Scientific paper

Synthesis and Spectroscopic Studies of Novel Rhodanine Azo Dyes: An Excellent Selective Chemosensor for Naked-eye Detecting of Cu^{2+} Ion

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Abstract

This study is first report on the synthesis of novel rhodanine based azo dyes and their fluorogenic and chromogenic sensing behaviors with metal ions (Li^+, Na^+, K^+, Rb^+, Pb^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}) by using UV-vis and fluorescence spectroscopy techniques. The results of spectroscopic experiments for rhodanine based azo dye **1a** exhibited excellent selectivity for Cu^{2+} over the other metal ions. Furthermore, anti-bacterial studies of rhodanine azo dyes were performed towards some selected bacteria via microbroth dilution method. Obtained results showed that rhodanine ionophore **1a** showed strong antibacterial activity against *S.aureus*.

Keywords*:* Rhodanine, copper(II) ion, chemosensor, azo-dye, antibacterial activity.

1. Introduction

Molecular recognition is the first step in the design and synthesis of molecular sensors for detection of anions, metal cations or neutral species in organic or aqueous media. The molecular sensor is designed to exhibit a physical response which must be easily detected in the presence of these target species. Rhodanine is an important part of heterocyclic azo dyes, which has been mainly used to determine noble metals.[1,2] According to the relationship between structures and chemiluminescence performances of organic azo dyes, many active groups have been introduced to rhodanine matrix to obtain satisfactory chemiluminescence properties.[3] Azo compounds, based on rhodanine, play a important role as chelating agents for a large number of metal ions.[4,5] The complexation studies of the rhodanine based azo dyes with various metal ions along with uranyl, ruthenium, copper, cobalt and nickel ions are documented in the literature.[6–9] Chemical properties of rhodanine and its derivatives are of interest due to coordination capacity and their use as metal extracting agents.[10] Careful examination of the literature reveals that considerable work has been reported on the spectrophotometric studies of the heterocyclic azo compounds, their metal complexes and their analytical applications.[11] But little information has appeared in the literature concerning azo compounds derived from rhodanine and their metal complexes. It is also accepted that knowledge of the stability constants of such azorhodanines and their metal complexes may eventually help to throw some light on the deactivation of essential trace metals in biological systems.[12] Furthermore, heterocyclic compounds based on thiazolidine are biologically active compounds having five membered rings, with different heteroatoms. A wide range of pharmacological activities has been attributed to these molecules. Among these include antimicrobial,[13] anticancer,[14,15] antiviral,[16] anticonvulsant,[17–19] antitubercular,[20] antifungal,[21,22] anti-inflammatory,[23] analgesic[24] and antiproliferative[25,26] activities.

Up to now, although several works about the effect of the rhodanine based azo dyes on the both metal complexation and pharmacological activities has been repor-

ted.[8,19] There is no other reported a chemosensor study between metal cations and rhodanine based azo dyes. Therefore, the aim of the present study was to explore the effect of rhodanine based azo dyes on the selective chemosensor studies for some selected metal cations such as Li^+, Na^+, K^+, Rb^+, Pb^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+}.

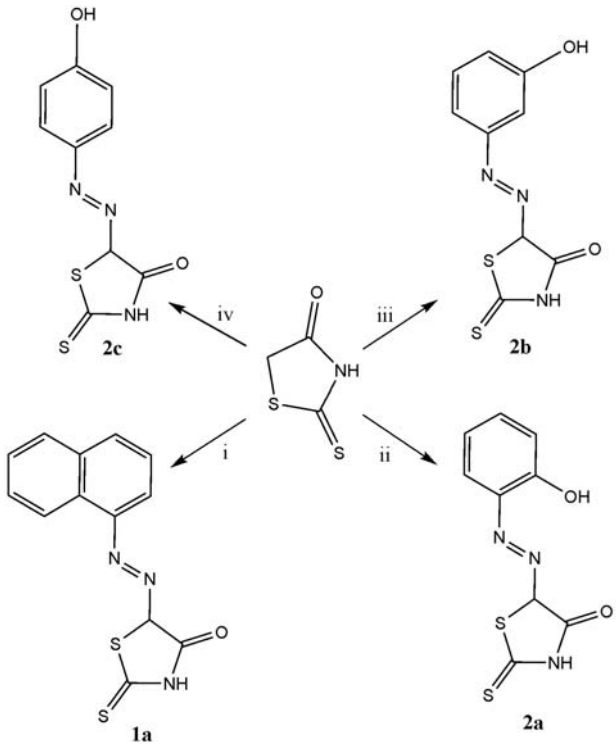
2. Experimental

2. 1. Materials

All of the reagents used in this study were obtained from Merck or Fluka and used without further purification. All the metal salts were used as perchlorate compounds ($MClO_4$, M : Li^+, Na^+, K^+, Rb^+, Pb^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}). Thin layer chromatography (TLC) was performed using silica gel on glass TLC plates (silica gel H, type 60, Merck). Column chromatographic separations were performed on Merck Silica gel-60 (230–400 mesh).

