1.0×10^{-2} M) stock solutions and acetate buffer with a pH of 4.2 (150 μL, 0.20 M) were added to a vial. Also, to equalize the conditions of measurement of the sample solutions, 45 μL of 0.05 M HCl solution (same volume used for Tl^{3+}) was added to all samples. The resulting mixture was used to make a measuring solution (3.0 mL, 7 : 3 (v/v) mixture of acetate buffer and DMSO) through dilution using DMSO and distilled water. The final concentration for the analyte and probe **1** was 1.5×10^{-4} M and 5.0×10^{-6} M, respectively, while that of the buffer was 1.0×10^{-2} M.

2.5 Preparation of Tl^{3+} signaling product 1

After dissolving probe **1** (43 mg, 0.01 mmol) in a 10 mL solution of acetonitrile, thallium(III) nitrate trihydrate (89 mg, 0.02 mmol) was added to 1.0 mL of 0.1 N HCl. This reaction mixture was stirred for 1 hour after which 10 mL of dichloromethane was added. The organic phase was separated and evaporated under reduced pressure. Purification of signaling product **4** was carried out by column chromatography (silica gel, CH_2Cl_2 : CH_3OH = 9 : 1, v/v).

2.6 Determination of the detection limit of Tl^{3+}

Calculation of the detection limit of Tl^{3+} ions was performed by applying the equation ($3s_{bl}/m$), where s_{bl} is the standard deviation of the blank measurement (n = 12) and m is the calibration sensitivity obtained from the slope of the calibration plot according to the IUPAC recommendations.[44]

2.7 Determination of Tl^{3+} in synthetic urine using a smartphone

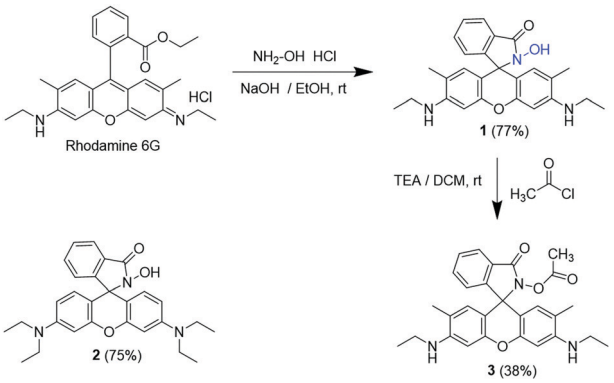
The reported literature was used as the foundation for determining Tl^{3+} ions in synthetic urine using a smartphone.[45] The smartphone is used as a readily available tool for measuring and processing signals. The conditions for all the experiments were adjusted using an acetate buffer solution with a pH of 4.2 containing 30% (v/v) DMSO.

A. Preparation of sample solutions. Samples were prepared through the addition of acetate buffer (150 μL, 0.20 M), Tl^{3+} stock solution (0, 7.5, 15, 22.5, and 30 μL, 5.0×10^{-4} M), and probe **1** (30 μL, 5.0×10^{-4} M) into a 10 mL vial. Distilled water and DMSO (3.0 mL, 7 : 3 (v/v)) were then used to dilute the resulting solution. The final concentration of the probe in the solution was 5.0×10^{-6} M, the buffer 1.0×10^{-2} M, and the Tl^{3+} ions 0–1.0×10^{-6} M.

B. Determination of Tl^{3+} using a smartphone. A cuboid with a square hole in the lid was used to measure the response of the samples. A Galaxy S10 smartphone, Samsung Electronics model, with no special settings, was used to take photographs of the samples under a hand-held UV lamp, VILBER, VL-4LC model. The RGB Grabber, Shunamicode smartphone application was used to estimate the red, green, and blue channel levels of the images from the fluorescence. Finally, Tl^{3+} calibration curve was obtained by plotting the changes in the green channel level. The green channel level showed the most distinct signal variation than the levels of the red and blue channels.

