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Fluorescence Signaling of Zr^{4+} by Hydrogen Peroxide Assisted Selective Desulfurization of Thioamide

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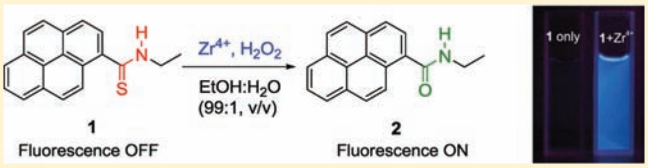
Supporting Information

ABSTRACT: Thioamide derivative with a pyrene fluorophore was smoothly transformed to its corresponding amide by Zr^{4+} ions in the presence of hydrogen peroxide. The transformation was evidenced by ^1H NMR spectroscopy and the signaling was completed within 10 min after sample preparation. Interference from Ag^+ and Hg^{2+} ions in Zr^{4+}-selective fluorescence signaling was readily suppressed with the use of Sn^{2+} as a reducing additive. Discrimination of Zr^{4+} from closely related hafnium, which is a frequent contaminant in commercial zirconium, was not possible. Prominent Zr^{4+}-selective turn-on type fluorescence signaling was possible with a detection limit of 4.6×10^{-6} M in an aqueous 99% ethanol solution.



■ INTRODUCTION

Zirconium is used in a wide range of applications within various industries due to its refractory and hardness characteristics, as well as its resistance to attack by common acids and bases.[1,2] It is increasingly being used as a corrosion-resistant material in the construction of chemical processing industry equipment.[3] It is also a component of some Ziegler–Natta catalysts used to produce polyethylene and polypropylene.[4] Zirconium dioxide (zirconia) is used in laboratory crucibles, ceramic materials,[5] metallurgical furnaces, and biomedical applications such as dental prostheses and femoral heads.[6,7] Particularly, zirconium alloys are used for the cladding of uranium fuel in a water-cooled nuclear power reactor.[8] Moreover, zirconium phosphate is known to be a highly efficient ion-exchanger, and is superior to other known organic exchangers with respect to thermal stability.[9]

Due to the widespread use of these industrial zirconium compounds, zirconium determination is a subject of considerable importance. Zirconium can be determined by inductively coupled plasma mass spectrometry.[10] It is also routinely analyzed by potentiometry using Alizarin Red S and cetyltrimethylammonium bromide ion pair or bis(diphenylphosphino)ferrocene incorporated in PVC matrix,[11] EDTA titration,[12] and gravimetry using mandelic acid.[13] Although the spectrophotometric technique might be more convenient in terms of required instruments and technical skill, selective optical signaling of Zr^{4+} ions is rarely reported. Among the few recent reports are those describing the spectrophotometric analysis of Zr^{4+} based on the complex it forms with Alizarin Red S and a ternary complex formed between Zr^{4+} and 5,7-dibromo-8-hydroxyquinoline in the presence of thiocyanate.[14]

There are many well designed molecular probes for the signaling or visualization of important chemical and biological species based on the selective reaction of the latent probes with the target analytes.[15] Among many sophisticated strategies for probe design, a number of sulfur-containing probes have been successfully used for the selective signaling of thiophilic metal ions.[16] A notable example is the signaling of Hg^{2+} ions via desulfurization of thio-functionalized probes based on a variety of molecular frameworks, such as anthracene,[17] rhodamines,[18] and coumarins.[19] This paper reports a simple Zr^{4+}-selective fluorescent signaling probe based on the hydrogen peroxide assisted desulfurization of pyrene-thioamide. The hydrogen peroxide–Zr^{4+} system has been used as an efficient reagent for the desulfurization of thioamides to amides.[20] The designed pyrene-thioamide **1** selectively signaled the Zr^{4+} ions in the presence of hydrogen peroxide in an aqueous 99% ethanol solution. Interference from Ag^+ and Hg^{2+} ions in Zr^{4+}-selective fluorescence signaling was readily suppressed with the use of Sn^{2+} as a reducing additive.

