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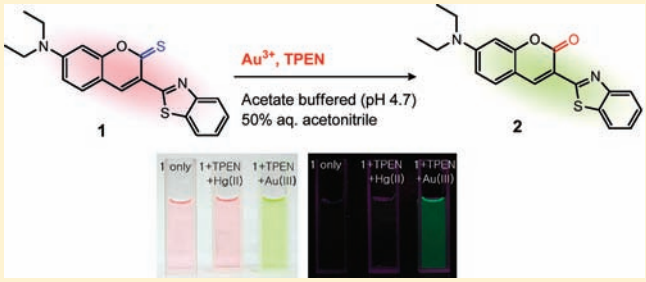
Colorimetric and Fluorescent Signaling of Au^{3+} by Desulfurization of Thiocoumarin

Ji Eun Park, Myung Gil Choi, and Suk-Kyu Chang*

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea

Supporting Information

ABSTRACT: We investigated the chemosignaling of Au^{3+} by the selective desulfurization of thiocoumarin. In the presence of a heavy metal ion chelator *N*,*N*,*N*′,*N*′-tetrakis-(2-pyridylmethyl)ethylenediamine, thiocoumarin was selectively converted to its oxo analogue by reaction with Au^{3+}, resulting in a pronounced chromogenic and fluorescent signaling. Selective signaling of Au^{3+} was possible in the presence of common alkali, alkaline earth, and transition metal ions, as well as Au^{+} in a mixed aqueous environment. The colorimetric determination of Au^{3+} was possible by the color change from pink to yellowish green of the designed probe. The detection limit for the determination of Au^{3+} in 50% aqueous acetonitrile was 1.1×10^{-7} M.



INTRODUCTION

Research on gold-related chemistry is currently one of the most rapidly growing fields in chemistry because of its relevance to a number of issues in material science.[1] Recently, a series of thorough reviews were published on various topics of gold chemistry,[2] such as catalysis,[3] selective oxidation,[4] nanoparticles in diagnostics and detection,[5] and photophysical perspective of this valuable element.[6]

The determination of precious metals of gold as well as other platinum group elements (Pt, Pd, Rh, Ir, Ru, and Os) in biological, clinical, and industrial samples has been of great interest.[7] Inductively coupled plasma mass spectrometry[8] has been a key technology for the sensitive and simultaneous determination of traces of these elements. Other techniques such as atomic absorption spectrometry and nuclear[9] and electrochemical[10] methods have also been reported. More recently, quantitative analysis of widely investigated gold nanoparticles has also been reviewed.[11] In spite of the ongoing efforts to develop versatile analytical techniques for gold analysis,[12] the optical signaling of Au^{3+} is more convenient in terms of the necessary instruments and technical skills and well discussed in a recent report.[13] Among the recently developed Au^{3+}-selective colorimetry and fluorescent signaling systems, selective chemical reaction based chemosignaling approach[14] which has been uniquely employed for the construction of many sophisticated signaling systems is interesting. Representative examples are Au^{3+}-induced intramolecular cyclization of the alkynes to yield a fluorescent ring-opened structure and cyclization of propargylamide to oxazolecarbaldehyde of rhodamines.[15] The other approach utilized the Au^{3+}-mediated hydroarylation reaction of a latent fluorophore of the alkyne derivative to yield a strongly fluorescent coumarin derivative[16] and the Kucherov reaction of 1,8-naphthalimide-alkyne conjugate to yield its methylketone derivative having ratiometrically analyzable signals via vinylgold intermediate.[17]

N,*N*,*N*′,*N*′-Tetrakis-(2-pyridylmethyl)ethylenediamine (TPEN) is known as an efficient Zn^{2+} chelator[18] and is a potential candidate for a practical and selective complexing agent for a variety of soft metal ions,[19] such as Hg^{2+},[20] Cd^{2+},[21] Cu^{2+},[22] and Pd^{2+}.[23] It also is frequently used as a separation tool for d- or f-block metal ions.[24] We have reported a dual signaling Hg^{2+}-selective probe based on the metal ion-induced desulfurization of thiocoumarins.[25] On the other hand, thioamide is known to be readily converted to its oxo amide by Au^{3+} ions.[26] On the basis of this, we devised a simple Au^{3+}-selective signaling system that uses the desulfurization of thiocoumarin to its oxo derivative, while utilizing TPEN as a masking agent for the possible interfering ions. In fact, significant Hg^{2+} response of thiocoumarin was effectively suppressed using TPEN,[27] and efficient Au^{3+}-selective signaling was realized. The developed system exhibited a pronounced chromogenic and fluorescence signaling behavior, which is typical of coumarin derivatives, toward Au^{3+} ions in an aqueous environment.

