

Sensing of Cyanide Using Highly Selective Thiazole-based Cu²⁺ Chemosensor

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The recognition and detection of anions is a field that has attracted increasing interest in recent years due to the fundamental importance of these species in many chemical and biological processes.¹ Cyanide (CN⁻) is a hazardous chemical that occurs naturally, both in the geologic and biologic world. Over 2,000 plants species, including fruits and vegetables, contain cyanogenic glycosides that release cyanide on acid hydrolysis (e.g., as occurs when ingested). Among them, cassava (tapioca, manioc) and sorghum are staple foods for hundreds of millions in tropical countries.² It causes damage by absorption through the lungs, gastrointestinal tract, and skin, and can kill mammals upon binding to a heme unit. The process of cellular respiration in mammals is inhibited by the cyanide anion, which interacts strongly with the heme unit at the active site of cytochrome *a3*.³ Hydrogen cyanide (HCN) produced by *Pseudomonas aeruginosa* (PA) is considered to be involved in the pathogenesis of Cystic Fibrosis (CF) lung disease.⁴ Thus the *in vivo* imaging of cyanide can be a valuable tool for elucidating the mechanism of bacterial cyanogenesis, as well as assessing the detriment of HCN to CF patients. Cyanides are industrially made in large quantities and used in electroplating, metallurgy, production of organic chemicals, plastics, photographic developing, fumigation, and mining.⁵ Cyanides have been used for unusual and not always admirable activities. Concentrated sodium cyanide (NaCN) solutions have been used to stun colorful fish to supply fish for aquaria releasing cyanide in water.⁶ So human being are exposed to cyanides from dietary, industrial, environmental, and other sources. Consequently, there is considerable interest in detecting the presence of the toxic cyanides by using chemosensors.⁷ A variety of colorimetric and fluorescent probes have been reported. For example, according to its strong co-ordination ability, some cyanide chemosensors were developed, by utilizing cyanide complexes including Zn(II)-porphyrin,^{8a} Ru(II)-pyridine,^{8b,c} and boronic acid derivatives.^{8d} Other strategies were also involved, such as hydrogen bonding interactions,^{8f} and copper-cyanide affinity.^{8h} Additionally, in order to minimize the influence of other anions, i.e. fluoride and acetate, the nucleophilic addition reactions of cyanide were applied for sensing of cyanide, including reactions with oxazine,^{9a,b} pyrylium,^{9c} squarane,^{9d} acyltriazene,^{9e} acridinium,^{9f} salicylaldehyde,^{9g,h,i} trifluoroacetophenone,^{9j,k} or trifluoroacetamide derivatives.^{9l,m,n} Among

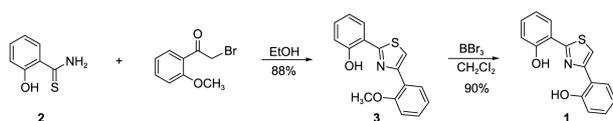
these especially, the copper-cyanide affinity demonstrated high sensitivity and good selectivity toward cyanide.

It is well known that chelating groups such as C = N and C-O exhibit a high affinity to transition and post-transition metal cations, but a lower binding affinity toward alkali metal and alkaline earth metal cations.¹⁰ Recently we have reported thiazole based chemosensors as anions,¹¹ ratiometric fluorescence sensing of zinc,¹² and chromogenic and fluorogenic sensing of Cu(II).¹³ In all of these compounds the thiazole ring is substituted by a phenol at position 2 and phenyl or pyridine or a coumarin at position 4. Both exhibit the same mechanism for fluorescence based on the anion or cation-induced inhibition of the excited-state intramolecular proton transfer (ESIPT). Thus, a heteroaromatic ring system such as a thiazole with two phenolic groups at position 2 and 4 can act as a -ONO- donor receptor with functionality highly selective to transitional metal cations.¹⁴ In this paper, the design and development of a novel thiazole and phenol based fluorescent chemosensor with phenolic substituent at position 2 and 4 of the thiazole ring is reported. The chemosensor **1** shows high selectivity toward Cu²⁺ and its complex with cyanide anion in aqueous ethanol (1:1) buffered at pH 7.4. The photophysical and binding properties of **1** and its copper complex are investigated.