■ EXPERIMENTAL METHOD

General. 1-Pyrenecarboxylic acid, ethylamine hydrochloride, oxalyl chloride, and Lawesson's reagent were purchased from Aldrich Chemical Co. and used without further purification. $ZrCl_4$ and $SnCl_2$ were obtained from Aldrich Chemical Co. and used as received. All solvents were purchased from Aldrich Chemical Co. as "anhydrous" or "spectroscopic grade". ^1H NMR (300 MHz) and ^{13}C NMR (150 MHz) spectra were obtained on a Varian Gemini 2000 and Varian VNS NMR spectrometer, respectively, and referenced to the residual solvent signal. Fluorescence spectra were measured on an Aminco-Bowman Series 2 spectrophotometer. Mass spectra were obtained on a JMS-AX505WA (JEOL) mass spectrometer. Elemental analysis data were obtained by Flash EA 1112 (Thermo Electron corporation) elemental analyzer.

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Preparation of Metal Ion and Anion Solutions. Stock solutions (0.1 M) of zirconium(IV) chloride and Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+} ions in perchlorate salts were prepared in deionized water. Stock solutions (0.1 M) of F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, SO_4^{2-}, NO_3^-, OAc^-, HCO_3^-, and ClO_4^- ions in sodium salts were prepared in deionized water.

Synthesis of 2. To a suspension of 1-pyrenecarboxylic acid (0.10 g, 0.41 mmol) in CH_2Cl_2 (10 mL) was added oxalyl chloride (0.11 mL, 1.2 mmol). One drop of *N,N*-dimethylformamide was injected as a catalyst. The resulting mixture was stirred at room temperature for 4 h. Evaporation of the volatiles yielded pyrene-1-carbonyl chloride which was used without purification for next reaction. To a dispersion of ethylamine hydrochloride (0.17 g, 2.0 mmol) in CH_2Cl_2 (10 mL) was added triethylamine (1.4 mL, 10 mmol) and stirred at room temperature for 10 min. To the resulting solution, pyrene-1-carbonyl chloride dissolved in CH_2Cl_2 (2 mL) was added dropwise. After 2 h of stirring, the reaction mixture was washed with water and evaporated to dryness followed by crystallization from CH_2Cl_2 and CH_3OH to obtain **2** (90 mg, 81%) as a light yellowish product. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.56 (d, $J = 9.3$ Hz, 1H), 8.23−8.01 (m, 8H), 6.15 (br m, 1H), 3.67 (qd, $J = 7.3$ and 5.6 Hz, 2H), 1.36 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.9, 132.4, 131.3, 131.1, 130.7, 128.6, 128.5, 128.5, 127.1, 126.3, 125.7, 125.7, 124.7, 124.4, 124.4, 124.4, 124.3, 35.2, 15.0. HRMS (DIP) *m/z* calcd for $C_{19}H_{16}NO$ $[M + H]^+$ 274.1232; found, 274.1234. Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.13; H, 5.26; N, 5.09.

Synthesis of 1. To a solution of **2** (71 mg, 0.26 mmol) in toluene (5 mL) was added Lawesson's reagent (110 mg, 0.27 mmol) and the solution was refluxed for 24 h. The solvent was evaporated, and the crude product was purified by flash column chromatography (silica gel, ethyl acetate/hexane = 1:3, v/v) to give yellow solid product **1** (54 mg, 73%). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.31 (d, $J = 9.3$ Hz, 1H), 8.24−8.01 (m, 8H), 7.63 (br m, 1H), 4.05 (qd, $J = 7.3$ and 5.4 Hz, 2H), 1.47 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 200.7, 138.7, 131.8, 131.3, 130.7, 128.6, 128.3, 127.2, 126.4, 126.3, 125.8, 125.5, 124.7, 124.7, 124.6, 123.7, 41.5, 13.4. HRMS (DIP) *m/z* calcd for $C_{19}H_{16}NS$ $[M + H]^+$ 290.1003; found, 290.0998. Anal. Calcd for $C_{19}H_{15}NS$: C, 78.86; H, 5.22; N, 4.84. Found: C, 78.80; H, 4.84; N, 4.82.