EXPERIMENTAL METHODS

General Methods. Coumarin 6 (**2**), *N*,*N*,*N*′,*N*′-tetrakis-(2-pyridylmethyl)ethylenediamine (TPEN), Lawesson's reagent, and $AuCl_3$ were purchased from Aldrich Chemical Co. AuCl was obtained from Alfa Aesar Co. Other inorganic salts were in perchlorate form and used as received. Acetonitrile was purchased from Aldrich Chemical Co. as "spectroscopic grade". ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained on a Varian gemini 2000 spectrometer and referenced to the residual solvent signal. UV−vis

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spectra were recorded with a Jasco V-550 spectrophotometer equipped with a Peltier temperature controller. Fluorescence spectra were measured on an Aminco-Bowman Series 2 spectrophotometer. Mass spectra were obtained on a Micromass Autospec mass spectrometer. Elemental analysis data were obtained by Flash EA 1112 (Thermo Electron corporation) elemental analyzer.

Preparation of 1. Thiocoumarin **1** was prepared by the reaction of coumarin 6 (**2**) with Lawesson's reagent following the reported procedure.[25] Yield, 65%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (br d, J = 0.6 Hz, 1H), 8.01 (ddd, J = 8.2, 1.1, and 0.7 Hz, 1H), 7.95 (ddd, J = 7.9, 1.3, and 0.6 Hz, 1H), 7.53 (d, J = 9.0 Hz, 1H), 7.48 (ddd, J = 8.2, 7.2, and 1.3 Hz, 1H), 7.37 (ddd, J = 8.1, 7.1, and 1.1 Hz, 1H), 6.73 (dd, J = 9.0 and 2.5 Hz, 1H), 6.67 (br d, J = 1.9 Hz, 1H), 3.45 (q, J = 7.1 Hz, 4H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.8, 164.4, 160.0, 153.1, 151.6, 139.0, 136.4, 131.4, 126.2, 124.8, 124.4, 122.1, 121.6, 111.9, 111.4, 96.4, 45.5, 12.7. HRMS (DIP) m/z calcd for $C_{20}H_{18}N_2OS_2$ $[M]^+$ 366.0861, found 366.0857. Anal. Calcd for $C_{20}H_{18}N_2OS_2$: C, 65.54; H, 4.95; N, 7.64; S, 17.50. Found: C, 65.56; H, 4.89; N, 7.50; S, 17.72.

Elucidation of Signaling Mechanism by ^{1}H NMR Spectroscopy. To have evidence for the Au^{3+}-assisted conversion from **1** to **2**, ^{1}H NMR spectra of **1**, **2**, and the reaction product of **1** with $AuCl_3$ in the presence of TPEN were obtained. To a solution of probe **1** (10 mM, in 50% aqueous acetonitrile) in the presence of TPEN (40 mM) was added $AuCl_3$ (20 mM), and the mixture was stirred at room temperature. After 30 min, the volatiles were evaporated under reduced pressure, and the residue was purified by column chromatography (silica gel, eluant: dichloromethane). ^{1}H NMR spectra of probe **1**, compound **2**, and the reaction product of **1**–TPEN–Au^{3+} were measured in D_2O/DMSO-d_6 (1:9, v/v).

Measurements of UV–Vis and Fluorescence Spectra. Stock solutions of probe **1** (0.50 mM) and TPEN (10 mM) were prepared in acetonitrile. Stock solutions of metal ions (10 mM) were prepared in deionized water by dissolving perchlorate salts of alkali (Li^+, Na^+, K^+), alkaline earth (Mg^{2+}, Ca^{2+}, Ba^{2+}), and transition metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Pb^{2+}, Hg^{2+}). Solutions (10 mM) of Au^+ and Au^{3+} were prepared from their chloride salts in deionized water.

The UV–vis spectrum of the probe **1** was measured in the presence and absence of metal ions. The measuring solution was prepared by mixing stock solutions of probe **1** (30 μL), metal ions (30 μL), and TPEN (60 μL) in 50% aqueous acetonitrile solution. Among the tested pH values, pronounced signaling behavior was observed around pH 4.7; thus, the solution was fixed at pH 4.7 by using an acetate buffer solution. Final concentrations of probe **1**, metal ions, and acetate buffer were 5.0 μM, 0.10 mM, and 10 mM in water–acetonitrile (1:1, v/v), respectively. After 1 min of each mixing, the UV–vis spectrum of the solution was measured. The discrimination between Au^{3+} and Hg^{2+} was attempted by using 2 equiv (with respect to the metal ions) of additional chelating agents of EDTA, 8-hydroxyquinoline, cyclam, and TPEN. To compensate the inherent absorbances of some transition metal ions, such as Co^{2+}, Cu^{2+}, and Fe^{3+} ions, in the analytes, the same amount of TPEN was added to the reference solution. The final concentration of added chelating agent was 0.20 mM. The fluorescence spectrum of **1** upon treatment with various metal ions in the absence and presence of TPEN was also obtained under the same conditions by excitation at 485 nm.