2. 2. Instrumentation

^{1}H NMR spectra were obtained using a Varian 400 MHz spectrometer operating at 400 MHz. IR spectra were obtained on a Perkin Elmer spectrum 100 FTIR spectrometer (ATR). UV-vis absorption and fluorescence spectra were recorded on a Shimadzu UV-1700 spectrophotometer and on a Perkin-Elmer LS-55 fluorescence spectrometer, respectively. Elemental analyses were performed using a Leco CHNS-932 analyzer. Melting points were determined on a Gallenkamp apparatus.



Scheme 1. Synthesis of azo dyes based rhodanine **1a** and **2a-c**. i: HCl, $NaNO_2$, CH_3COOH, CH_3COONa, 1-Aminonaphthalene, 0 °C. ii: HCl, $NaNO_2$, CH_3COOH, CH_3COONa, 2-Aminophenol, 0 °C. iii: HCl, $NaNO_2$, CH_3COOH, CH_3COONa, 3-Aminophenol, 0 °C. iv: HCl, $NaNO_2$, CH_3COOH, CH_3COONa, 4-Aminophenol, 0 °C.

2. 3. Synthesis

Rhodanine based azo dyes (**1a** and **2a-c**) were synthesized according to the following modified literature procedure (Scheme 1).[27,28] All of the reactions were monitored with thin layer chromatography.

2. 4. Synthesis of Rhodanine Based Azo Dyes 1a and 2a-c

2. 4. 1 General Procedure

25 ml of distilled water containing hydrochloric acid (12 M, 32.19 mmol) were added to corresponding amin compounds such as 2-naphthylamine or *o*-, *p*-, *m*-amino phenol (5 mmol) respectively. To the cooled (0 °C) and stirred mixture, a solution of sodium nitrite (5.1 mmol, in 10 mL of water) was added dropwise for 10 min. Then, to the formed diazonium chloride mixture, a solution of 2-thioxo-4-thiazolidinone (5 mmol) in 25 mL of glacial acetic acid was added dropwise for 20 min with cooling so that the mixture was maintained 0–5 °C. The mixture containing both the rhodanine and the diazonium salt was then added with stirring to a cold solution of 15 grams of sodium acetate in 50 mL of water. After addition, the resulting slurry was stirred for 2 hours at 5 °C. The mixture was allowed to stand for overnight. Then the obtained dark red precipitates were filtered, washed several times with water. The crude product was purified by recrystallization from hot ethanol.

5-(naphthalen-2-yldiazenyl)-2-thioxothiazolidin-4-one (1a)

Yield = 65%, dark red; Mp 107 °C; IR (ν_{max}, cm^{-1}): 1721 (C=O), 1665 (C=C), 1450 (N=N), 1325 and 1211 (C=S). ^{1}H NMR ($CDCl_3$): δ 8.53 (bs, 1H, NH), 6.85–6.96 (m, 7H, ArH), 3.51 (bs, 1H, CH). Anal. Calc.: $C_{13}H_9N_3OS_2$. C, 54.34; H, 3.16; N, 14.62%. Found: C, 54.29; H, 3.12; N, 14.68%.

5-(2-hydroxyphenyl) diazenyl-2-thioxothiazolidin-4-one (2a)

Yield = 68%, dark red; Mp 80–82 °C; IR (ν_{max}, cm^{-1}): 1720 (C=O), 1671 (C=C), 1440 (N=N), 1317 and 1195 (C=S). ^{1}H NMR ($CDCl_3$): δ 10.03 (s, 1H, OH), 8.71 (s, 1H, NH), 6.77–6.90 (m, 4H, ArH), 3.33 (s, 1H, CH). Anal. Calc.: $C_9H_7N_3O_2S_2$. C, 42.68; H, 2.79; N, 16.59%. Found: C, 42.59; H, 2.77; N, 16.63%.