The chemosensor **1** was obtained in a good yield by the Hantzsch condensation reaction of 2-hydroxythiobenzamide with 2-bromo-2'-methoxyacetophenone in refluxing ethanol, followed by deprotection of the methoxy group with boron tribromide as shown in Scheme 1. ¹H NMR, ¹³C NMR and elemental analysis confirmed the structure of **1**.

An UV-vis study was carried out in 50% (v/v) water/ethanol buffered by 10 mM HEPES at pH 7.4 at a concentration level of 20 μM. Sensor **1** displayed an obvious absorption band at 334 nm. This can be attributable to a π - π* transition; this is favored by the planar orientation enforced by the intramolecular hydrogen bonding.^{11,15} However, upon addition of Cu²⁺ to the solution of **1**, a new absorption band at 381 nm becomes enhanced gradually, while the absorption band at 334 nm decreased synchronously, due to the disruption of hydrogen bonding between the phenolic hydrogen and thiazole nitrogen (Scheme 2). As shown in Figure 1 only the addition of CN⁻ to the **1**-Cu²⁺ complex solution (20 μM) causes a blue shift to 334 nm due to the displacement of Cu²⁺ by the CN⁻. Fluorescence titration of **1** with Cu²⁺ was also carried out in 50% (v/v) water/ethanol buffered by 10 mM HEPES at pH 7.4 at a concentration level of 20 μM. Addition

*This paper is dedicated to Professor Eun Lee on the occasion of his honourable retirement.



Scheme 1. Synthesis of chemosensor 1.

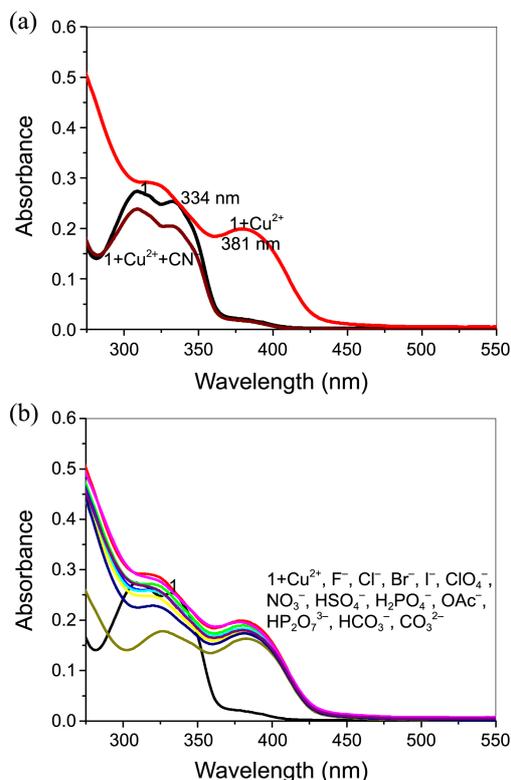


Figure 1. Changes in UV-vis spectra of **1** (20 μM) and **1-Cu²⁺** upon (a) addition of CN^- , and (b) different anions in EtOH:H₂O (1:1) containing HEPES buffer (10 mM, pH 7.4).

of Cu^{2+} to the solution of **1** results in a simultaneous quenching of fluorescent emission at 492 nm when excited at 340 nm (Figure 2). Like the benzothiazole derivatives¹⁶ sensor **1** contains an intramolecular hydrogen bond that undergo ESIPt and yields a highly Stokes' shifted emission from the proton-transfer tautomer.¹⁷