3. Results and discussion

The Tl^{3+}-selective reaction-based probe was designed considering the fact that hydroxamic acid function is smoothly transformed into carboxylic acid by common oxidants.[33] We incorporated hydroxamic acid as a signaling switch into the rhodamine dye, expecting that the transformation could induce the conversion of the ring-closed hydroxamate form of the probe to ring-opened rhodamine dye, which would revive the dye's characteristic colorimetric and fluorescence properties. Another feature of the designed probe is that the hydroxamic acid ligating subunit is capable of forming a stable complex with Tl^{3+} ions,[14] which would act favorably for promoting the interaction with the probe for the expected hydrolysis reaction. As described earlier, the basic framework of rhodamine–hydroxamate **2** has been previously used for the analysis of oxidizing agents (hypochlorous acid and IBX) and nerve gas agents.[33–35] We believe that the response toward these species is not a problem for the analysis of Tl^{3+} ions in typical applications because IBX and nerve gas agents are not common targets and the use of these relevant species do not overlap. Furthermore, the response of hypochlorous acid could readily be suppressed by relying on the scavenging effect of DMSO. The reaction between rhodamine 6G and rhodamine B base with hydroxylamine hydrochloride was used to prepare probes **1** and **2**, respectively (Scheme 1).[33,34] Compound **3** was obtained by the acetylation of **1**.



Scheme 1 Synthesis of probes **1** and **2** and acetylated derivative **3**.

UV-vis and fluorescence experiments were used to examine the Tl^{3+} signaling properties of the probe. To gain insight into the optimized structure of the probe, two similar but differently structured rhodamine-based hydroxamic acids (**1** and **2**) and one acetylated derivative **3** were tested. The signaling speed for Tl^{3+} of rhodamine 6G-based probe **1** was faster than that of rhodamine B-based probe **2** (pseudo first-order rate constant: 0.24 min^{-1} for compound **1** and 0.19 min^{-1} for compound **2**)[46] (Fig. S1 and S2, ESI†); this observation is similar to the previous report for the determination of hypochlorous acid.[33] Furthermore, the Tl^{3+} signaling contrast of probe **1** was considerably more pronounced than that of probe **2** (Fig. S3, ESI†). Meanwhile, acetylated derivative **3** did not reveal any noticeable responses, which implies the importance of the unfunctionalized hydroxamic acid group of the probe in the Tl^{3+} signaling process (Fig. S4, ESI†). We also investigated the pH-dependency of the Tl^{3+} signaling of compound **3** and found that the acetylated derivative showed no meaningful fluorescence changes in the presence and absence of Tl^{3+} ions (Fig. S5, ESI†). Therefore, all the signaling experiments were performed with rhodamine 6G-based hydroxamate probe **1**.

To obtain optimal signaling conditions for the Tl^{3+} analysis, we systematically optimized the pH, solvent, and composition of the analytical procedure. Fig. S6 (ESI†) shows the pH profile between the pH of 4.2 and 7.0 obtained from the fluorescence results. The pH-profile of the thallium signaling indicated that the response was strongly pH-dependent and progressively diminished from pH 4.1 to 5.0, then remained relatively constant up to pH 7.0. Under strongly acidic conditions, the hydroxamate function of the probe is likely to convert into a ring-opened form, which resulted in undesirable background colorimetric and fluorescent responses. Meanwhile, in basic solutions, Tl^{3+} is unstable and is known to be converted into an oxide, Tl_2O_3.[47]

Probe **1** exhibited a noticeable change in the fluorescence spectrum exclusively toward Tl^{3+} ions among the tested common metal ions (Fig. 1). Treatment with Tl^{3+} significantly increased

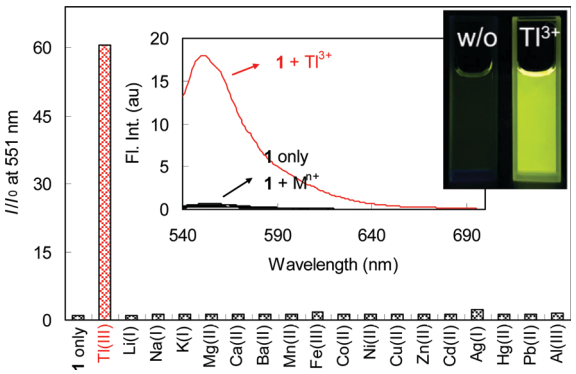
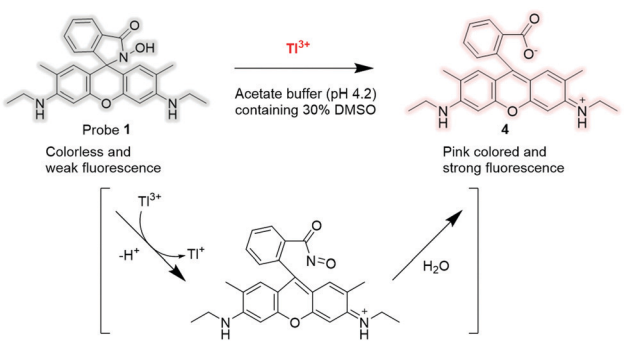