5-(3-hydroxyphenyl) diazenyl-2-thioxothiazolidin-4-one (2b)

Yield = 59%, red; Mp 86–89 °C; IR (ν_{max}, cm^{-1}): 1720 (C=O), 1658 (C=C), 1445 (N=N), 1315 and 1211

(C=S). ^{1}H NMR ($CDCl_3$): δ 8.81 (s, 1H, OH), 8.58 (s, 1H, NH), 7.02 (s, 1H, ArH) 6.87–7.00 (m, 3H, ArH), 3.56 (s, 1H, CH). Anal. Calc.: $C_9H_7N_3O_2S_2$. C, 42.68; H, 2.79; N, 16.59%. Found: C, 42.61; H, 2.84; N, 16.66%.

5-(4-hydroxyphenyl) diazenyl-2-thioxothiazolidin-4-one (2c)

Yield = 66%, red; Mp 101–104 °C; IR (ν_{max}, cm^{-1}): 1717 (C=O), 1665 (C=C), 1445 (N=N), 1321 and 1213 (C=S). ^{1}H NMR ($CDCl_3$): δ 8.21 (s, 1H, OH), 8.10 (s, 1H, NH), 7.00–7.13 (m, 4H, ArH), 3.50 (s, 1H, CH). Anal. Calc.: $C_9H_7N_3O_2S_2$. C, 42.68; H, 2.79; N, 16.59%. Found: C, 42.66; H, 2.82; N, 16.65%.

2. 5. Absorption and Fluorescence Measurements

Stock solutions of the metal perchlorates and rhodanine based azo dyes **1a** or **2a-c** were prepared 7.0×10^{-3} M and 7.0×10^{-4} M in DMF, respectively. For UV-vis and fluorescence measurements, sample solutions were obtained by mixing appropriate amount of stock solution of receptors **1a** or **2a-c** with stock solution containing metal perchlorate, and finally diluted with DMF to make the solution having desired concentrations of chemosensor and metal ions in the solution. For the Job plot analyses, a series of solutions in DMF with varying concentrations of receptors **1a** and Cu^{2+} were prepared, and the measurements were performed under the condition of [**1a**] + [Cu^{2+}] = 7.0×10^{-5} M in final solution (5 mL). All the measurements were taken at room temperature about 25 °C. UV-vis absorption spectra and fluorescence spectra of the mixed solutions were recorded against DMF at the end of the completed reaction between the metal ions and **1a**. For the fluorescence measurements, excitation wavelength was 293 nm, with a slit width of 5 nm.

2. 6. Antibacterial Studies

The minimal inhibition concentration (MIC) values of the chemicals were studied for the microorganisms. The inocula of microorganisms were prepared from 12-h broth cultures and suspensions were adjusted to 0.5 McFarland standard turbidity. Mueller Hinton Broth (100 μL) were placed into each 96 wells of the microplates. Chemical solutions at a concentration of 20 mg mL^{-1} were added into the first rows of microplates and two fold dilutions of the chemicals were made by dispensing the solutions to the remaining wells. Culture suspensions (100 μL) were inoculated into each wells. Gentamicin solution was used as positive control. The sealed microplates were incubated at 37 °C for 18 h. Microbial growth was determined by adding 20 μL of 2,3,5-triphenyl-tetrazolium chloride (0.5%) after incubation to each well and incubating for 30 minutes at 37 °C.[29]

3. Results and Discussion

Rhodanine based azo dyes **1a** and **2a-c** were synthesized according to modified literature procedure[27,28] as shown in Scheme 1. The formation of 5-arylidenerhodanines and 5-arylazorhodanines can be carried out both in an alkaline medium and in acetic acid in the presence of sodium acetate, while the corresponding 5-substituted derivatives of thiazolidine-2,4-dione and 2-thiohydantoin can be obtained only in an alkaline medium.[27] All of the newly synthesized compounds **1a** and **2a-c** were characterized by IR, ^{1}H NMR and elemental analysis. Spectroscopic data were in full agreement with those expected. In the IR spectra of the compounds **1a** and **2a-c**, peaks were seen around 1710–1720 cm^{-1} attributable corresponding C=O bond and 1320 and 1210 cm^{-1} attributable C=S bond stretching.[30–32] Additionally, the occurrence of new bands around 1440–1450 cm^{-1} region attributable azo N=N bond stretching in the IR spectra of the compounds **1a** and **2a-c** confirmed the completion of the reactions. In the ^{1}H NMR spectra of newly synthesized rhodanine based azo dyes **1a** and **2a-c**, new peaks attributable aromatic protons were observed around 6.90–7.10 ppm. Furthermore, it was observed that new signals attributed to the phenolic hydroxyl protons were seen around 10.03 ppm for **2a**, 8.81 ppm for **2b** and 8.21 ppm for **2c** respectively. Although, rhodanine ring existed in three tautomeric forms: ketone, enol and thioenol, due to a significant polarity of the rhodanine N–H bond and to the possibility of the proton migration to the oxygen or sulfur atoms of the C=O and C=S groups, we found that the most stable form of the rhodanine ring in crystalline state was the ketone form for compounds **1a** and **2a-c**. This is not surprisingly results. Because, it is well known that rhodanine ring exists mainly as the ketone form, which is due to the low probability of keto-enol and keto-thioenol transformations.[33] The limiting stage of the tautomeric transformation is the heterolytic dissociation of the rhodanine N–H bond.[34] Also, this situation is supported by quantum-chemical calculations in literature.[33,35]

