



Selective colorimetric assay of cyanide ions using a thioamide-based probe containing phenol and pyridyl groups



Eun Joo Song^{a,†}, Soojin Kim^{b,†}, Gyeong Jin Park^a, Sol Ji Park^b, Ye Won Choi^a, Cheal Kim^{a,*}, Jinheung Kim^{b,*}

^a Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul, Republic of Korea

^b Department of Chemistry and Nano Science, Global Top 5 Research Program, Ewha Womans University, Seoul 120-750, Republic of Korea

ARTICLE INFO

Article history:

Received 20 May 2014

Revised 4 September 2014

Accepted 10 September 2014

Available online 20 September 2014

Keywords:

Colorimetric sensor

Cyanide ion

Phenol

Pyridyl

Deprotonation

ABSTRACT

The selective assay of cyanide ions with a thioamide compound (HNPTU) containing phenol and pyridine as a chemosensor is reported using absorbance changes in a buffered aqueous solution (50 mM HEPES, pH 7.4) containing ethanol. Upon treatment with cyanide ions, the colorless solution of HNPTU turned yellow. No significant changes were observed with other comparable anions, such as F⁻, Cl⁻, Br⁻, I⁻, and CH₃COO⁻. The color change of HNPTU upon treatment with CN⁻ was maintained even in the presence of the comparable monovalent anions. The complex stability constant ($K_3 = 2.6 \times 10^3$) for the stoichiometric 1:1 complexation of HNPTU with cyanide ions was obtained based on absorbance titrations. The interaction of HNPTU with cyanide ions was proposed to be deprotonation, as shown by NMR and Cu(II) treatment experiments.

© 2014 Elsevier Ltd. All rights reserved.

Introduction

Free cyanide is the most toxic form of all cyanide compounds. The cyanide anion derives from alkali metal salt and hydrogen cyanide either in a gaseous or aqueous state. Cyanide is very reactive and forms ionic complexes with various metal cations. The salts of sodium, potassium, and calcium cyanide are quite toxic as they are highly soluble in water to generate free CN⁻. Although metal–cyanide complexes are expected to be less toxic than free CN⁻, the aqueous dissociation of metal–cyanide salts releases free cyanide. Even in the neutral pH, metal–cyanide complexes can dissociate sufficiently to be environmentally harmful.^{1,2}

Cyanide ions form complexes with gold, mercury, cobalt, iron ions, etc., that are very stable even under mildly acidic conditions. However, both ferrous and ferric–cyanide complexes decompose to release free cyanide ions when exposed to direct ultraviolet light in aqueous solutions.

The World Health Organization (WHO) advises the cyanide concentration in drinking water to be maintained lower than ca. 2 μM.³ Chemical products containing cyanide ions are widely used in electroplating, gold mining, polymer products, etc. Recently, fluorescent chemosensors of various chemical structures have

been reported to show specificity for cyanide ions which have significant meaning due to toxicity of cyanide in biological and environmental systems.^{4–11} Relatively, colorimetric sensors specific for cyanide ions are small in number.^{12–17} Colorimetric probes for selective detection of various biologically and environmentally relevant small anions and metal cations have attracted an increasing interest due to easy handling and detection. More examples of selective chemosensors for cyanide ions exhibiting clear color changes are needed to develop fast and accurate detection methods in various situations.

In this study, we report the anion-binding properties of a new thioamide-based probe bearing phenol and pyridyl groups (HNPTU). This probe exhibited a color change with high selectivity upon interaction with cyanide ions in ethanol/H₂O buffered with HEPES.

