

## Known compounds of thiourea as dual naked-eye nano scale detectors of $\text{N}_3^-/\text{I}^-$ and $\text{Cu}^{2+}$ ions

Halimeh Hajighasemi<sup>a</sup>, Naser Foroughifar<sup>b\*</sup>, Alireza Khajeh-Amiri<sup>c\*</sup> and Ebrahim Balali<sup>a</sup>

<sup>a</sup>Department of Organic Chemistry, Faculty of pharmaceutical chemistry, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran

<sup>b</sup>Department of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, Iran

<sup>c</sup>Aja University of Medical Sciences, Toxicology Research Centre, Tehran, Iran

Received: February 2023; Revised: March 2023; Accepted: April 2023

**Abstract:** Some colorimetric sensors containing the thiourea motif were synthesized and applied as naked-eye detectors in dimethyl sulfoxide/water solution. The ion detection studies displayed that the prepared compounds (**1-4**) act as selective, dual-sensitive chromogenic sensors to detect  $\text{Cu}^{2+}$ ,  $\text{N}_3^-$ , and  $\text{I}^-$  ions. These chemosensors distinguish  $\text{I}^-$  and  $\text{N}_3^-$  *via* naked-eye color changing from colorless to yellow, and red respectively in a paper test strips, besides a distinct red shift in UV-Vis. spectrum in nano scale. The result of Job's plot indicates that the stoichiometry binding ratios of compound **1** to corresponded ions are 1:1.

**Keywords:** Colorimetric probe; Ion sensing; Dual sensor; Naked-eye detection, thiourea.

### Introduction

Copper, as a plentiful transition metal, is a vital micronutrient, which its role in industries such as the processing of drugs, fertilizers, machine parts, batteries, electrical wires, making of alloys, etc. is very prominent and well known. Due to the direct relationship between industry and the environment, we can expect the uptake of copper by plants and its entry into the environmental cycle. Today, it has been proven that copper as a redox agent is effective in various genetic diseases, including Huntington, Parkinson's, Alzheimer's, Menkes, and Wilson. It should be noted that, although copper pollutants cause serious problems, copper deficiency also increases the risk of coronary heart disease [1-6].

Iodine is a chemical element that is essential for normal human growth and plays an important role in thyroid function. Both iodide excessive and deficiency intake could lead to thyroid diseases [7-9].

It is notable that, the iodine and related ions, in addition to affecting the function of the thyroid gland, could create serious environmental problems and physical diseases. Lacking iodine during early pregnancy can lead to cretinism, and spontaneous abortion. Also, its effective impress on brain functions, nerve system, and increasing infant mortality is well established [10,11].

Azide derivatives are used in explosives, propellants, anti-corrosion agents, radical scavengers' preparation on a large-scale. While, those are potentially fatal species, which *via* irreversibly binding to the heme cofactor prevent cytochrome oxidase activity and lead to severe hypotensive, comparable with carbon monoxide function. The small amount of sodium azide as a sodium salt of corresponded ion can be disastrous similar to sodium cyanide. It can lead to arrhythmia, bradycardia, shock, convulsions, coma pulmonary edema, and finally asystole in less than half an hour. However, exposure to a slight amount can cause skin and eye

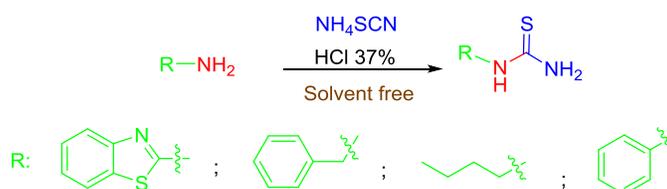
\*Corresponding author: E-mail: n\_foroughifar@yahoo.com

irritation, nausea, headache, blurred vision, shortness of breath, dizziness, low blood pressure, or kidney damage [12–14]. Considering the above, the efficient detection of cations, besides the anions, in the environment, food, biological, and industrial samples, is an important topic for researchers. So that, various techniques and methods have been developed for effective detection. Among them, recently, colorimetric chemosensors have been extensively utilized due to their benefits, such as easy and efficient usage with the naked eye without the requisiteness for special equipment, fast response along with the low cost for it [15–21].

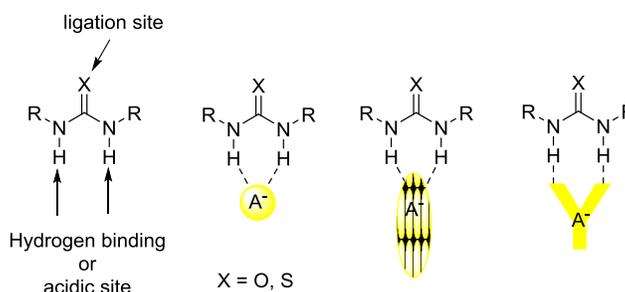
To design colorimetric chemosensors, researchers extremely employed the structures having mono, bis, tris, tetrakis, and cyclic urea/thiourea [22–27]. These

compounds interact by having two active sites both through the formation of hydrogen bonds and through the chelation with neutral species, cations, and anions. The spatial arrangement of the urea/thiourea is such that it bonds effectively with all three types of spherical, liner, and Y shape anions [22] (Figure 1).