3. 1. UV-Vis Studies

The sensing ability of chemosensor **1a** for various alkali and heavy metal ions (Li^+, Na^+, K^+, Rb^+, Pb^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) in DMF was investigated by UV-vis measurements. In the absence of the metal ions, rhodanine based azo dye **1a** showed an absorption band at 414 nm attributed to the n-π* transitions of the rhodanine moiety. Upon addition of Cu^{2+}, the band at 414 nm decreased and a new red-shifted absorption band at 492 nm appeared as shown in Fig. 1a. Correspondingly, the solution color changed from orange to dark brown. The significant color change indicates that compound **1a** is a sensitive naked-eye indicator for Cu^{2+}(Fig. 1b). On the other hand, no significant change at 414 nm was observed upon the addition of the

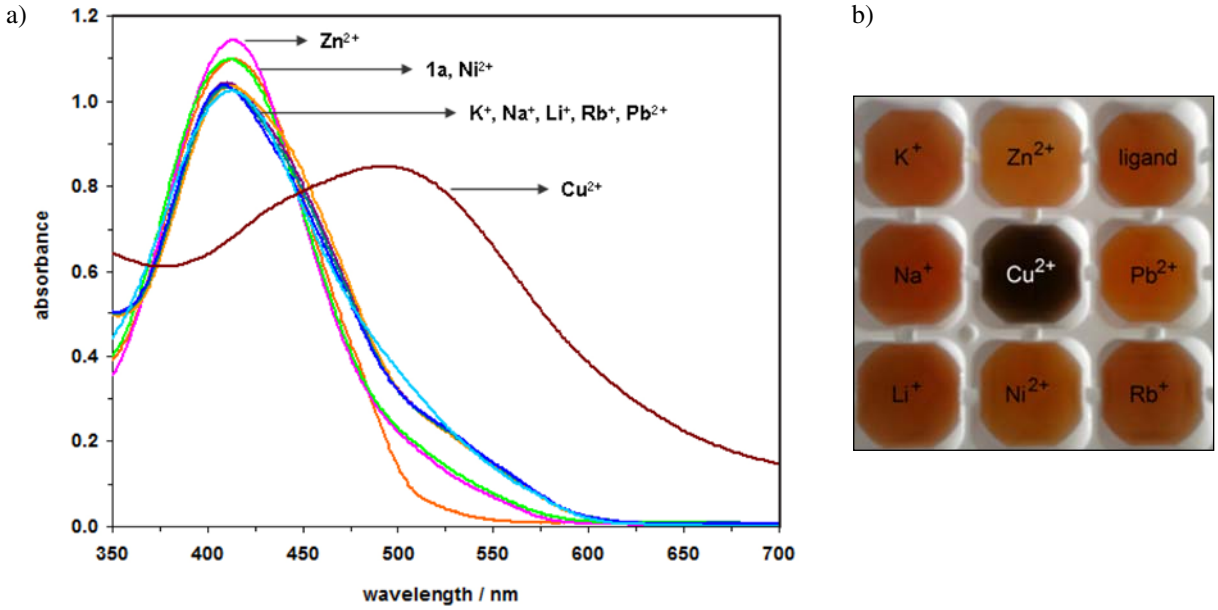


Fig. 1. (a) UV-vis absorption spectra of receptor **1a** (7.0×10^{-5} M) with various metal ions (6 eq.) in DMF. (b) Chromogenic changes of receptor **1a** (7.0×10^{-5} M) in the presence of various metal ions (6 eq.) in DMF.

other metal ions, indicating that receptor **1a** shows high selectivity for Cu^{2+} over these metal ions. This indicated that Cu^{2+} binding with chemosensor **1a** blocked the electron withdrawing ability of the rigid naphthalene group and resulted in a shorter absorption wavelength.