Coordination of Cu^{2+} removes the phenolic proton and disrupts the ESIPt, thus causing full quenching. The binding mode of **1** with Cu^{2+} from the results of fluorescence titration spectra (Fig. 2 inset) showed to be 1:1 with a binding constant $1.15 \times 10^4 \text{ M}^{-1}$ (error limits $\leq 10\%$).¹⁸ Cu^{2+} being a paramagnetic transition-metal cation coordinate to **1** and completely quench the fluorescence emission (Figure 3). The quenching results obtained with addition of Cu^{2+} suggest that the open shell d-orbitals of Cu^{2+} provide a very fast and efficient nonradiative decay of the excited states due to the electron or energy transfer between the metal cation and **1**. Competition binding experiment carried out with different metal ions (1.0 equiv) and Cu^{2+} showed that they did not interfere with the quenching of Cu^{2+} by **1** (Figure 3).

This selectivity is due to the fact that although transition

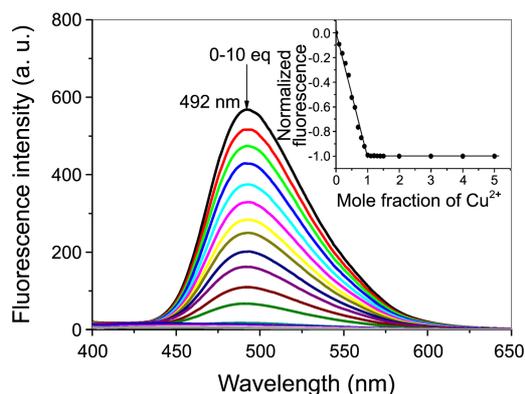


Figure 2. Changes in fluorescence spectra of **1** (20 μM) in EtOH:H₂O (1:1) containing HEPES buffer (10 mM, pH 7.4) upon addition of $\text{Cu}(\text{ClO}_4)_2$. ($\lambda_{\text{ex}} = 340 \text{ nm}$) Inset: mol ratio plots of fluorescence at 492 nm.

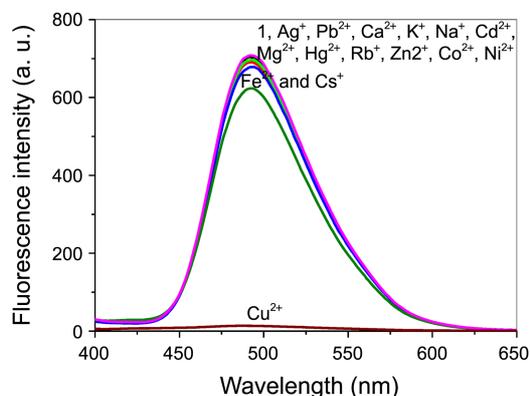


Figure 3. Fluorescence spectra of **1** (20 μM) upon addition of 10 equiv of various cations in EtOH:H₂O (1:1) containing HEPES buffer (10 mM, pH 7.4). $\lambda_{\text{ex}} = 340 \text{ nm}$.

metals do not differ too much in size, they can establish coordinative interactions at very different energies, which can be used for discriminative purposes, especially for fluorescent sensing.¹⁹ This phenomenon is consistent with copper that occurs highest on the Irving-Williams series.²⁰ Copper(II) has a particularly high thermodynamic affinity for the typical -ONO- donor, i.e., the imino nitrogen of the thiazole ring, and a strong tendency to promote deprotonation of the phenolic protons during complex formation,¹⁰ with fast metal-to-ligand binding kinetics that are not possible with the other transition metal ions.

The fact that CN^- is known to form strong complexes with Cu^{2+} , the possibility of implementing **1-Cu²⁺** complex as chemosensor for CN^- detection was explored. Initial fluorescence experiments were carried with **1-Cu²⁺** complex at a concentration level of 20 μM . On slow addition of the CN^- , the peak at 492 nm, which was quenched due to the Cu^{2+} , was enhanced as shown in Figure 4. The enhancement continues until the addition of 2 equiv of CN^- after that however, higher CN^- concentration did not lead to any further emission enhancement.