Competition Signaling Behaviors. Under the same measurement conditions, competitive signaling behavior of **1** toward Au^{3+} ions in the presence of coexisting metal ions as background was studied. Final concentrations of probe **1**, TPEN, Au^{3+}, and all the other competing metal ions and anions were 5.0 μM, 0.20 mM, 0.10 mM, and 0.10 mM, respectively, in a mixture of acetate buffered water (pH 4.7, 10 mM)–acetonitrile solution (1:1, v/v).

Time Course Plot of Signaling. The time course of the signaling of **1** for Au^{3+} ions was followed by measuring the absorbance of the measuring solution at 463 nm. The concentrations of the probe **1**, TPEN, Hg^{2+}, and Au^{3+} ions were 5.0 μM, 0.20 mM, 0.10 mM, and 0.10 mM, respectively, in a mixture of acetate buffered water (pH 4.7, 10 mM)–acetonitrile solution (1:1, v/v).

Detection Limit. The detection limit was estimated by plotting the fluorescence changes of **1** in the presence of TPEN as a function of log[Au^{3+}] following the reported procedure.[28] 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.

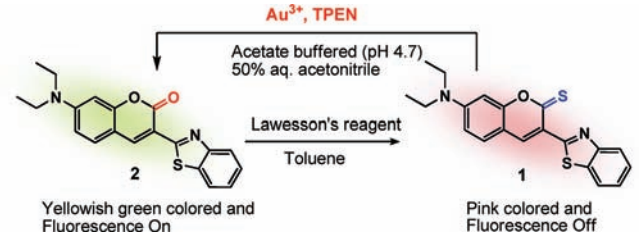
pH Effect on Au^{3+} Signaling. The pH effect on Au^{3+} signaling of **1** was investigated by measuring the UV–vis absorption spectra in a series of buffered solutions between pH 4.0–9.0. The pH of the solution was fixed by using acetate (pH 4.0–6.0), phosphate (pH 7.0–8.0), and tris (pH 9.0) buffer solutions. Final concentrations of probe **1**, TPEN, Au^{3+}, and each buffer solution were 5.0 μM, 0.20 mM, 0.10 mM, and 10 mM, respectively, under the same measurement conditions.

Interference from Au^+ at Higher Temperature. The possibility of the interference from Au^+ by the transformation of Au^+ to Au^{3+} at higher temperature was tested. The signaling of AuCl solution by **1** was measured after treatment of the solution at 50 and 80 °C for 2 h in a water bath. Final concentrations of probe **1**, TPEN, and AuCl were 5.0 μM, 0.20 mM, and 0.10 mM, respectively, under the same measurement conditions.

RESULTS AND DISCUSSION

Thiocoumarin derivative **1** was prepared by the reaction of coumarin 6 (**2**) with Lawesson's reagent following a previously reported procedure (Scheme 1).[25] The structural motif of coumarin 6 was selected as a probe because of its prominent chromogenic change from pink to yellowish green and its marked off-on type fluorogenic behavior due to the Au^{3+}-induced conversion of thiocarbonyl to carbonyl function.

Scheme 1. Preparation of Thiocumarin 1 and its Au^{3+}-Selective Signaling



Compound **1** had absorption bands at 366 and 520 nm in a 1:1 mixture of acetonitrile and acetate buffer solution (10 mM, pH 4.7). Upon treatment with various metal ions, prominent changes in the absorption behavior were observed exclusively with Au^{3+} and Hg^{2+} ions (Figure 1 and Figure S1, Supporting Information). With 20 equiv of Au^{3+} or Hg^{2+} ions, the absorption band of **1** at 520 nm disappeared almost completely, and a new band at 463 nm developed. Concomitantly, the solution color changed from pink to yellowish green. The absorbance ratio at the two characteristic wavelengths 520 and 463 nm (A_{520}/A_{463}) of **1** significantly changed from 3.29 to about 0.01 for Au^{3+} and Hg^{2+} ions (Figure S2, Supporting Information). The Hg^{2+} response of **1** was previously reported by us,[25] but the response of thiocoumarin toward Au^{3+} is unprecedented. Other metal ions revealed almost no responses, and the ratio A_{520}/A_{463} varied in a narrow range between 3.02 (for Au^+) and 3.47 (for Ba^{2+}). One more thing to note is that probe **1** could discriminate the two common oxidation states of gold(I) and gold(III): compound **1** exhibited a significant response to Au^{3+} but almost no responses toward Au^+. On the other hand, Au^+ ions are known to be unstable to disproportionation to Au^{3+} and Au. We checked the possibility