Synthesis of 3. Compound **3** was prepared by following a previously reported procedure.[21]

Signaling of Zr^{4+} Ions. Due to the rather uninformative UV−vis absorption responses of **1** toward surveyed metal ions, signaling behavior was assessed by fluorescence measurements. For all measurements, the excitation wavelength was 340 nm.

(a). Without H_2O_2. Stock solution of **1** (5.0×10^{-4} M) was prepared in ethanol. Test solutions were prepared by placing 30 μL of stock solution of **1** and 3.0 μL of metal ion solution consecutively in a vial. The resulting solutions were diluted to 3.0 mL with ethanol and deionized water to make a final composition of 99:1, v/v. The final concentration of **1** and metal ion was 5.0×10^{-6} M and 1.0×10^{-4} M, respectively.

(b). With H_2O_2. Stock solution of H_2O_2 (0.5 M) was prepared in deionized water. Test solutions were prepared by placing 30 μL of stock solution of **1**, 3.0 μL of H_2O_2 solution, and 3.0 μL of metal ion solution consecutively in a vial. The resulting solutions were diluted to 3.0 mL with ethanol and deionized water to make a final composition of 99:1, v/v. The final concentration of **1**, H_2O_2, and metal ion was 5.0×10^{-6} M, 5.0×10^{-4} M, and 1.0×10^{-4} M, respectively.

(c). With Reducing Agent $SnCl_2$. Stock solution of stannous chloride (0.1 M) was prepared in deionized water. Test solutions were prepared by placing 30 μL of stock solution of **1**, 6.0 μL of Sn^{2+} solution, 9.0 μL of H_2O_2 solution, and 3.0 μL of metal ion solution successively in a vial. The resulting solutions were diluted to 3.0 mL with ethanol and deionized water to make a final composition of 99:1, v/v. The final concentration of **1**, H_2O_2, Sn^{2+}, and metal ion was 5.0×10^{-6} M, 1.5×10^{-3} M, 2.0×10^{-4} M, and 1.0×10^{-4} M, respectively.

Detection Limit. Detection limit was estimated by plotting the changes in fluorescence intensities of **1** at 382 nm as a function of log $[Zr^{4+}]$ following the reported procedure.[22] A linear regression curve was fitted to the intermediate values of the sigmoidal plot. The point at which this line crossed the ordinate axis was taken as the detection limit.

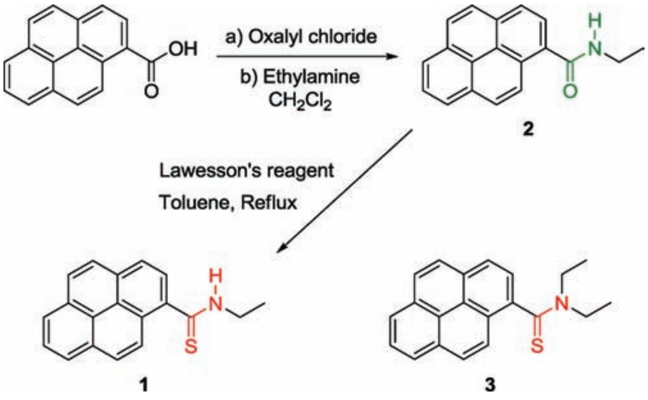
Competition Experiment. Test solutions were prepared by placing 30 μL of stock solution of **1**, 3.0 μL of H_2O_2 solution, 3.0 μL of metal ion or anion solution, and 3.0 μL of Zr^{4+} solution consecutively in a vial. The resulting solutions were diluted to 3.0 mL with ethanol and deionized water to make a final composition of 99:1, v/v. The final concentration of **1**, H_2O_2, M^{n+} or A^{n-}, and Zr^{4+} was 5.0×10^{-6} M, 5.0×10^{-4} M, 1.0×10^{-4} M, and 1.0×10^{-4} M, respectively.