Considering this category, we designed dual-functional naked-eye chemosensors **1-4** containing thiourea motif for visual detection of  $\text{Cu}^{2+}$ ,  $\text{N}_3^-$ , and  $\text{I}^-$  ions (Scheme 1 and Table 1). The sensing processes can be recognized by naked-eye detection, with a color change from colorless to yellow, and colorless to red in the presence of  $\text{I}^-$  and  $\text{N}_3^-$  ions, respectively. Furthermore, the accessible strip papers of probes **1-4** allow the qualitative sensing of the ions utilizable.



**Scheme 1.** Synthesis of compounds **1-4**.



**Figure 1.** Possible binding sites in urea/thiourea.

**Table 1.** Yields and melting points of compounds **1-4**.

	Amine	Product <sup>[a]</sup>	Time (min)	Yield (%) <sup>[b]</sup>	mp (°C) found	Reported <sup>[Ref]</sup>
<b>1</b>		<b>4a</b>	60	87	171-173	172-174 [28]
<b>2</b>		<b>4b</b>	65	85	162-164	163-165 [29]
<b>3</b>		<b>4c</b>	70	93	146-148	-[30]
<b>4</b>		<b>4d</b>	55	88	147-149	148-150 [31]

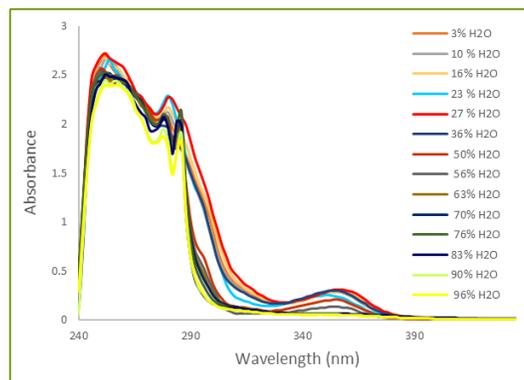
[a] The compound **4a-d** were known and their structures were deduced by comparison of melting points and spectral data with authentic samples.

[b] Yields refer to the pure isolated products.

## Results and Discussion

As our knowledge about molecular structures designing, here we designed some structures containing thiourea motif *via* reaction of Ammonium thiocyanate with heterocyclic, aromatic, and aliphatic amines to investigate, and compare different thiourea skeleton impact on sensing behavior of designed structures.

At the first step, compound **1** was selected as a model compound and the UV-Vis. absorption of it (0.35  $\mu\text{M}$ ) was measured during the increasing of water percent in dimethyl sulfoxide media to select the best ratio of H<sub>2</sub>O-DMSO for continuation. The results demonstrated that with a minor difference, 27% H<sub>2</sub>O would be the best (Figure 2).



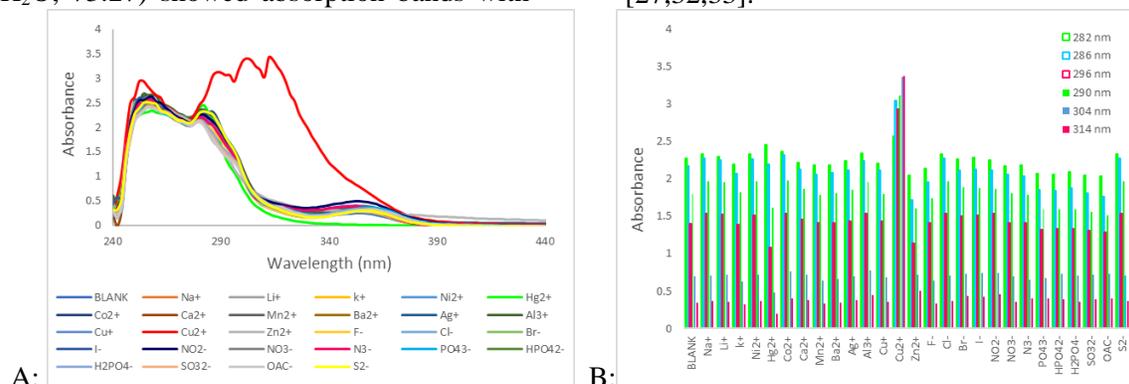
**Figure 2.** Solvent effect according to H<sub>2</sub>O percentage.

The colorimetric manner of compounds **1-4** was investigated *via* examination of their ability to sense sodium salts of anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, N<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>3</sub><sup>2-</sup>, OAc<sup>-</sup>, S<sup>2-</sup>), and chloride salts of cations (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cu<sup>+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ag<sup>+</sup>, Zn<sup>2+</sup>, and Al<sup>3+</sup>) by UV-Vis. absorption spectrometry in DMSO-H<sub>2</sub>O (73:27 v/v) solution.