Fig. 1 Changes in fluorescence enhancement (I/I_0) of probe **1** at 551 nm where ions of common metals are present. Insets: (middle) fluorescence spectra of **1** with metal ions present, (right) photograph of probe in the presence and absence of Tl^{3+} using a UV lamp for illumination. [**1**] = 5.0×10^{-6} M, [M^{n+}] = 1.5×10^{-3} M in a solution of acetate buffer (pH 4.2, 10 mM) containing 30% (v/v) DMSO. λ_{ex} = 527 nm.

the fluorescence intensity of the probe at 551 nm. The increase was close to 60-fold. Simultaneously, there was a color change in the solution to fluorescent greenish-yellow from dark when illuminated with a UV lamp (λ_{ex} = 365 nm). Fig. S7 (ESI†) shows that inconsequential results were also observed for most of the anions tested.

Oxidative hydrolysis of the hydroxamate component to a carboxylic acid resulted in the signaling of Tl^{3+} by probe **1** (Scheme 2). The conversion was preliminarily confirmed by TLC (Fig. S8, ESI†). For the acquisition of more positive evidence concerning the postulated conversion, the product from the Tl^{3+} signaling was purified using a column chromatogram with silica gel, solvent: CH_2Cl_2 : CH_3OH = 9 : 1, v/v. There was a close similarity between the ^{1}H NMR spectral data of the reference compound **4** and the purified product (Fig. 2). This is further evidenced by a relevant peak of the signaling product at m/z = 415.2018 (calculated for $[C_{26}H_{27}N_2O_3]^+$ m/z = 415.2016) (Fig. S9, ESI†).

The probe's response to other commonly used oxidants were measured since the functional group of hydroxamic acid can be hydrolyzed when oxidative conditions are present. Most of the tested oxidants, except for IBX, did not induce any measurable changes in the fluorescence spectrum (Fig. S10, ESI†). The response induced by IBX surpassed that of Tl^{3+} ions and the



Scheme 2 Signaling of Tl^{3+} ions by oxidative hydrolysis of probe **1**.

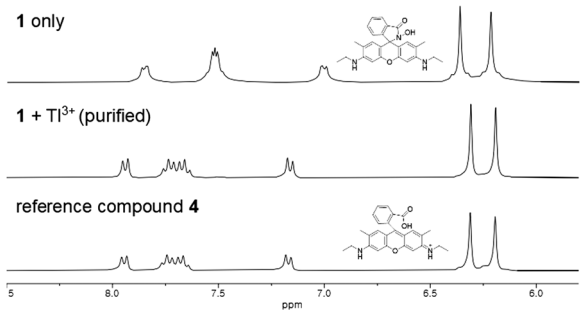


Fig. 2 Partial ^{1}H NMR spectra of **1**, purified signaling product, and reference compound **4**. The middle spectrum was acquired after purifying the product of the signaling process. [**1**] = [**4**] = 5.0×10^{-3} M in DMSO-d_6.

signaling speed for IBX was similar to that of Tl^{3+} ions (Fig. S11, ESI†). However, as previously described, we believe that the response from IBX is not so relevant for the analysis of Tl^{3+} ions in routine chemical applications.[48] The undesirable response from hypochlorous acid, which was observed in aqueous acetonitrile and THF solution, was successfully suppressed, employing the HOCl scavenging effect of DMSO (Fig. S12, ESI†).[24,49] After a preliminary survey using varying compositions of DMSO in acetate buffer solution, we found that 30% DMSO solution is the optimal condition in terms of the selectivity and signal contrast of the probe toward Tl^{3+} ions.