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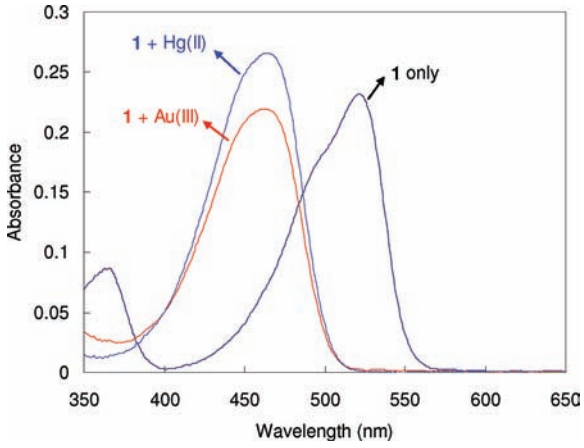

Figure 1. UV−vis spectra of **1** in the presence of Au^{3+} and Hg^{2+} ions. [**1**] = 5.0×10^{-6} M, [M^{n+}] = 1.0×10^{-4} M. In a mixture of CH_3CN and acetate buffer solution (pH 4.7, 10 mM) (1:1, v/v).

of interference from this transformation by measuring the responses toward Au^+ after treatment of the solution at 50 and 80 °C for 2 h. There was no noticeable change in signaling behavior of **1** toward Au^+ solution at 50 °C; however, some responses were observed at 80 °C (Figure S3, Supporting Information).[29] We also tested another Au^{3+} species, $NaAuCl_4$, and found that there was no difference in signaling behavior of **1** between the two species $AuCl_3$ and $NaAuCl_4$ (Figure S4, Supporting Information).

Based on this observation, we aimed to develop an Au^{3+}-selective signaling system using an extra additive that could provide discrimination between the two responding metal ions of Au^{3+} and Hg^{2+}. Surveyed additives include representative chelating agents for Hg^{2+} ions, such as TPEN, EDTA, 8-hydroxyquinoline, and cyclam. Among the tested additives, TPEN effectively suppressed the Hg^{2+} response of **1** (Figure 2

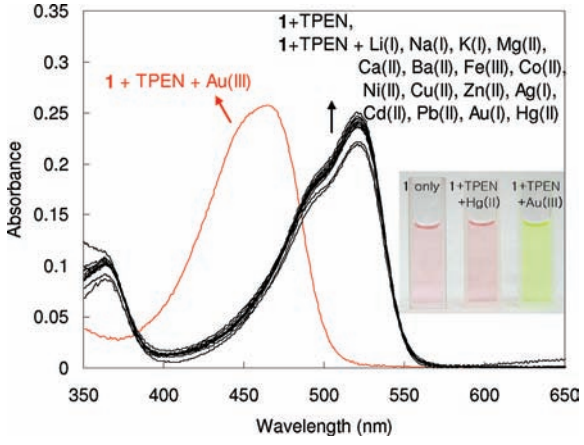

Figure 2. UV−vis spectra of **1** in the presence of various metal ions with additional chelating agent TPEN. [**1**] = 5.0×10^{-6} M, [M^{n+}] = 1.0×10^{-4} M, [TPEN] = 2.0×10^{-4} M. In a mixture of CH_3CN and acetate buffer solution (pH 4.7, 10 mM) (1:1, v/v).

and Figure S5, Supporting Information). In the presence of cyclam, quite effective suppression of Hg^{2+} signaling of **1** was also observed (Figure S6, Supporting Information). With other surveyed chelating agents of EDTA and 8-hydroxyquinoline, the desired exclusive Au^{3+} selectivity was not realized because the Hg^{2+}-induced signaling was still significant (Figures S7 and S8, Supporting Information).