Fig. 2a shows UV-vis absorption spectra of receptor **1a** with various concentrations of Cu^{2+}. The absorption peak at 414 nm gradually decreased with increasing amounts of Cu^{2+} (0–6 eq.). A well-defined isosbestic point at 450 nm indicates the formation of a new compound. By plotting the changes of receptor **1a** in the absorbance intensity at 492 nm as a function of Cu^{2+} concentration, sigmoidal curve was obtained and the stoichiometry between receptor **1a** and Cu^{2+} ion was determined as 1:1 complex formation as shown in Fig. 2b. To evaluate the stoichiometry between **1a** and Cu^{2+}, Job's plot analysis was also executed. The maximum point occurred at the molar fraction of [**1a**] / ([Cu^{2+}] + [**1a**]) of ~ 0.53, confirming the 1:1

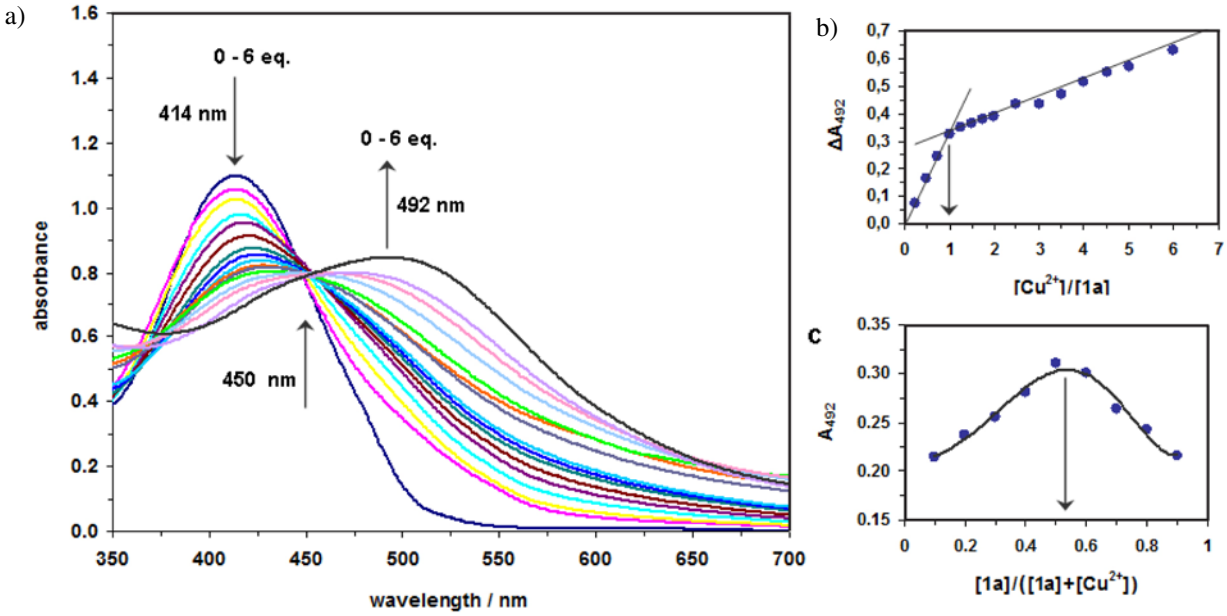


Fig. 2. (a) UV-vis titrations of 7.0×10^{-5} M receptor **1a** with increasing amounts of Cu^{2+} (0–6 eq.) in DMF. (b) The absorbance change at 492 nm as a function of Cu^{2+} concentration. (c) Job's plot of a 1:1 complex of receptor **1a** and Cu^{2+}.

stoichiometry (Fig. 2c). The association constant of the complex of compound **1a** and Cu^{2+} was determined to be 7.2×10^4 M^{-1} by the Benesi-Hildebrand equation.[36]

$$1/\Delta A = 1/(K\varepsilon[D]_0[A]_0) + 1/(\varepsilon[D]_0) \quad (1)$$

where $[D]_0$ is the initial concentration of receptor **1a** (donor), $[A]_0$ is the initial concentration of Cu^{2+} (acceptor), is the molar coefficient of the complex, K is the association constant of the complex, ΔA is the change in the absorbance of the interaction of receptor **1a** and Cu^{2+} after adding Cu^{2+} ions.