Upon the addition of 10 equiv. Cu<sup>2+</sup> ions to compound **1** (0.35  $\mu\text{M}$ ) as a heterocyclic molecule containing thiourea motif, a remarkable hypochromic shift accompanied by a little bathochromic shift observed.

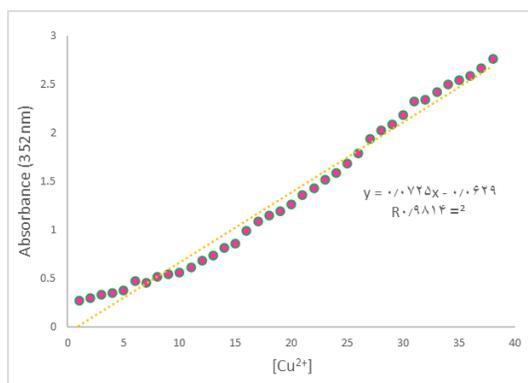
The UV-Vis. spectra of probe **1** in selected media (DMSO-H<sub>2</sub>O, 73:27) showed absorption bands with

the  $\lambda_{\text{max}}$  centered at 282, 286, and 296 nm, which are assigned to intramolecular charge transfer (ICT) of thiourea and benzothiazole skeleton ( $n \rightarrow \pi^*$ , and  $\pi \rightarrow \pi^*$ ) (Figure 3). Instantly, with the addition of Cu<sup>2+</sup> ions to probe **1** due to their interaction, the ICT bands appeared at 290, 304, and 314 nm ( $\Delta\lambda_{\text{max}} = 8 \text{ nm}$ ). As it can be observed, these bands have not appeared for other ions, which revealed that synthesized probe **1** can be used as selective Cu<sup>2+</sup> indicators. Also, in the presence of Hg<sup>2+</sup>, the band at 356 nm disappeared, but it wasn't so obvious, and it can be ignored (Figure3). Unexpectedly, against the previous report about urea/thiourea containing structures, compound **1**, didn't show a distinct response to F<sup>-</sup>, and OAc<sup>-</sup> ions [27,32,33].



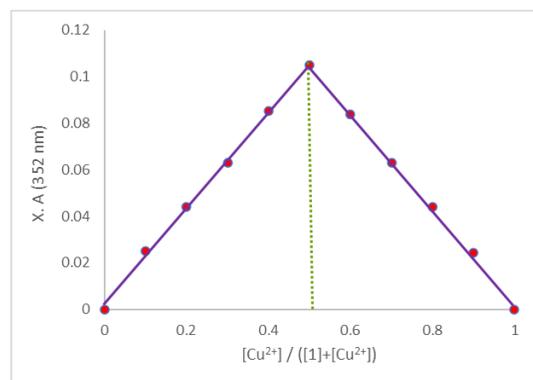
**Figure 3.** (A) UV-Vis spectral responses of probe **1** (0.35  $\mu\text{M}$ ) After adding of 10 equiv. of different ions in DMSO-H<sub>2</sub>O (73:27 v/v); (B) UV-Vis spectral responses of probe **1** (0.35  $\mu\text{M}$ ) After the addition of 10 equiv. of different ions in selected wavelength.

Intending to achieve more awareness of the sensing manner of the compound **1** to  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$  the UV-Vis. spectrophotometric titrations experiment was carried out. As shown in Figure 4, following the addition of  $\text{Cu}^{2+}$  ions to the solution of probe **1**, a hypochromic shift accompanied by a little bathochromic shift occurred, which slowly grew with increment of  $\text{Cu}^{2+}$  concentration. The measured limit of detection ( $\text{LOD} = 3\sigma/m$ ) for  $\text{Cu}^{2+}$  was  $0.11 \mu\text{M}$ . The  $\text{Hg}^{2+}$  ions addition gradually led to a hypochromic shift, which wasn't so distinct. The measured LOD of considerate ion was  $2.4 \mu\text{M}$ .



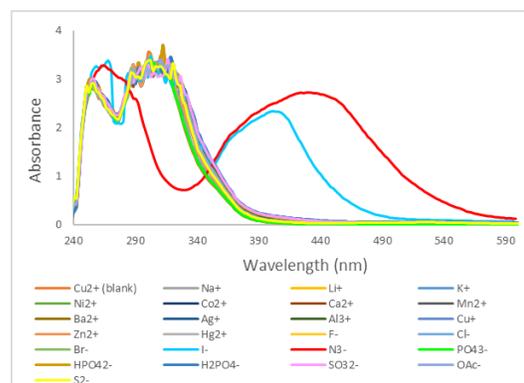
**Figure 4.** The UV-Vis. changes of the chemosensor **1** ( $0.35 \mu\text{M}$ ) with various amounts of  $\text{Cu}^{2+}$  ions.