^1H NMR Evidence. To a solution of **1** (49 mg, 0.17 mmol) in ethanol (5 mL) was added H_2O_2 (30%, 0.084 mL, 0.84 mmol) and $ZrCl_4$ (79 mg, 0.34 mmol). The mixture was stirred at room temperature for 5 min and water (10 mL) was added to the solution. The solid product was filtered and dried in vacuum. The product was dissolved in $CDCl_3$ to obtain the ^1H NMR spectrum for (**1** + Zr^{4+} + H_2O_2).

■ RESULTS AND DISCUSSION

Pyrene-ethylthioamide derivative **1** was prepared by the reaction of *N*-ethylpyrene-1-carboxamide **2**, which was obtained from the reaction of 1-pyrenecarboxylic acid with ethylamine (yield, 81%), with Lawesson's reagent in toluene (yield, 73%) (Scheme 1). Diethylthioamide derivative **3**[21] which we used as a probe for the important oxidant Oxone was also tested, but the signaling behavior toward the surveyed metal ions was significantly inferior to the ethylthioamide derivative **1**.

Scheme 1. Preparation of Pyrene-Ethylthioamide Derivative 1 and the Structure of Diethylthioamide Derivative 3



The fluorescence spectrum of probe **1** showed a very weak emission around 372−455 nm in an aqueous 99% ethanol solution (EtOH:H_2O = 99:1, v/v) (Figure S1, Supporting Information). This is due to the quenching nature of thioamide functional groups.[23] Treatment of **1** with 20 equiv of metal ions or anions resulted in a significant fluorescence enhancement for Ag^+ (82-fold) and Hg^{2+} (96-fold) ions at 382 nm (Figure 1 without H_2O_2 and Figure S1, Supporting Information). This observation is easily understood due to the desulfurization of thioamide by these ions.[17] The presence of Zr^{4+} exhibited almost no signaling for **1**, which was also the case for the other surveyed metal ions. The use of only 1% water for the signaling was due to the greatly reduced fluorescence signaling of the present system with increasing water content. Therefore, a minimum amount of water, which is requisite for the analysis of aqueous analytes but did not significantly influence the fluorescence behavior of **1**, was used in the signaling experiments.

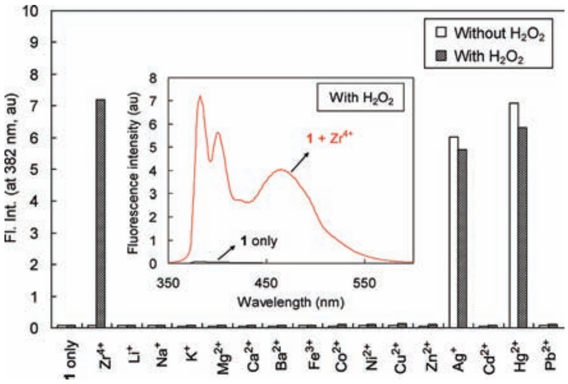
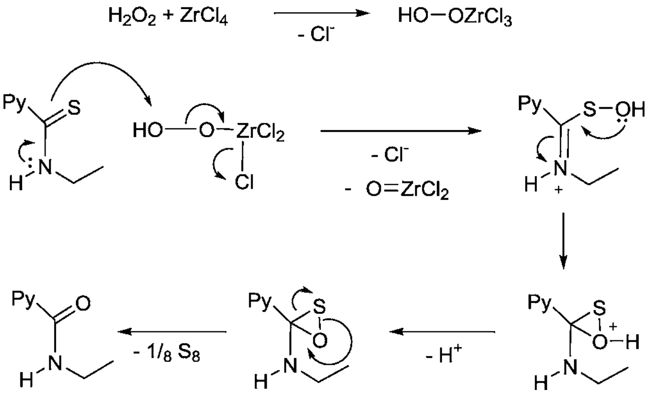


Figure 1. Changes in fluorescence intensity at 382 nm of **1** toward representative metal ions in the absence and presence of H_2O_2. Inset: fluorescence spectra of **1** and **1** upon treatment with Zr^{4+} in the presence of H_2O_2. [**1**] = 5.0×10^{-6} M, [H_2O_2] = 5.0×10^{-4} M, [Zr^{4+}] = [M^{n+}] = 1.0×10^{-4} M in aqueous 99% ethanol; λ_{ex} = 340 nm.