On the other hand, the absorption behaviors of the other rhodanine derivatives (**2a-c**) were investigated under the same conditions. The UV-vis spectra of receptors **2a-c** showed new absorption bands at 300 nm, 298 nm, 299 nm, respectively. Excess perchlorate salts of 6 eq. Cu^{2+} were tested to evaluate the metal ion-binding properties of receptors **2a-c**. Interestingly, we found that receptors **2a-c** do not show any UV and color (light yellow) changes, whereas receptors **1a** show a significant selectivity for Cu^{2+} over the other metal ions. The results obtained are summarized in Table 1. Upon the addition of Cu^{2+}, UV-vis absorption spectra of the Cu-complexes exhibited similar photochemical changes compared to those of receptors **2a-c**.

Table 1. UV-vis absorption properties of receptors **2a-c** (7.0×10^{-5} M) for Cu^{2+} ion (6 eq.) in DMF. λ is the maximum wavelength of the compound. A_0 is the absorbance of receptors **2a-c**. A is the absorbance of (**2a** + Cu^{2+}), (**2b** + Cu^{2+}) or (**2c** + Cu^{2+}).

Parameter	2a	2a + Cu^{2+}	2b	2b + Cu^{2+}	2c	2c + Cu^{2+}
λ (nm)	300	297	298	296	299	296
A/A_0		0.804		0.725		0.793

3. 2. Fluorescence Studies

The fluorescence spectra of receptor **1a** in the absence and presence of various metal ions (Li^+, Na^+, K^+, Rb^+, Pb^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) in DMF were recorded at excitation wavelength of 293 nm, and the emission spectrum of free receptor **1a** displays a significant band in fluorescence intensity at 360 nm. As shown in Fig. 3a, upon addition of Cu^{2+}, emission intensity of receptor **1a** was quenched. In many chemosensing systems, paramagnetic Cu^{2+} ions can strongly quench the emission of a fluorophore via a photoinduced metal-to-fluorophore electron or electronic energy transfer.[37,38] In addition, among the more paramagnetic metal ions, Cu^{2+} has a particularly high thermodynamic affinity for ligands with žžN" or žžO" as chelating element, and fast metal-to-ligand binding kinetics.[38,39] Zn^{2+} has a little effect on the fluorescence intensity of receptor **1a**. This behavior can be explained by some factors like an increased rigidity in complex structure[40] and a restriction in the photoinduced electron transfer (PET).[41,42] Addition of the other metal ions almost did not constitute a change in the fluorescence spectra of receptor **1a**, in terms of fluorescence intensity at 360 nm and general peak shape (Fig. 3b).

Fig. 4a shows fluorescence spectra of receptor **1a** with various concentrations of Cu^{2+}. The fluorescence titration resulted in a gradual decrease in the fluorescence intensity of receptor **1a** with the addition of Cu^{2+} (0–4