Next, the effect of foreign ions on Tl^{3+} signaling was substantiated to test the practical applicability of **1**. In general, the presence of ions of common metals is inconsequential to the Tl^{3+} signaling activity of the probe as seen in the slight variation in the fluorescence intensity ratio $I_{Metal+Tl(III)}/I_{Tl(III)}$ at 551 nm of 0.86 (for Cd^{2+}) and 1.15 (for Fe^{3+}) (Fig. 3). There was no significant interference from the anions with a limited variation for the $I_{Anion+Tl(III)}/I_{Tl(III)}$ between 0.91 (for F^-) and 1.08 (for Br^-) (Fig. S13, ESI†). We further confirmed that there is no significant anion-dependency of Tl^{3+} signaling properties (Fig. S14, ESI†) by the experiments using nitrate or acetate salt of Tl^{3+} ions. On the other hand, due to the redox-active properties of the iodide ion, it was not tested. Tl^{3+} ions are standardized routinely relying on the redox reaction with iodide through iodometric titration.[41]

The quantitative analytical profile of the probe for Tl^{3+} signaling was elucidated by measuring concentration-dependent fluorescence changes. The intensity of fluorescence at 551 nm increased proportionally with the increase in thallium ions (Fig. S15, ESI†). Based on these results, the linear correlation (R^2 = 0.9821) up to 2.0×10^{-5} M Tl^{3+} ions of the analysis was acquired. The limit of detection for thallium ions of the probe was found to be 2.9×10^{-7} M after estimation using the IUPAC recommendation $3s_{bl}/m$.[44] In addition, signaling of Tl^{3+} with the probe was fast and completed within 5 minutes under the employed conditions (Fig. S1a, ESI†). Meanwhile, the probe itself did not exhibit any measurable changes in fluorescence over 3 hours after sample preparation.

Probe **1** also showed prominent colorimetric signaling behavior toward Tl^{3+} ions, as illustrated by the results of UV-vis measurements. Under the same optimal conditions of pH 4.2

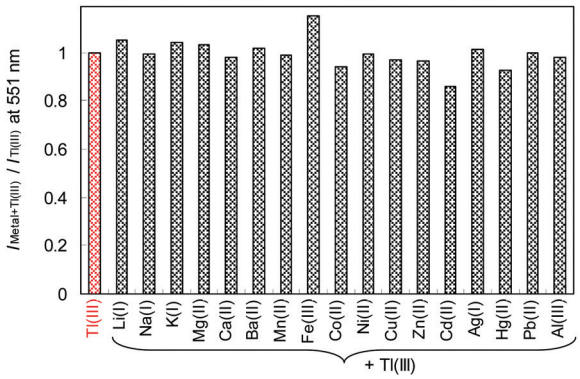


Fig. 3 Changes in the fluorescence intensity ratio ($I_{Metal+Tl(III)}/I_{Tl(III)}$) of Tl^{3+} signaling by probe **1** at 551 nm in the presence of common metal ions under competitive conditions. [**1**] = 5.0 × 10^{-6} M, [Tl^{3+}] = [M^{n+}] = 1.5 × 10^{-3} M in acetate buffer solution (pH 4.2, 10 mM) containing 30% (v/v) DMSO. λ_{ex} = 527 nm.

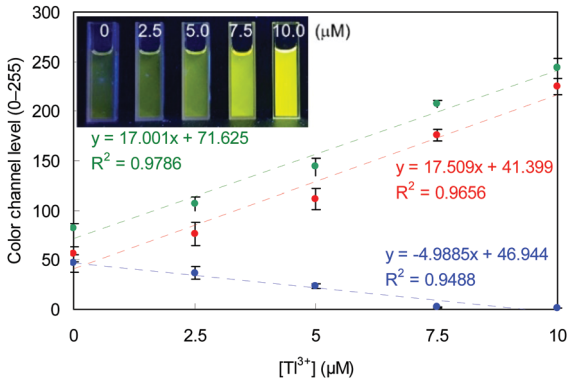


Fig. 5 Fluctuations in the red, green, and blue color channel level of probe **1** when the concentration of thallium ions is varied. Inset: Picture of solutions for thallium ion signaling. [**1**] = 5.0 × 10^{-6} M, [Tl^{3+}] = 0–10 μM in acetate buffer solution (pH 4.2, 10 mM) containing 30% (v/v) DMSO. A UV lamp (λ_{ex} = 365 nm) was used for illumination.

acetate-buffered solution containing 30% DMSO, probe **1** showed no measurable absorption bands above 400 nm. A significant enhancement in absorbance at 527 nm was observed with thallium ions alone following interactions with different metal ions (Fig. 4), oxidants apart from IBX (Fig. S16, ESI†), and anions (Fig. S17, ESI†). There was a concurrent color change of the solution to pink from colorless. The presence of ions of common metals did not affect the signaling of Tl^{3+} ions (Fig. S18, ESI†), and anions (Fig. S19, ESI†) as a background. These outcomes indicate the possibility of colorimetric analysis of thallium ions in the routine physiological and chemical analytes using probe **1**.