However, in the presence of hydrogen peroxide, Zr^{4+} signaling was observed for **1** in addition to Ag^+ and Hg^{2+} ions (Figure 1 with H_2O_2 and Figure S2, Supporting Information). Although H_2O_2 itself is known to have a tendency for desulfurization of thioamide, it did not reveal any noticeable signaling behavior of thioamide **1** under the present conditions (Figure 1).[24] Upon the treatment of **1** with Zr^{4+} in the presence of 100 equiv of H_2O_2, a prominent fluorescence enhancement in the monomer and excimer emission region was observed (inset of Figure 1). The large fluorescence change was due to the H_2O_2 assisted desulfurization of thioamide by the Zr^{4+} ions, and the proposed reaction mechanism is shown in Scheme 2. As has been reported for the Zr^{4+}-H_2O_2 induced desulfurization of alkyl and aryl thioamides, the reaction proceeds probably through a cyclic intermediate that undergoes sulfur extrusion.[20] The nucleophilic attack of H_2O_2 on $ZrCl_4$ makes the oxygen atom of peroxide more electrophilic for the reaction.

A prominent increase in the excimer region of pyrene around 465 nm was also observed for Zr^{4+} as well as Hg^{2+} and less pronouncedly for Ag^+ ions (Figure S2, Supporting Information). We attempted to apply ratiometry for the quantification of Zr^{4+} signaling based on these variations in the monomer and excimer regions. However, ratiometry was rather uninformative, and following the changes in monomer emission was more favorable for understanding the selective signaling of the Zr^{4+} ions by **1**. The appearance of the excimer emission of **1** in the presence of Zr^{4+} and Hg^{2+} ions might be due to the metal ion induced association of the pyrene moieties[25] by the interaction of the metal ions with the amide carbonyl groups of the converted amide **2**, that is possibly facilitated by the subtle changes in medium exerted by the desulfurization process. To summarize, probe **1** showed a relatively broad signaling behavior toward Hg^{2+}, Ag^+, and Zr^{4+} ions in the presence of H_2O_2 (see Figure 1, with H_2O_2).

Scheme 2. Proposed Mechanism for the Desulfurization of 1 by Zr^{4+}-H_2O_2 (Py = pyrene)[20]



Based on this observation, we attempted to achieve selective Zr^{4+} signaling of **1** using different potential masking agents for Hg^{2+} and Ag^+ ions including iodide, EDTA, *N,N,N′,N′*-tetrakis-(2-pyridylmethyl)-ethylenediamine, and Chelex-100 resin. In most cases, the signaling toward Zr^{4+} was deteriorated in the presence of the tested masking agents or chelating resin. Conversely, when the solution was treated with a well-known reducing agent $SnCl_2$, this resulted in the effective suppression of the Hg^{2+} and Ag^+ responses by reductive transformation to elemental Hg and Ag, respectively.[26,27] In this case, treatment of thioamide derivative **1** with Sn^{2+} ions alone did not induce any signaling (Figure 2) as well as reduction of the Zr^{4+}, which is known to be difficult to reduce;[3] that resulted in an exclusive Zr^{4+} selectivity of probe **1** (Figure S3, Supporting Information). We also tested the possibility for the discrimination of Zr^{4+} from the rare earth element Hf^{4+}, which is typically contained 1−2.5% in commercial zirconium metal. However, probe **1** exhibited similar Hf^{4+} signaling behavior which is comparable to