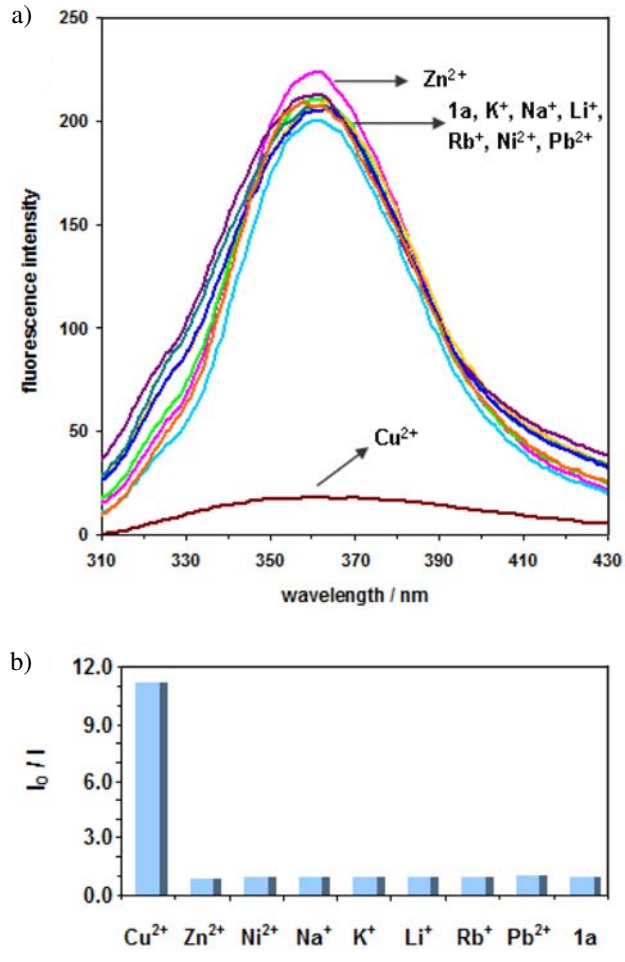


Fig. 3. (a) Fluorescence spectra of receptor **1a** (5.0×10^{-6} M) in the absence and presence of various metal ions (6 eq.) in DMF. (b) Changes in the fluorescence intensity ratio (I_0/I) at 360 nm of receptor **1a** (5.0×10^{-6} M) in the presence of various metal ions (6 eq.). I_0 is the fluorescence intensity of receptor **1a**. I is the fluorescence intensity of (**1a** + M^{n+}). λ_{ex} : 293 nm.

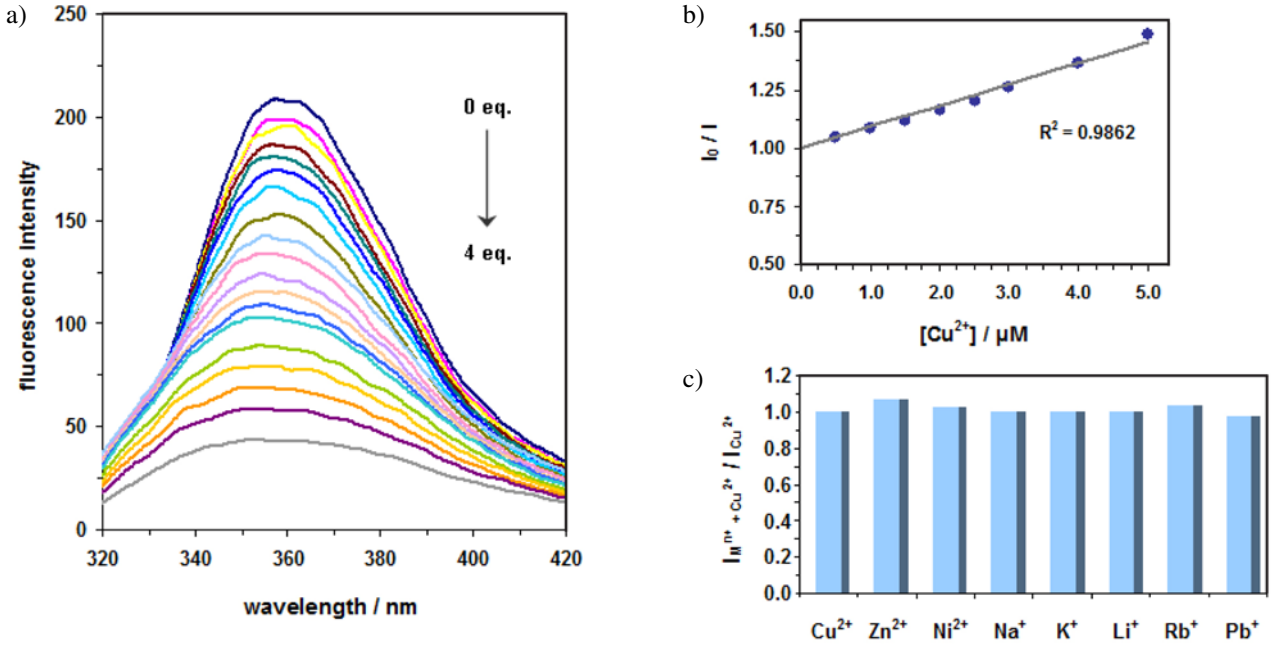


Fig. 4. (a) Fluorescence titrations of receptor 1a (5.0×10^{-6} M) with increasing amounts of Cu^{2+} (0–4 eq.) in DMF. (b) Changes in the fluorescence intensity ratio (I_0/I) at 360 nm as a function of Cu^{2+} concentration. (c) The fluorescence change profiles of receptor 1a (5.0×10^{-6} M) in the presence of Cu^{2+} (6 eq.) and miscellaneous ions including Li^+, Na^+, K^+, Rb^+, Pb^{2+}, Ni^{2+} and Zn^{2+} (6 eq.). λ_{ex}: 293 nm.