The Job's plot analyses, which show the changes in adsorption intensity versus concentration changes, were used to determine the binding stoichiometry of compound **1** with  $\text{Cu}^{2+}$  ions. According to the diagram, the maximum adsorption was observed in 0.50 molar fraction of  $\text{Cu}^{2+}$  ions, which means the binding ratio of compound **1** to  $\text{Cu}^{2+}$  is 1:1 (Figure 5).



**Figure 5.** Job's plot between probe **1** and  $\text{Cu}^{2+}$  ions in  $\text{DMSO-H}_2\text{O}$  (73:27 v/v).

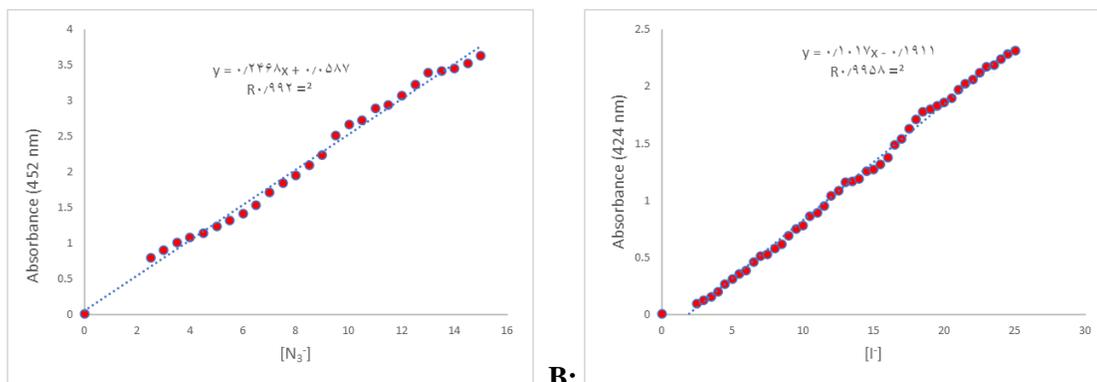
In continues, the interaction of **1**- $\text{Cu}^{2+}$  with the competitive ions (10 equiv.) was investigated (Figure 6). For this purpose, the UV-Vis. spectrum of compound **1** in the presence of  $\text{Cu}^{2+}$ , and other species was recorded, which illustrated that the addition of 10 equivalent  $\text{I}^-$ , and  $\text{N}_3^-$  ions could lead to a strong bathochromic shift.



**Figure 6.** UV-Vis spectral responses of probe **1**- $\text{Cu}^{2+}$  after the addition of 10 equiv. of different ions in  $\text{DMSO-H}_2\text{O}$  (73:27 v/v).

As reported by Hosseinjani et al., typically, the interaction of colorimetric probes with anions stabilizes the excited state of the chromophore, so induce a redshift to the charge-transfer absorption band.[20] In this case, with the addition of 10 equivalent  $\text{N}_3^-$  new bands with the  $\lambda_{\text{max}}$  centered at 264, and 432 nm appears, while the **1**- $\text{Cu}^{2+}$  bands that were talked about before are disappearing, which was demonstrated with the naked-eye color change from colorless to red, and with the addition of 10 equivalent  $\text{I}^-$  new bands with the  $\lambda_{\text{max}}$  centered at 266, and 402 nm appear, while the **1**- $\text{Cu}^{2+}$  bands remain in place. This interaction was illustrated with the naked-eye color change from colorless to yellow. It is notable that, the extra amount of desired ions led to more bathochromic shifts. The mechanism of the reaction was investigated by  $^1\text{H}$  NMR spectroscopy.

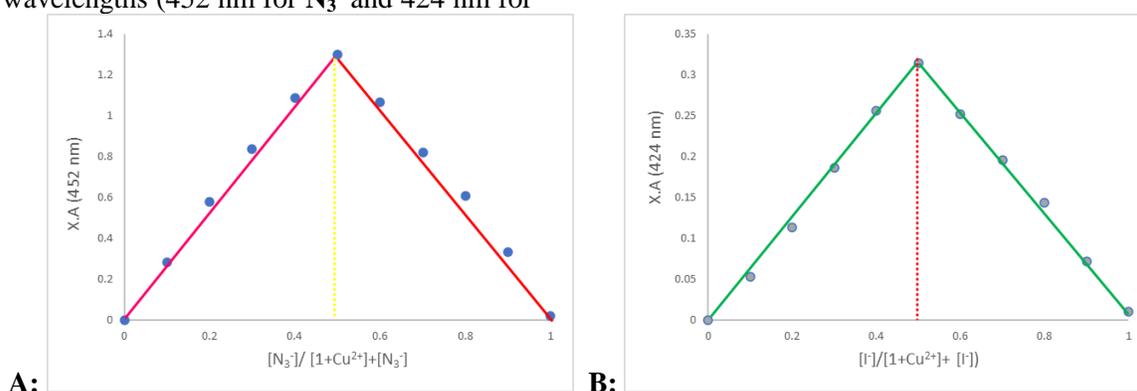
The spectrophotometric titrations experiment for **1**- $\text{Cu}^{2+}$  and  $\text{N}_3^-/\text{I}^-$  was performed. As shown in Figure 7, upon the addition of  $\text{N}_3^-/\text{I}^-$  ions to the solution of compound **1**- $\text{Cu}^{2+}$ , the bathochromic shift occurred, which gradually grew with increasing concentration of  $\text{N}_3^-/\text{I}^-$ . The measured limit of detection for  $\text{N}_3^-$ , and  $\text{I}^-$  were 31, and 76 nM, respectively.