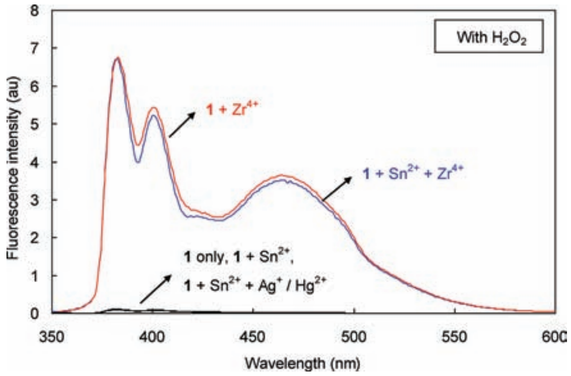
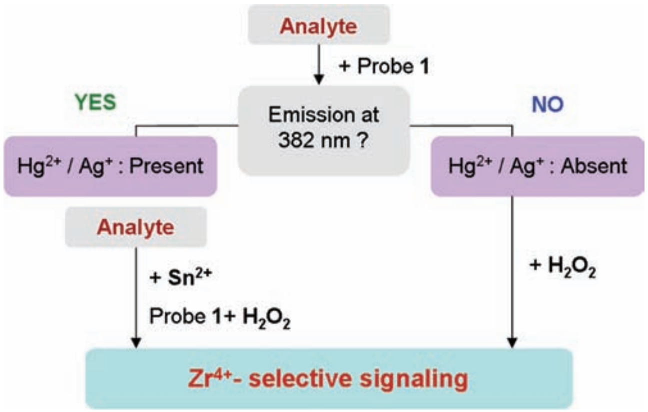


Figure 2. Effect of Sn^{2+} on fluorescence signaling of **1** toward Zr^{4+}, Hg^{2+}, and Ag^+ in the presence of H_2O_2. [**1**] = 5.0×10^{-6} M, [H_2O_2] = 1.5×10^{-3} M, [Zr^{4+}] = [M^{n+}] = 1.0×10^{-4} M, [Sn^{2+}] = 2.0×10^{-4} M in aqueous 99% ethanol; λ_{ex} = 340 nm.

that of Zr^{4+} ions (Figure S4, Supporting Information), which might be due to the rather similar chemical properties of zirconium and hafnium.[28]

The procedure to circumvent interference from Ag^+ and Hg^{2+} ions in Zr^{4+} signaling by **1** using $SnCl_2$ is outlined in Scheme 3. The presence of these interferences was easily monitored by the response of probe **1** toward analytes in the absence of H_2O_2 (Figure 1, without H_2O_2). If the analyte solution did not exhibit a response of the probe **1** at 382 nm, then the absence of Ag^+ and Hg^{2+} was confirmed. In this case, the simple addition of H_2O_2 to the analytes signaled the Zr^{4+} concentration selectively. Conversely, when the signal of **1** was observed without H_2O_2 (Figure 1, without H_2O_2), it implied the presence of these interfering ions. Then, Zr^{4+}-selective signaling of **1** could be achieved by the addition of an extra reducing agent Sn^{2+} in addition to H_2O_2 as oulined in Scheme 3.

Scheme 3. Outline of the Procedure for Zr^{4+}-Selective Signaling by 1



The suggested desulfurization of thioamide by Zr^{4+} in the presence of H_2O_2 was verified by ^1H NMR measurements. The ^1H NMR spectrum of the purified reaction product of **1** with Zr^{4+} in the presence of H_2O_2 was almost identical to that of **2** (Figure 3). The resonances of the methylene protons of the ethyl group at 4.05 ppm (blue star), the thioamide NH proton at 7.63 ppm (green star), and a doublet corresponding to the pyrene moiety at 8.31 ppm (red star) were shifted to 3.67, 6.15, and 8.56 ppm, respectively.

The fluorescence signaling behavior of **1** toward Zr^{4+} was not significantly affected by the presence of surveyed commonly encountered metal ions (Figure 4 and Figure S5, Supporting