Thiocoumarin **1** showed a weak emission at 511 nm due to the presence of a strongly quenching thiocarbonyl function.[30] After treatment with metal ions, particularly with Au^{3+} and Hg^{2+} ions, prominently enhanced fluorescence of **1** at 511 nm was observed (Figure S9, Supporting Information). On the other hand, in the presence of TPEN, the response of **1** toward Hg^{2+} ions at 511 nm completely disappeared, resulting in an exclusive Au^{3+} selectivity with a 49.7-fold fluorescence enhancement (Figure 3). Other metal ions did not induce

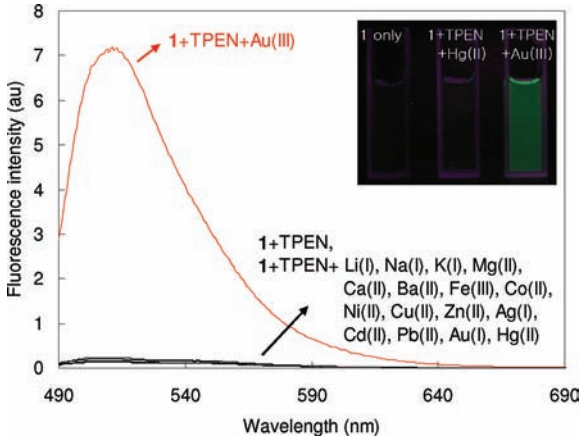

Figure 3. Fluorescence spectra of **1** in the presence of various metal ions with additional chelating agent TPEN. [**1**] = 5.0×10^{-6} M, [M^{n+}] = 1.0×10^{-4} M, [TPEN] = 2.0×10^{-4} M. In a mixture of CH_3CN and acetate buffer solution (pH 4.7, 10 mM) (1:1, v/v). λ_{ex} = 485 nm.

any noticeable signaling, and the fluorescence intensity ratio of **1** in the presence versus absence of metal ions I/I_o at 511 nm varied in a narrow range between 0.92 for Ni^{2+} and 1.58 for Hg^{2+} (Figure S10, Supporting Information). Although using a masking agent is less desirable for the practical applications in terms of simplicity and convenience, these observations imply that a new Au^{3+}-selective fluorescence signaling system can be achieved using the heavy metal chelator TPEN as a masking agent for the interfering metal ions.

The observed signaling is due to the Au^{3+}-assisted desulfurization of the thiocarbonyl function of **1**, as has been previously reported for Hg^{2+} ions. Desulfurization of thiocarbonyl groups with Hg^{2+} and Au^{3+} ions is already known.[31] However, in the presence of TPEN, Hg^{2+} ions are efficiently sequestered (K_d for Hg^{2+}−TPEN = $\sim 10^{-25}$ M)[32] to suppress the desulfurization of **1**, and the exclusive signaling of Au^{3+} was realized. It is known that Au^{3+} also forms a complex with TPEN; however, the stability of the complex is not sufficiently high (K_d for Au^{3+}−TPEN = $\sim 10^{-10}$ M),[33] and thus gold ions could react with the thiocarbonyl group of **1** under the signaling conditions.

The postulated conversion was evidenced by ^{1}H NMR, UV−vis, and fluorescence measurements. The ^{1}H NMR spectrum of reaction product of **1** with Au^{3+} in the presence of TPEN (**1**−TPEN−Au^{3+}) was almost the same as that of **2** under the measurement conditions (Figure 4). In addition, UV−vis and fluorescence measurements of **1** in the presence of TPEN and Au^{3+} ions also support the postulated desulfurization of **1** to **2** as depicted in Scheme 1.

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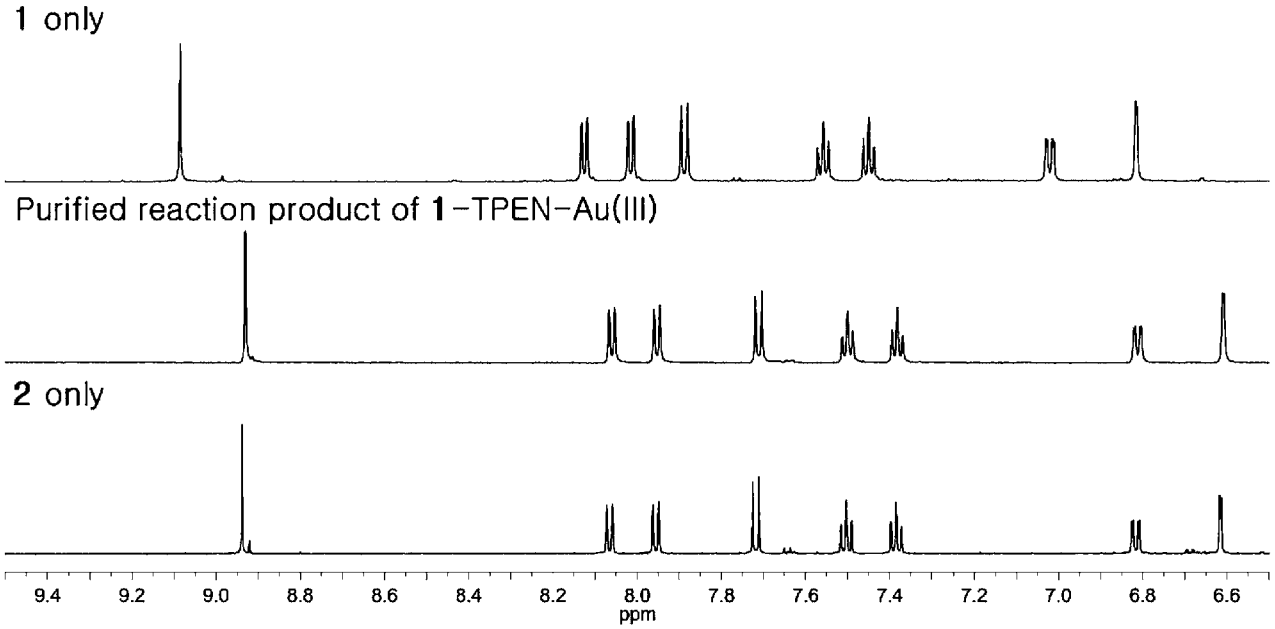