The levels of thallium ions in synthetic urine were determined as a practical application of the probe. Urinary thallium levels, along with hair thallium levels, are essential parameters for the diagnosis of thallium exposure and poisoning.[21,50] Synthetic urine solutions[42,43] with varying concentrations of Tl^{3+} were treated with the probe solution under the same signaling conditions, and the developed responses were captured using a smartphone. The fluorescence images of the solutions were analyzed using color analysis software (RGB Grabber, Shunamicode). The values for the red, green, and blue channels of the image were plotted against the concentration of thallium. The calibration curves were not perfect (R^2 = 0.9656, 0.9786, and 0.9488 for the plots using the red, green, and blue channels of the image, respectively) owing to the slight curvature of the plots (Fig. 5). We found that Tl^{3+} levels down to 5.0 × 10^{-6} M in synthetic urine could be discerned simply by obtaining a smartphone image. Concerning the IUPAC recommendation ($3s_{bl}/m$), the detection limit of the probe to determine thallium ions was assessed using the plot's green channel value. The obtained detection limit (2.9 × 10^{-7} M, 57 μg L^{-1}) was not sensitive enough for the determination of Tl^{3+} in normal urine samples (1.32 × 10^{-8} M, 2.6 μg L^{-1}). However, we believe that the present analytical method could be used for preliminary screening of elevated thallium levels in acute thallium poisoning by a simple urine test. Recent toxicology research reported that the median urinary thallium level in acute poisoning cases was 1959 μg L^{-1} (8.10 × 10^{-6} M) in a range of 452–2909 μg L^{-1} (1.87 × 10^{-6}–1.20 × 10^{-5} M).[51] We also confirmed that the Tl^{3+} calibration curve and the detection limit of the probe obtained from the smartphone image were quite similar to the results obtained by independent fluorescence measurements (Fig. S20, ESI†). As mentioned in the introduction, the analysis of the urinary thallium levels is now routinely carried out using procedurally complicated heavy instruments such as an ICP-MS and atomic absorption spectrometer with complicated procedures.[10] By relying on the present method, elevated urinary thallium levels in accidental acute poisoning cases could be rapidly assessed from images obtained using a readily available smartphone.

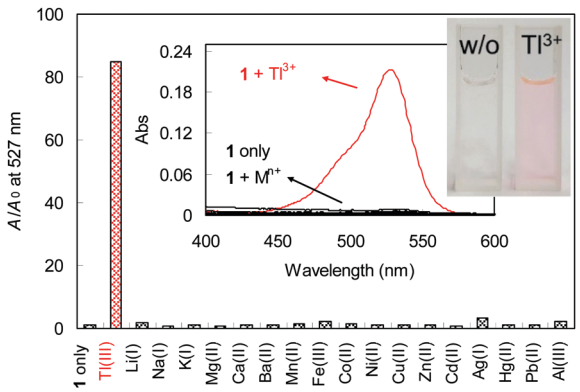


Fig. 4 Changes in absorbance enhancement (A/A_0) of probe **1** at 527 nm when the ions of common metals are present. Insets: (middle) absorption spectra of **1** when metal ions are present, (right) photograph of the probe in the presence and absence of thallium ions. [**1**] = 5.0 × 10^{-6} M, [M^{n+}] = 1.5 × 10^{-3} M in acetate buffer solution (pH 4.2, 10 mM) containing 30% (v/v) DMSO.

4. Conclusions

A simple, small molecule-based probe was developed for the selective and sensitive detection of toxic thallium ions. The basis of signaling was oxidative hydrolysis, stimulated by thallium ions, of the hydroxamate moiety of the probe based on rhodamine fluorophore to restore the fluorescence and colorimetric activity of

the parent dye. The presence of ions of common metals, oxidants, or anions apart from iodide ions that are redox-active, did not influence thallium ion-selective signaling. Smartphone images were used to successfully visualize the levels of thallium ions in synthetic urine with a detection limit of 290 nM. The method developed through this research can be used for the early diagnosis of elevated levels of thallium in urine in cases of acute poisoning.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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