From fluorescence titration, the binding constant of **1-Cu²⁺**

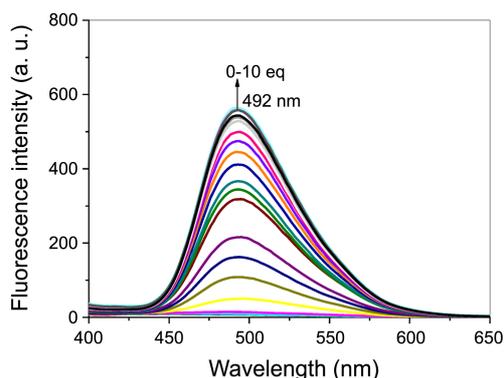


Figure 4. Fluorescence titration spectra of **1**-Cu²⁺ (20 μM) upon addition of CN⁻ (0-10 equiv) in EtOH:H₂O (1:1) containing HEPES buffer (10 mM, pH 7.4). λ_{ex} = 340 nm.

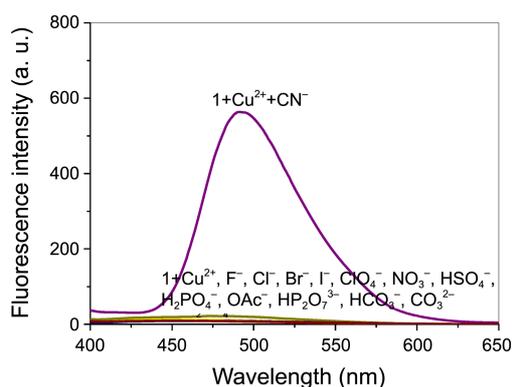


Figure 5. Fluorescence spectra of **1**-Cu²⁺ (20 μM) upon addition of 10 equiv of various anions in EtOH:H₂O (1:1) containing HEPES buffer (10 mM, pH 7.4). λ_{ex} = 340 nm.

with CN⁻ was calculated to be $4.48 \times 10^4 \text{ M}^{-1}$ (Error limits $\leq 10\%$).¹⁸ This is explained by the fact that CN⁻ react with Cu²⁺ to form a very stable Cu(CN)₂ species (Scheme 2).

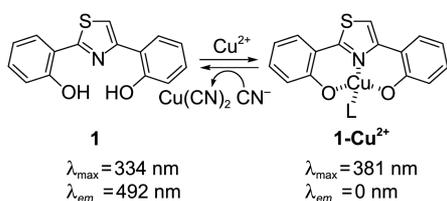
The fluorescence responses of **1**-Cu²⁺ with different anions were recorded in EtOH:H₂O (1:1) containing HEPES buffer (10 mM, pH 7.4) with excitation at 340 nm. Due to the high copper-cyanide affinity, only CN⁻ causes the revival of the fluorescence via the displacement of the Cu²⁺ (Figure 5). Moreover the sensitivity of **1** in the presence of Cu²⁺ ion toward the CN⁻ is not interfered by the presence of CO₃²⁻, HCO₃⁻ or any other anions even when their concentrations are as high as 10-fold than CN⁻. This indicates that **1**-Cu²⁺ complex system has a high selectivity and sensitivity for CN⁻ ions. The detection limits of **1** and its Cu²⁺ complex for Cu²⁺ and CN⁻ were found to be 19 ppm and 7.9 ppm, respectively.²¹ In addition to these we also checked several amino acids with the **1**-Cu²⁺ complex, but it did not induce any significant change in its fluorescence.

An NMR study for complexation was not available due to the magnetic-silent nature,¹³ originating from the paramagnetic property of Cu²⁺. So we prepared the complex of **1** with Cu²⁺ in ethanol and characterized by HR-FAB mass in which the molecular ion peak was found at m/z 330.9724, that responds to (C₁₅H₉CuNO₂S + 1)⁺ m/z 330.9728.