Figure 4. Partial ^{1}H NMR spectra of **1**, the purified reaction product of **1**−TPEN−Au^{3+}, and **2**. [**1**] = [**2**] = 5.0×10^{-3} M. In D_2O/DMSO-d_6 (1:9, v/v).

The quantitative analytical behavior of **1** in the signaling of Au^{3+} ions was investigated by UV−vis titration. The large difference in absorption bands of **1** induced by Au^{3+} allowed a convenient ratiometric analysis of the concentration-dependent signaling behavior (Figure 5). A plot of the absorbance ratio at

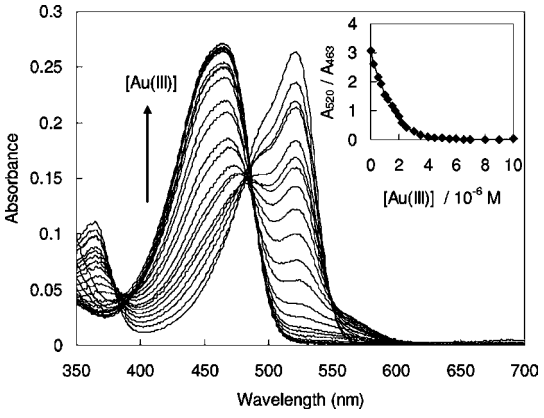

Figure 5. Changes in UV−vis spectra of **1**−TPEN as a function of Au^{3+} concentration. [**1**] = 5.0×10^{-6} M, [TPEN] = 2.0×10^{-4} M. In a mixture of CH_3CN and acetate buffer solution (pH 4.7, 10 mM) (1:1, v/v). Inset shows the ratiometric (A_{520}/A_{463}) behavior of **1** as a function of [Au^{3+}].

520 and 463 nm (A_{520}/A_{463}) as a function of [Au^{3+}] showed a prominent change up to 4×10^{-6} M of Au^{3+}. From this concentration dependent response, the detection limit of **1** for the determination of Au^{3+} ions was estimated as 1.1×10^{-7} M in 50% aqueous acetonitrile solution.[28]

Signaling of Au^{3+} by **1** was completed within 1 min under the measurement conditions (Figure S11, Supporting Information). Under the same conditions, however, thiocoumarin **1** was stable and did not show any significant signaling at 24 h after sample preparation. Possibly interfering Hg^{2+} ions also induced an insignificant response to **1** in the presence of TPEN even 24 h after the sample preparation. To check the pH effect on the signaling of Au^{3+} ions by the **1**−TPEN system, signaling measurements were carried out by using a series of buffer solutions (pH 4.0−9.0). The Au^{3+}-selective signaling behavior was not significantly affected in acidic conditions (pH 4.0−6.0) without any noticeable interference from Hg^{2+} ions (Figure S12, Supporting Information) as well as other metal ions.