**Figure 7.** The UV-Vis. changes of the chemosensor **1**-Cu<sup>2+</sup> with various amounts of N<sub>3</sub><sup>-</sup> ions (A), and I<sup>-</sup> ions (B).

Job's plot analyses were used to determine the binding stoichiometry of compound **1** in the presence of Cu<sup>2+</sup> with I<sup>-</sup> and N<sub>3</sub><sup>-</sup> (Figure 8). The maximum absorption at selected wavelengths (452 nm for N<sub>3</sub><sup>-</sup> and 424 nm for

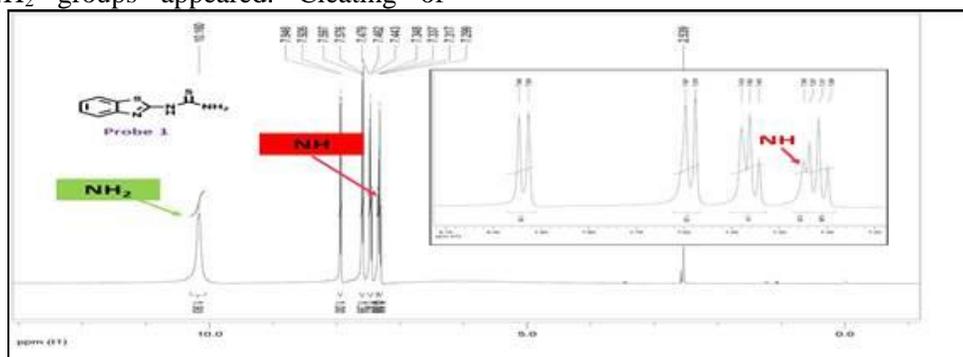
I<sup>-</sup>) was observed when the mole fraction of N<sub>3</sub><sup>-</sup> and I<sup>-</sup> ions reached about 0.50, inferring that the binding ratio of compound **1**-Cu<sup>2+</sup> to N<sub>3</sub><sup>-</sup>, and I<sup>-</sup> is 1:1.