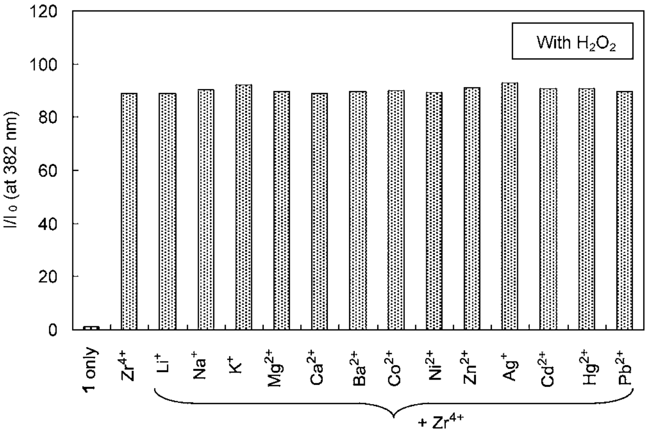


Figure 4. Fluorescence signaling of Zr^{4+} by **1** in the presence of coexisting metal ions. [**1**] = 5.0×10^{-6} M, [H_2O_2] = 5.0×10^{-4} M, [Zr^{4+}] = [M^{n+}] = 1.0×10^{-4} M in aqueous 99% ethanol; λ_{ex} = 340 nm.

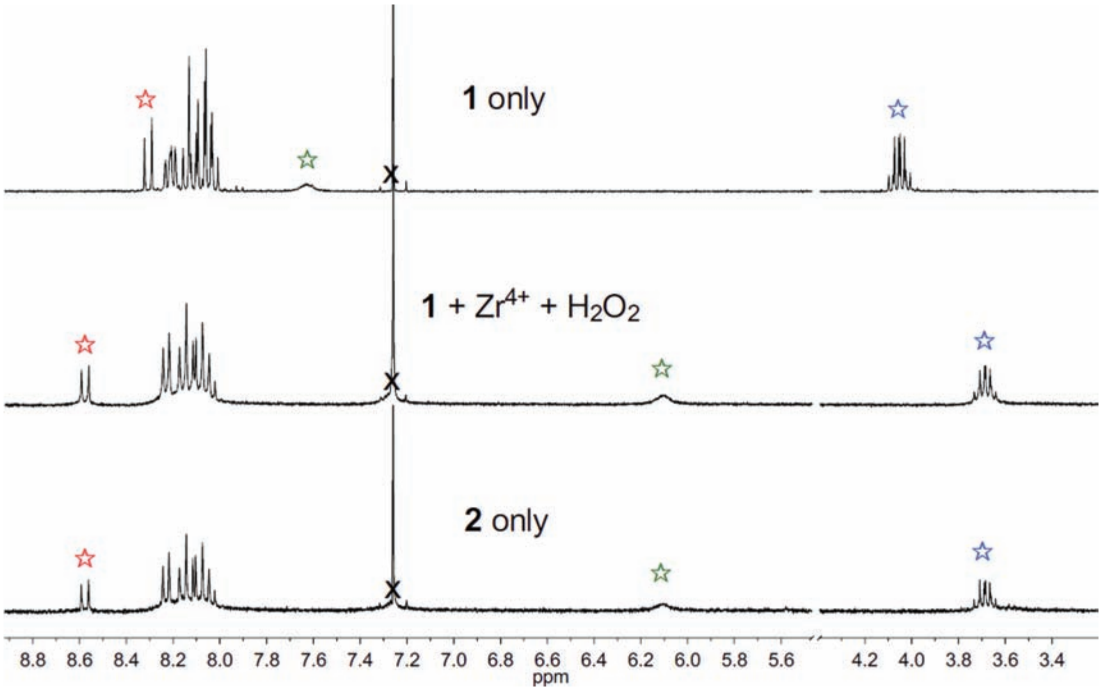


Figure 3. Partial ^1H NMR spectra of **1**, reaction product of **1** with Zr^{4+} in the presence of H_2O_2, and **2** in $CDCl_3$. [**1**] = [**2**] = 5.0×10^{-3} M. The middle spectrum (**1** + Zr^{4+} + H_2O_2) was obtained using a purified reaction product between **1** and Zr^{4+} in the presence of H_2O_2 in aqueous 99% ethanol.