Finally, we performed a competition experiment for Au^{3+} signaling of **1** in the presence of TPEN with potentially interfering metal ions and anions as background. Alkali and alkaline earth metal ions showed no significant interference (Figure 6). Potential interference from transition metal ions,

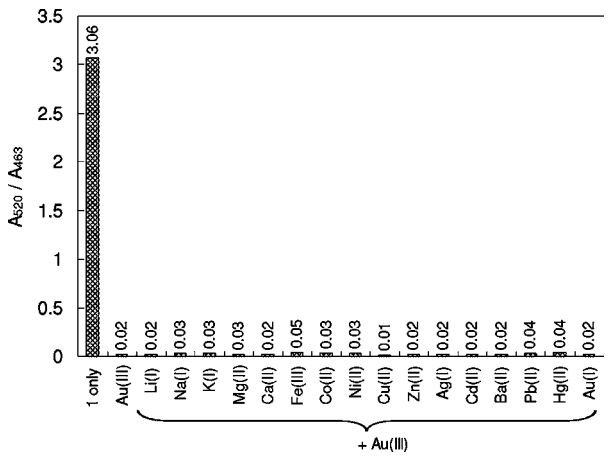

Figure 6. Competitive signaling of Au^{3+} by **1**−TPEN in the presence of representative metal ions as background. [**1**] = 5.0×10^{-6} M, [Au^{3+}] = [M^{n+}] = 1.0×10^{-4} M, [TPEN] = 2.0×10^{-4} M. In a mixture of CH_3CN and acetate buffer solution (pH 4.7, 10 mM) (1:1, v/v).

particularly Hg^{2+} ions, also was not observed. Representative anions also induced no noticeable interferences for the selective signaling of Au^{3+} by **1** (Figure S13, Supporting Information). All these observations clearly suggest that the designed

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thiocoumarin−TPEN system could selectively signal the valuable Au^{3+} ions in the presence of commonly coexisting metal ions.

CONCLUSIONS

A simple thiocoumarin derivative was developed for a gold-selective chemosignaling system. Au^{3+}-induced desulfurization of thiocarbonyl function resulted in a colorimetric and an "off−on"-type fluorescence signaling of Au^{3+} ions in a mixed aqueous media. Marked color change from pink to yellowish green allowed naked-eye detection of Au^{3+}. Selective signaling of Au^{3+} was possible in the presence of common alkali, alkaline earth, and transition metal ions, as well as Au^{+} in a mixed aqueous environment. Interference from Hg^{2+} ions was successfully eliminated by using a chelating agent TPEN. The detection limit was 1.1×10^{-7} M in 50% aqueous acetonitrile. Gold(III) induced transformation from thiocoumarin to coumarin was confirmed by ^{1}H NMR measurements. The signaling was fast and detectable by the naked eye, so the thiocoumarin−TPEN system can be used as a convenient Au^{3+}-selective colorimetric probe system.

ASSOCIATED CONTENT

Supporting Information

Additional chemosignaling behavior, ^{1}H NMR, and ^{13}C NMR spectra of **1** are reported. These materials are available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: skchang@cau.ac.kr.

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REFERENCES

(1) (a) *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley: Chichester, 1999. (b) *Gold Chemistry Applications and Future Directions in the Life Sciences*; Mohr, F., Ed.; Wiley-VCH: Weinheim, 2009. (c) *Modern Supramolecular Gold Chemistry: Gold-Metal Interactions and Applications*; Laguna, A., Ed.; Wiley-VCH: Weinheim, 2008.

(2) Hutchings, G. J.; Brust, M.; Schmidbaur, H. *Chem. Soc. Rev.* **2008**, *37*, 1759−1765.

(3) Hashmi, A. S. K.; Rudolph, M. *Chem. Soc. Rev.* **2008**, *37*, 1766−1775.

(4) Pina, C. D.; Falletta, E.; Prati, L.; Rossi, M. *Chem. Soc. Rev.* **2008**, *37*, 2077−2095.

(5) (a) Wilson, R. *Chem. Soc. Rev.* **2008**, *37*, 2028−2045. (b) Sardar, R.; Funston, A. M.; Mulvaney, P.; Murray, R. W. *Langmuir* **2009**, *25*, 13840−13851.

(6) Yam, V. W.-W.; Cheng, E. C.-C. *Chem. Soc. Rev.* **2008**, *37*, 1806−1813.

(7) Barefoot, R. R.; Van Loon, J. C. *Talanta* **1999**, *49*, 1−14.

(8) Scheffer, A.; Engelhard, C.; Sperling, M.; Buscher, W. *Anal. Bioanal. Chem.* **2008**, *390*, 249−252.

(9) Noguiera, C. A.; Figueiredo, M. G. *Analyst* **1995**, *120*, 1441−1443.

(10) Messerschmidt, J.; Alt, F.; Tolg, G. *Anal. Chim. Acta* **1994**, *291*, 161−167.

(11) Yu, L.; Andriola, A. *Talanta* **2010**, *82*, 869−875.