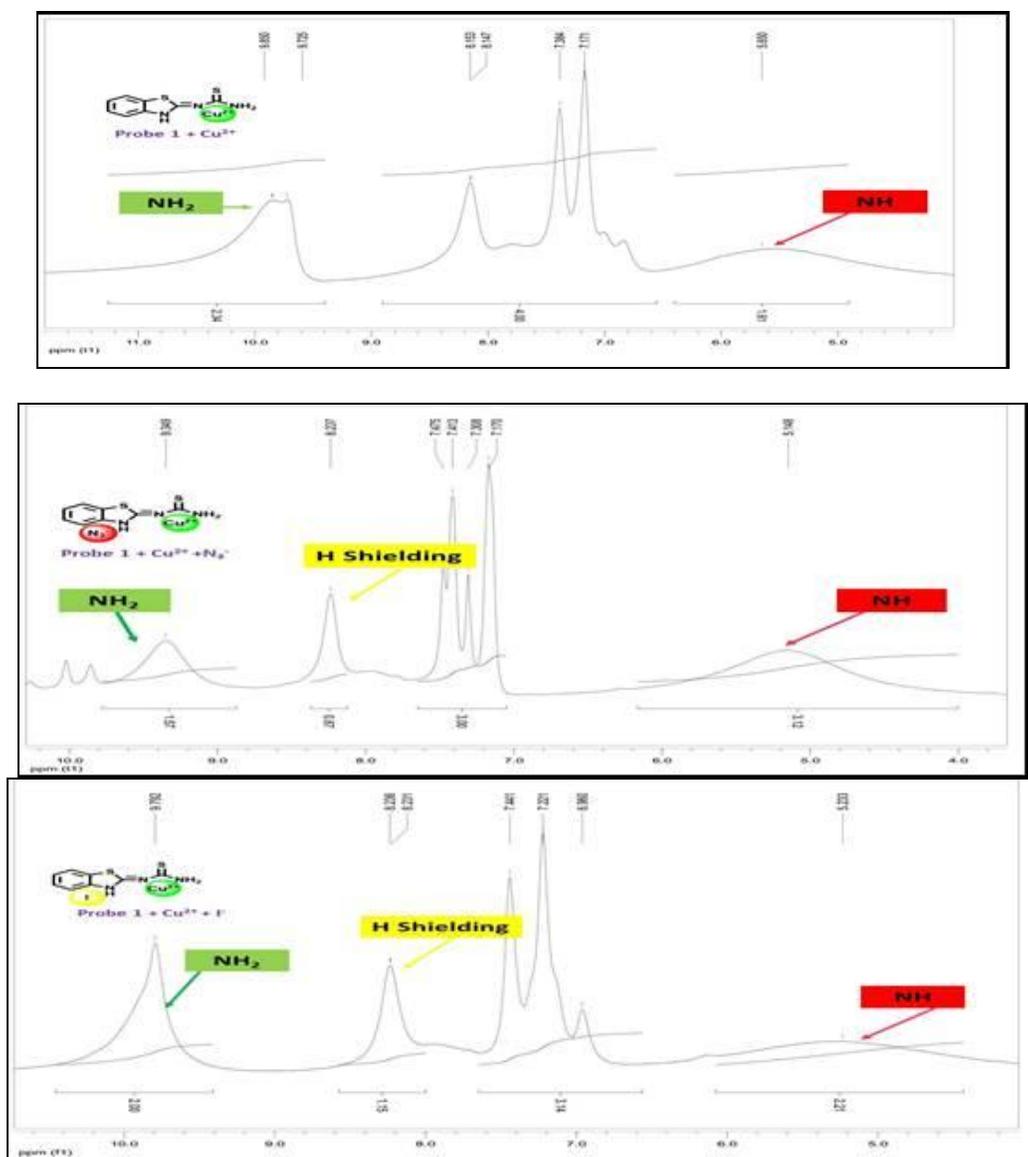


**Figure 8.** Job's plot between probe **1**-Cu<sup>2+</sup>, N<sub>3</sub><sup>-</sup> (A) and I<sup>-</sup> (B) ions in DMSO-H<sub>2</sub>O (73:27 v/v).

For more information, and find out more about the mechanism of interaction between compound **1** and Cu<sup>2+</sup>, N<sub>3</sub><sup>-</sup>/I<sup>-</sup> ions, the <sup>1</sup>H NMR titration in DMSO-*d*<sub>6</sub> solution was carried out. As shown in Figure 9, The NH<sub>2</sub>, and NH single signals appeared at 10.16, 7.35 ppm, respectively. With the addition of the 1 equiv. Cu<sup>2+</sup> ions a significant shift for the NH band (~ 2 ppm) and a small shift belong side converting to a doublet for NH<sub>2</sub> groups appeared. Cleaving of

nitrogen-bonded pair electrons with Cu<sup>2+</sup> ions reduce their focus on hydrogens, which is expected to increase tautomerization. This phenomenon can be explained by the shift of hydrogens signals, in both NH, and NH<sub>2</sub>, to a lower field and getting broad. On the other hand, Cleaving prevents the free rotation of NH<sub>2</sub> hydrogen groups, so the hydrogens are no longer the same, and the NH<sub>2</sub> peak is seen as a doublet peak.



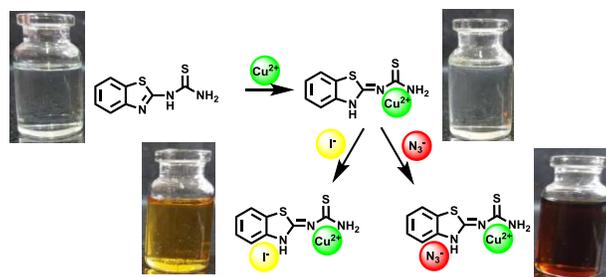


**Figure 9.**  $^1\text{H}$  NMR spectra of compound **1**, **1** + 1 equiv.  $\text{Cu}^{2+}$ ,  $(\mathbf{1}\text{-Cu}^{2+})$  + 1 equiv.  $\text{I}^-$ , and  $(\mathbf{1}\text{-Cu}^{2+})$  + 1 equiv.  $\text{N}_3^-$  in  $\text{DMSO-}d_6$ .

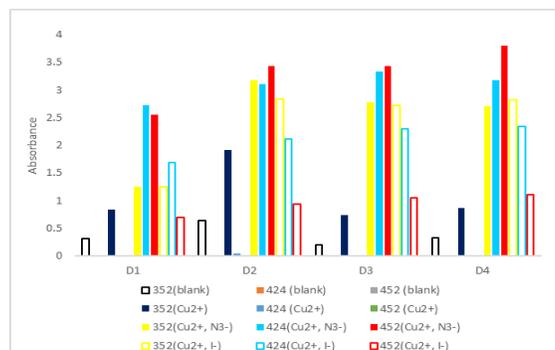
A tentative mechanism for this transformation is proposed in Scheme 2.

Subsequently, azide, and iodine ions were added to the probe  $\mathbf{1}\text{-Cu}^{2+}$  solution. With the addition of these two ions, in addition to more deshielding of NH, and  $\text{NH}_2$  groups *via* second complex formation, it was seen that one hydrogen of the aromatic ring was slightly shielded. This observation can be attributed to the placement of this hydrogen in the rich electron space of iodide and azide ions [22].