Information). The I/I_o, which is the ratio of the fluorescence intensity at 382 nm of the **1**–Zr^{4+}–H_2O_2 system in the presence and absence of background metal ions, varied within a narrow region between 89 (for Ca^{2+}) and 93 (for Ag^+). However, Fe^{3+} and Cu^{2+} ions are found to significantly interfere with the Zr^{4+}-selective signaling due to the Fenton-like reaction with added H_2O_2.[29,30] Possible influence of coexisting anions on the signaling was also examined (Figure S6, Supporting Information). Almost no interferences were observed with commonly encountered anions except for SO_4^{2-} and $H_2PO_4^{2-}$, which might be due to the hydrolysis of zirconium sulfate[31] and formation of insoluble zirconium phosphate (K_{sp} of $Zr_3(PO_4)_4$ = 1×10^{-132}).[32] Signaling of Zr^{4+} by probe **1** was completed within 10 min (Figure 5). Conversely, under the same conditions, probe **1** did not show any responses after 2 h of sample preparation.

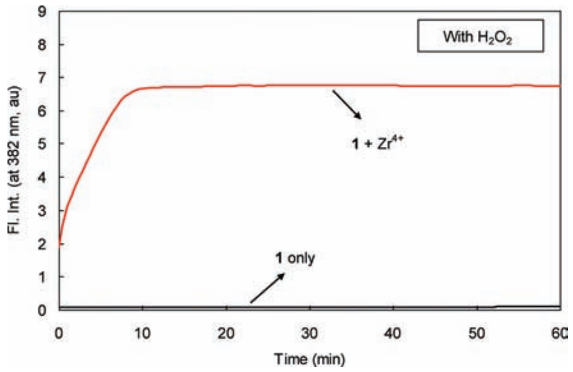


Figure 5. Time trace for the changes in fluorescence intensity of **1** in the absence and presence of Zr^{4+}. [**1**] = 5.0×10^{-6} M, [H_2O_2] = 5.0×10^{-4} M, [Zr^{4+}] = 1.0×10^{-4} M in aqueous 99% ethanol; λ_{ex} = 340 nm. Fluorescence intensities were measured at 382 nm.

Finally, concentration-dependent signaling of Zr^{4+} was investigated by the treatment of **1** with varying amounts of Zr^{4+} analytes. The fluorescence intensity at 382 and 465 nm increased linearly as a function of Zr^{4+} concentration up to 4.0×10^{-5} M (Figure 6). From this concentration-dependent signaling behavior at 382 nm, the detection limit of **1** for the determination of Zr^{4+} was estimated to be 4.6×10^{-6} M in an aqueous 99% ethanol solution.[22]

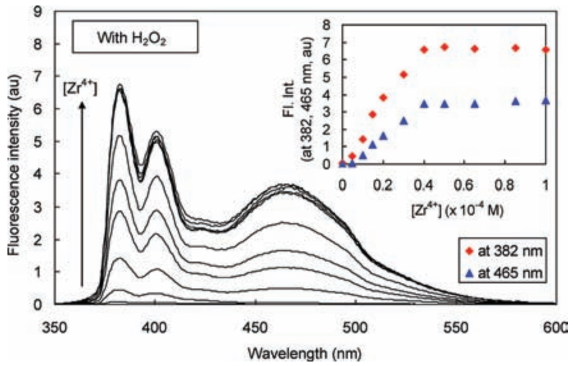


Figure 6. Concentration-dependent fluorescence signaling of Zr^{4+} by **1** in the presence of H_2O_2. [**1**] = 5.0×10^{-6} M, [H_2O_2] = 5.0×10^{-4} M in aqueous 99% ethanol; λ_{ex} = 340 nm. Inset: fluorescence intensities were measured at 382 and 465 nm.

■ CONCLUSIONS

A new chemosignaling system for Zr^{4+} ions was developed based on the Zr^{4+} induced desulfurization of thioamide to amide. The pyrene-ethylthioamide derivative exhibited selective fluorogenic signaling toward the Zr^{4+} ions via H_2O_2-assisted transformation to amide. The devised system also showed a pronounced and selective signaling behavior in the presence of common metal ions except for Ag^+ and Hg^{2+}. Interference from Ag^+ and Hg^{2+} ions was readily suppressed with the use of Sn^{2+} as a reducing additive. Although interference from closely related hafnium exists, the designed compound could be useful as a convenient fluorescent probe for the determination of industrially important Zr^{4+} ions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional chemosignaling behaviors of **1** toward Zr^{4+}, Hf^{4+}, common metal ions and anions, and ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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