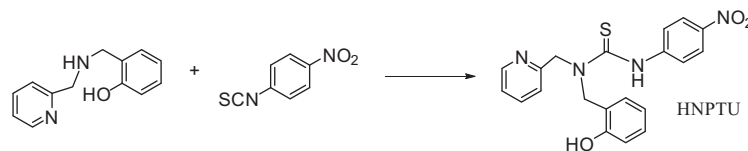
Results and discussion

The new thioamide-based chemosensor, HNPTU, was prepared with 72% yield by the reaction of 1-hydroxy-2-naphthaldehyde and *para*-thiocyanate-nitrobenzene (Scheme 1 and Experimental section). HNPTU was characterized by electrospray mass spectrum, showing a negative ion [HNPTU–H⁺]⁻, $m/z = 393.13$ (Fig. S1). In contrast with a colorless solution of HNPTU in ethanol/H₂O buffered with 50 mM HEPES (pH 7.4), the solution turned yellow upon addition of cyanide ions. The absorption maximum shifted from

* Corresponding authors. Tel.: +82 2 32774453; fax: +82 2 32773419.

E-mail addresses: chealkim@snust.ac.kr (C. Kim), jhkim@ewha.ac.kr (J. Kim).

† Both authors contributed equally to this work.

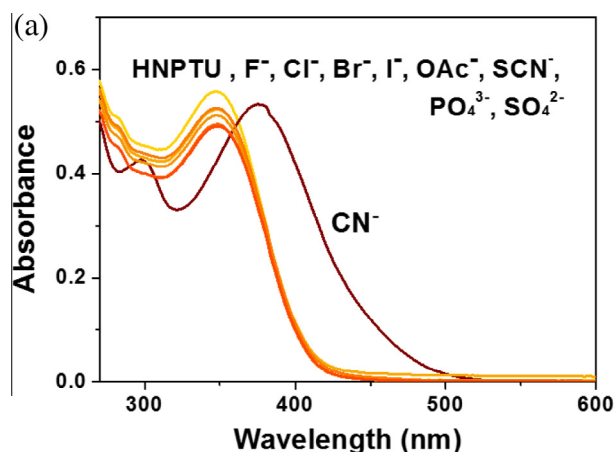


Scheme 1. Synthesis of the sensor HNPTU.

348 to 376 nm upon treatment with 50 equiv CN^- (Fig. 1). No clear color changes observed with other monovalent anions, such as F^- , Cl^- , Br^- , I^- , and CH_3COO^- (each 50 equiv, used as tetraethylammonium salts), demonstrate the high selectivity of HNPTU for cyanide in comparison with other anions.

The anion binding affinity of HNPTU was evaluated by monitoring their absorption properties as a function of anion concentration. The changes in the UV–vis spectra of HNPTU were observed as a function of CN^- concentration (Fig. 2). The band at 348 nm decreased and one at 376 nm progressively increased. The clear isosbestic point observed at 358 nm indicated a clean conversion throughout the cyanide titration. Previously, some organic receptors have been reported as colorimetric sensors for cyanide ions, in which most probes were known to make a covalent bond with cyanide by nucleophilic addition.^{14–17} The absorbance changes of HNPTU and HNPTU-CN^- were most significant around pH 7–8 (Supporting information, Fig. S2); this probe was somewhat pH-insensitive in the biologically relevant pH range.

Figure 3 illustrates the absorbance response of HNPTU (at 376 nm) to CN^- in the presence of other competing anions. The color change to yellow upon addition of cyanide ions was maintained in the presence of the same amount of other anions, indicating that most anions do not interfere with the detection of CN^- by HNPTU in ethanol/ H_2O buffered with 50 mM HEPES.



(b)

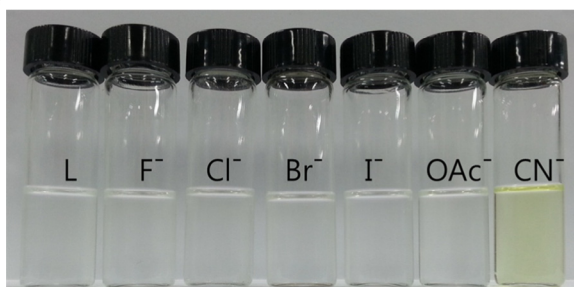


Figure 1. (a) UV–vis spectra of HNPTU (40 μM) in the absence and presence of 50 equiv various anions, CN^- , F^- , Cl^- , Br^- , I^- , and CH_3COO^- , in ethanol/ H_2O (8:2, v/v) buffered at pH 7.4 with HEPES (50 mM). (b) The images of the solutions of HNPTU treated with different anions. L stands for HNPTU.