In order to generalize the sensing behavior of compounds containing thiourea substitution, aromatic and aliphatic derivatives containing thiourea **1-4** were prepared. The behavior of the synthesized compounds **2-4** against  $\text{Cu}^{2+}$ ,  $\text{I}^-$ , and  $\text{N}_3^-$  ions was investigated according to model **1** (Figure 10). As expected, all compounds **2-4** showed a significant bathochromic shift in UV-Vis. spectrum besides the naked-eye color changing against  $\text{Cu}^{2+}$ ,  $\text{I}^-$ , and  $\text{N}_3^-$  ions.

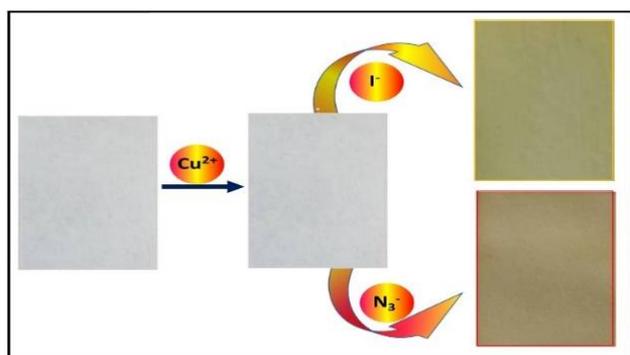


**Scheme 2.** Suggested mechanism of interaction between probe **1** and  $\text{Cu}^{2+}$ ,  $\text{I}^-$ , and  $\text{N}_3^-$ .



**Figure 10.** The UV-Vis. absorbance of probes **1-4** ( $3.5 \mu\text{M}$ ) after the addition of  $\text{Cu}^{2+}$ ,  $\text{I}^-$ , and  $\text{N}_3^-$  ions (according to the model) in  $\text{DMSO-H}_2\text{O}$  (73:27 v/v).

The paper test strips of probe **1** with  $\text{Cu}^{2+}$ ,  $\text{I}^-$  and  $\text{N}_3^-$  ions were checked for qualitative application. In doing this, filter papers were submerged in a probe **1** solution ( $35 \mu\text{M}$ ) and dried in the air. Then, submerged in aqueous solutions of  $\text{Cu}^{2+}$ , dried in the air, and again immersed in  $\text{I}^-$  /  $\text{N}_3^-$  ions ( $0.35 \text{ mM}$ ). The color-changing from colorless for **1**, and  $\text{1-Cu}^{2+}$  to yellow for  $(\text{1-Cu}^{2+})\text{-I}^-$  and red for  $(\text{1-Cu}^{2+})\text{-N}_3^-$  demonstrated a rapid detection of  $\text{I}^-$  and  $\text{N}_3^-$  ions in the real samples (Figure 11).



**Figure 11.** The test strips of compound **1** for detecting  $\text{Cu}^{2+}$ ,  $\text{I}^-$  and  $\text{N}_3^-$  ions.

## Experimental Section

Melting points were determined with an Electrothermal 9100 apparatus and are uncorrected. All chemicals and solvents were prepared from Mojllali, Samchun, and Merck companies, and used without more purification.  $^1\text{H}$  NMR (300 MHz) spectra were obtained using Bruker DRX-300 AVANCE spectrometers. Ultraviolet-Visible (UV-Vis) spectra were recorded with a Rayleigh UV-2601 double-beam spectrophotometer. The microwave irradiation experiments were done using microwave oven MW939.

### General procedure for the preparation of compounds 1-4

A mixture of amine (1.0 mmol), ammonium thiocyanate (1.0 mmol, 76 mg), and hydrochloric acid 37% (3-4 drops) were added to a vial containing a magnetic stirring bar. The mixture of was stirred at  $90^\circ\text{C}$  in the oil bathroom until the reaction was completed (monitored by TLC). Then was cooled and a solid product appeared. The considerate solid was filtrated and washed with n-hexane. For more purification, the compounds **1-4** were recrystallized by ethanol.

### Preparation of solution of probe and analyst

A stock solution of probe (3.5 mM) got ready in DMSO and the stock solutions of various analytes (NaCl, LiCl, KCl, NiCl<sub>2</sub>, HgCl<sub>2</sub>, CoCl<sub>2</sub>, CaCl<sub>2</sub>, MnCl<sub>2</sub>, BaCl<sub>2</sub>, AgCl, AlCl<sub>3</sub>, CuCl, CuCl<sub>2</sub>, ZnCl<sub>2</sub>, NaF, NaBr, NaI, NaNO<sub>2</sub>, NaNO<sub>3</sub>, NaN<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>SO<sub>3</sub>, NaOAc, Na<sub>2</sub>S) were provided from (3.5 mM) using deionized water.