(12) (a) Blyth, K. M.; Phillips, D. N.; van Bronswijk, W. *J. Chem. Educ.* **2004**, *81*, 1780−1782. (b) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103−1169. (c) Pitcairn, I. K.; Warwick, P. E.; Milton, J. A.; Teagle, D. A. H. *Anal. Chem.* **2006**, *78*, 1290−1295.

(13) Jang, G.-G.; Roper, D. K. *Anal. Chem.* **2011**, *83*, 1836−1842.

(14) Jun, M. E.; Roy, B.; Ahn, K. H. *Chem. Commun.* **2011**, 7583−7601.

(15) (a) Yang, Y.-K.; Lee, S.; Tae, J. *Org. Lett.* **2009**, *11*, 5610−5613. (b) Jou, M. J.; Chen, X.; Swamy, K. M. K.; Kim, H. N.; Kim, H.-J.; Lee, S.-G.; Yoon, J. *Chem. Commun.* **2009**, 7218−7220. (c) Egorova, O. A.; Seo, H.; Chatterjee, A.; Ahn, K. H. *Org. Lett.* **2010**, *12*, 401−403.

(16) Do, J. H.; Kim, H. N.; Yoon, J.; Kim, J. S.; Kim, H.-J. *Org. Lett.* **2010**, *12*, 932−934.

(17) Dong, M.; Wang, Y.-W.; Peng, Y. *Org. Lett.* **2010**, *12*, 5310−5313.

(18) Haas, K. L.; Franz, K. J. *Chem. Rev.* **2009**, *109*, 4921−4960.

(19) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533−3539.

(20) Nolan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **2007**, *129*, 5910−5918.

(21) Fukuoka, S.; Kida, T.; Nakajima, Y.; Tsumagari, T.; Watanabe, W.; Inaba, Y.; Mori, A.; Matsumura, T.; Nakano, Y.; Takeshita, K. *Tetrahedron* **2010**, *66*, 1721−1727.

(22) (a) Hirayama, N.; Iimuro, S.; Kubono, K.; Kokusen, H.; Honjo, T. *Talanta* **1996**, *43*, 621−626. (b) Gagne, R. R.; Kreh, R. P.; Dodge, J. A.; Marsh, R. E.; McCool, M. *Inorg. Chem.* **1982**, *21*, 254−261.

(23) Ogata, T.; Takeshita, K.; Fugate, G. A.; Mori, A. *Sep. Sci. Technol.* **2008**, *43*, 2630−2640.

(24) (a) Takeshita, K.; Ishida, K.; Nakano, Y.; Matsumura, T. *Chem. Lett.* **2007**, *36*, 1032−1033. (b) Takeshita, K.; Matsumura, T.; Nakano, Y. *Prog. Nucl. Energy* **2008**, *50*, 466−469.

(25) Choi, M. G.; Kim, Y. H.; Namgoong, J. E.; Chang, S.-K. *Chem. Commun.* **2009**, 3560−3562.

(26) (a) Hall, J.; Satchell, D. P. N. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1351−1353. (b) Micallef, J. V.; Satchell, D. P. N. *J. Chem. Soc., Perkin Trans. 2* **1982**, 971−977. (c) Micallef, J. V.; Satchell, D. P. N. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1379−1382.

(27) Lin, W.; Cao, X.; Ding, Y.; Yuan, L.; Yu, Q. *Org. Biomol. Chem.* **2010**, *8*, 3618−3620.

(28) Shortreed, M.; Kopelman, R.; Kuhn, M.; Hoyland, B. *Anal. Chem.* **1996**, *68*, 1414−1418.

(29) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; p 938. A reviewer suggested the possibility of probe **1** for the monitoring of this Au(I) to Au(III) transition. In fact, after 2 h at 80 °C, there were some changes in the UV−vis spectral behavior of **1**, which might be due to the transformed Au(III) species (Figure S3, Supporting Information). We suppose that the selective response of probe **1** toward Au(III), in principle, could be applicable for the monitoring of the progress of the disproportionation of Au(I).

(30) Goldberg, J. M.; Batjargal, S.; Petersson, E. J. *J. Am. Chem. Soc.* **2010**, *132*, 14718−14720.

(31) Corsaro, A.; Pistara, V. *Tetrahedron* **1998**, *54*, 15027−15062.

(32) Anderegg, G.; Hubmann, E.; Podder, N. G.; Wenk, F. *Helv. Chim. Acta* **1977**, *60*, 123−140.

(33) Takeshita, K.; Kondo, M. The 227th ACS National Meeting, Anaheim, CA, March 28−April 1, 2004. I&EC 146.