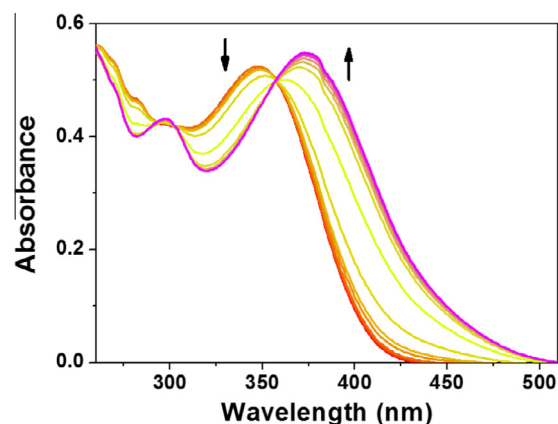


Figure 2. Changes in the UV–vis spectra of HNPTU (40 μM) as a function of the cyanide concentration in ethanol/ H_2O (8:2, v/v) buffered at pH 7.4 with HEPES (50 mM).

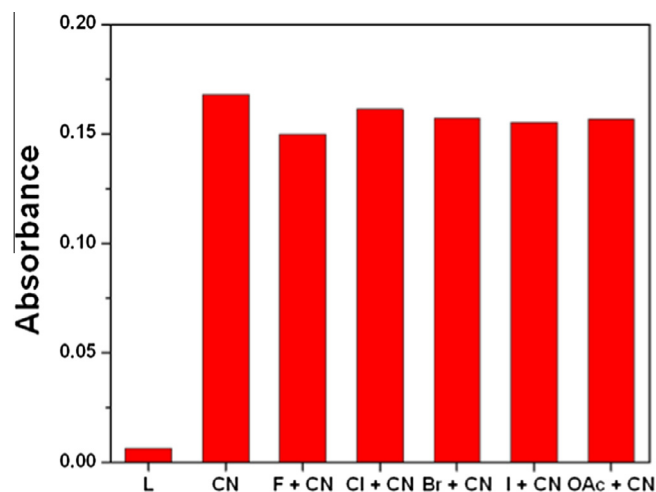


Figure 3. Cyanide-ion response of 40 μM HNPTU in the absence and presence of each competing anion (200 μM) in H_2O /ethanol (2:8, v/v) buffered at pH 7.4 with HEPES (50 mM). L stands for HNPTU. The absorbance maximum of a HNPTU-CN^- complex was observed at 376 nm.

Further insights into the nature of interaction of HNPTU and cyanide were studied by ^1H NMR titration experiments. Addition of cyanide ions to HNPTU did not show any significant changes in the NMR spectra (Fig. 4). Aromatic protons of HNPTU in the 6.5–9.0 ppm region were clearly influenced upon addition of cyanide ions. The methylene protons of HNPTU also shifted from 5.08 to 5.25 ppm upon treatment with CN^- .

A Job's plot as well as binding analysis using the Benesi–Hildebrand plot established a 1:1 complex of HNPTU (Fig. 5). Cyanide ions could be detected down to 20 μM based on the 3α /slope when 5 μM HNPTU was employed. Based on UV–visible titration experiments, the association constant (K_a) of $7.5 \times 10^2 \text{ M}^{-1}$ was obtained by using the nonlinear least-squares method (Supporting information, Fig. S3).

Download English Version:

<https://daneshyari.com/en/article/5263587>

Download Persian Version:

<https://daneshyari.com/article/5263587>

[Daneshyari.com](https://daneshyari.com)