In conclusion we have developed thiazole-based highly selective copper chemosensor **1** whose copper complex is used as an “On-Off” type highly selective and sensitive cyanide chemosensor *via* the displacement approach of the copper ion.

Experimental Section

Melting points were determined using a Thomas-Hoover



Scheme 2. Proposed mechanism for cyanide sensing.

capillary melting point apparatus and are uncorrected. The ¹H and ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer using Me₄Si as the internal standard. HR-FAB mass was taken at the KBSI Daegu branch. The UV-vis absorption spectra were determined on a Shimadzu UV-1650PC spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5301 fluorescence spectrometer equipped with a xenon discharge lamp and 1 cm quartz cells. All of the measurements were operated at 298 K. All other materials for synthesis were purchased from Aldrich Chemical Co. and used without further purification. The 2-hydroxythiobenzamide (**2**) was prepared by the procedure in the literature.¹¹ The solutions of metals and anions were prepared from their perchlorate (ClO₄⁻) and tetrabutylammonium (TBA) salts of analytical grade, and then subsequently diluted to prepare working solutions. The 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer solutions of differing pH were prepared using a proper amount of HEPES, KOH (1 N), and HCl (1 N) (all of analytical grade) under adjustment by a pH meter.

Synthesis of Chemosensor 1: A solution of 2-bromo-2'-methoxyacetophenone (180 mg, 0.78 mmol) and **2** (100 mg, 0.65 mmol) in ethanol (15 mL) was refluxed for 4 h and cooled down at room temperature. The solid precipitated was separated by filtration and washed with distilled water and then methanol to remove unreacted reagents to provide **3** in an 88% yield. A solution of BBr₃ (106 mg, 0.42 mmol) in dry CH₂Cl₂ (15 mL) was slowly added to a solution of **3** (100 mg, 0.35 mmol) in dry CH₂Cl₂ (20 mL) at -78 °C for 1 h. The cold bath was removed and the mixture was stirred at room temperature for 5 h, then the mixture was poured into water and stirred for 1 h. The aqueous layer was extracted with CH₂Cl₂ washed with brine, and dried over anhydrous Na₂SO₄ and concentrated. The residue was purified by column chromatography (SiO₂, 20% EtOAc in hexane) to give **1** in a 90% yield. mp 192-193 °C (CH₂Cl₂-hexane); ¹H NMR (CDCl₃) δ 8.25 (s, 1H), 8.13 (dd, *J* = 2.0, 1.5 Hz, 1H), 8.06 (dd, *J* = 2.0, 1.5 Hz, 1H), 7.38 (m, 1H), 7.25 (m, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 6.98 (m, 3H); ¹³C NMR (CDCl₃) δ 162.5, 155.5, 155.5, 150.7, 131.6, 129.6, 128.3, 127.5, 120.0, 119.6, 119.4, 118.9,

117.0, 117.0, 116.5; MS (relative intensity, %) m/z 269 (M^+ , 100), 236 (30), 121 (31); Anal. Calcd for $C_{15}H_{11}NO_2S$: C, 66.89; H, 4.12; N, 5.20; S, 11.91, Found: C, 66.65; H, 4.05; N, 5.18; S, 11.52.

Synthesis of 1-Cu²⁺ Complex. A mixture of **1** (100 mg, 0.37 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (164 mg, 0.44 mmol) in ethanol (10 mL) was refluxed for 10 h. The mixture was cooled to room temperature and the precipitated complex was filtered. The filtered cake was washed thoroughly with water, ethanol, and dried under vacuum to provide the complex (100 mg, 81% yield). HR-FAB Mass: calcd for $(C_{15}H_9CuNO_2S^+)^+$ 330.9728; found: 330.9724.

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