## Conclusion

In conclusion, four optical probes featuring thiourea construction were prepared via a modified method, and employed for naked-eye detection of Cu<sup>2+</sup>, I<sup>-</sup>, and N<sub>3</sub><sup>-</sup>. The mechanism of this interaction was studied by <sup>1</sup>H NMR titration experiments, which indicated complex formation between synthesized compounds and desired ions. For further study, quantitative measurements including stoichiometric ratio and detection limit were performed, which indicated a 1:1 ratio and LOD = 0.11 μM (Cu<sup>2+</sup>), 76 nM (I<sup>-</sup>), and 31 nM (N<sub>3</sub><sup>-</sup>). Finally, the paper strips were performed to evaluate the applicability of the prepared probes as naked-eye sensors in the real samples.

## Acknowledgements

We want to thank our colleagues in Research Council of Tehran Medical Science, Islamic Azad University for providing a good contribution to all aspects of the project.

## References

- [1] Ozdemir, M. *J Photochem. Photobio. A: Chem.* **2019**, 369, 54.
- [2] Lee, H.Y.; Son, H.; Lim, J. M.; *Analyst.* **2010**, 135, 2022.
- [3] Kaur, N.; Kumar, S. *Tetrahedron Lett.* **2006**, 47, 4109.
- [4] Liu, M-X.; Wei, T-B.; Lin, Q. *Spectrochimica Acta Part A: Mol. Biomol. Spect.* **2011**, 79, 1837.
- [5] Gupta, V. K.; Mergu, N.; Kumawat, L. K. *Sens. Actuators B: Chem.* **2016**, 223, 101.
- [6] Zhang, J.; Zhang, L.; Wei, Y. *Spectrochem. Acta Part A: Mol. Biomol. Spect.* **2014**, 132, 191.
- [7] Chen, L.; Lu, W.; Wang, X. *Sens. Actuators B: Chem.* **2013**, 182, 482.
- [8] Zimmermann, M. B.; Ito, Y.; Hess, S. Y. *Am. J. Clin. Nutr.* **2005**, 81, 840.
- [9] Ohashi T, Yamaki M, Pandav CS, *Clin. Chem.* **2000**, 46, 529.
- [10] Abdel-Latif MS, Al-Saraj MR. *Anal. Lett.* **2007**, 40, 729.
- [11] Li Z, Liu R, Xing G, *Biosens. Bioelect.* **2017**, 96, 44.
- [12] Dhara K, Saha UC, Dan A, *Chem. Commun.* **2010**, 46, 1754.
- [13] Friscourt F, Fahrni CJ, Boons G-J. *J. Am. Chem. Soc.* **2012**, 134, 18809.
- [14] Puthiyedath T, Bahulayan D. *Sens. Actuators B: Chem.* **2017**, 239, 1076.
- [15] Kaur N, Kumar S. *Tetrahedron Lett.* **2008**, 49, 5067.
- [16] Cao C, You X, Feng L, *Can. J. Chem.* **2020**, 98, 659.
- [17] Chen C, Men G, Bu W, *S Sens. Actuators B: Chem* **2015**, 220, 463.
- [18] Cheng Y-F, Zhao D-T, Zhang M, *Tetrahedron Lett.* **2006**, 47, 6413.
- [19] Hosseini-Pirdehi H, Mahmoodi NOA, Taheri A, *Spectrochimica Acta Part A: Mol. Biomol. Spect.* **2019**, 117989.
- [20] Hosseini-Pirdehi H, Mahmoodi NO, Nadamani MP, *J. Photochem. Photobiology A: Chem.* **2020**, 112365.
- [21] Hosseini-Pirdehi H, Mahmoodi NOA, Taheri A. *J. Photochem. Photobiology A: Chem.* **2021**, 421, 113524.
- [22] Kumar V. *Bull. Chem. Soc. Japan.* **2021**, 94, 309.
- [23] Kumar V, Kaushik MP, Srivastava AK, *Anal. Chin. Acta.* **2010**, 663, 77.
- [24] Lee DH, Lee HY, Hong J-I. *Tetrahedron Lett.* **2002**, 43, 7273.
- [25] Jose, D. A.; Kumar, D. K.; Ganguly, B. *Org. Lett.* **2004**, 6, 3445.
- [26] Li, L.; Li, H.; Liu, G. *Luminescence.* **2017**, 32, 1473.
- [27] Shao, J.; Lin, H.; Lin, H-K. *Talanta.* **2008**, 75, 1015.
- [28] Yapati, H.; Devineni, S. R.; Chirumamilla, S. J. *Chem. Sci.* **2016**, 128, 43.
- [29] Herr, R. J.; Kuhler, J. L.; Meckler, H. *Synthesis.* **2000**, 2000, 1569.
- [30] Bagherzadeh, N.; Sardarian, A. R.; Inaloo, I. D. *New J. Chem.* **2021**, 45, 11852.
- [31] Revankar, V. M.; Kulkarni, M.V. *Zeitschrift für Naturforschung B.* **2015**, 70, 483.
- [32] Kato, R.; Nishizawa, S.; Hayashita, T. *Tetrahedron Lett.* **2001**, 42, 5053.
- [33] Vinithra, G.; Suganya, S.; Velmathi, S. *Tetrahedron Lett.* **2013**, 54, 5612.