eq.). The values of (I_0/I) at 360 nm were plotted against the concentration of Cu^{2+}. I_0 and I are the fluorescence intensity of receptor **1a** and the fluorescence intensity of (**1a** + Cu^{2+}), respectively. The curve obtained exhibites a linear range between 0.5 μM and 5 μM Cu^{2+} with a correlation coefficient of 0.9862 (Fig. 4b). Furthermore, to explore the utility of receptor **1a** as a ion-selective fluoregenic chemosensor, fluorescence spectral changes of receptor **1a** in competitive metal ion complexation were investigated in the presence of Cu^{2+}(6 eq.) and miscellaneous cations (6 eq.) including Li^+, Na^+, K^+, Rb^+, Pb^{2+}, Ni^{2+} and Zn^{2+} in DMF. These miscellaneous competitive cations did not lead to any significant spectral change, in the presence of miscellaneous competitive cations, Cu^{2+} ions still resulted in the similar changes (Fig. 4c). All these results imply that receptor **1a** can be useful as a fluorogenic-sensing material for selective detection of Cu^{2+} in the presence of other competitive metal ions.

3. 3. Antibacterial Activity of Receptors 1a and 2a-c

Antibacterial activities of receptors **1a** and **2a-c** were investigated by microbroth dilution method according to previously published literature procedure[29] towards some selected bacterias such as *Escherichia coli* ATCC 25922, *Staphylococcus aureus* (MSSA) ATCC 25923, *Pseudomonas aeruginosa* ATCC 15442 and *Klebsiella pneumoniae* ATCC 10031. The obtained results are presented in Table 2. All of the receptors were found to be moderate antibacterial against all test bacteria at 1.25 mg mL^{-1} dose level. These chemicals were determined as equally effective against pathogen microorganisms tested. MIC values of receptors **2a** and **2b** were determined as 1.25 mg mL^{-1} against *E. coli, P. aeruginosa* and *K.pneumoniae*. Comparing the other bacterias and *S. Aureus*, receptor **2c** more affected the *S. Aureus* and MIC value was determined as 0.625 mg mL^{-1} for *S. aureus*. On the other hand, receptor **1a** exhibited very strong antibacterial activity against *S. aureus* at a concentration of 0.0195 mg mL^{-1}. It manifested a moderate antibacterial activity against *E. coli* at 1.25 mg mL^{-1} dose level and against *P. aeruginosa* and *K. pneumoniae* at a concentraiton of 2.50 mg mL^{-1}. While receptor **1a** showed similar antibacterial activity against *E. coli*, it was less effective against *P. aeruginosa* and *K. pneumoniae* when compared with receptors **2a-c**. According to the obtained results, it was determined that compound **1a** revealed strong antibacterial activity against *S. aureus* strain used in this study. *S. aureus* is the most sensitive strain against receptor **1a**.

4. Conclusion

In summary, new rhodanine based azo dye derivatives **1a** and **2a-c** were prepared and their metal ion-selective chemosensing and antibacterial behaviors were investigated. Receptor **1a** exhibited a selective change in UV-vis absorption and fluorescence spectra toward Cu^{2+}. The metal-binding properties of **1a**-Cu^{2+} complex were determi-

Table 2. Results of antibacterial activities of receptors **1a** and **2a-c** and standard antibiotic

Tested microorganisms	MIC values of chemicals (μg mL^{-1})				MIC values of Gentamicin (μg mL^{-1})
	1a	2a	2b	2c	
Escherichia coli ATCC 25922	1250	1250	1250	1250	9.76
Pseudomonas aeruginosa ATCC 15442	2500	1250	1250	1250	1.22
Staphylococcus aureus (MSSA) ATCC 25923	19.5	1250	1250	625	2.44
Klebsiella pneumoniae ATCC 10031	2500	1250	1250	1250	4.88

ned by spectrophotometric methods. The stoichiometry between receptor **1a** and Cu^{2+} was 1:1 complex formation, and the association constant was determined to be 7.2×10^4 M^{-1} by the Benesi-Hildebrand equation. Addition of Cu^{2+} to receptor **1a** solution resulted in an obvious color change from orange to dark brown, which made it possible to detect Cu^{2+} by the naked-eye. Moreover, receptor **1a** exhibited a good selectivity toward Cu^{2+} in the presence of competitive cations (Li^+, Na^+, K^+, Rb^+, Pb^{2+}, Ni^{2+} and Zn^{2+}). Furthermore, rhodanine based azo dyes **1a** showed strong antibacterial activity against *S.aureus*. As a conclusion, this study can be a good example for designing a variety of optical sensing devices based on metal ion detection.

5. Acknowledgements

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Povzetek

Predstavljena študija je prvo poročilo o sintezi novih azo barvil na osnovi rodanina ter o njihovih fluorogenih in kromogenih lastnostih, uporabnih za zaznavanje kovinskih ionov (Li^+, Na^+, K^+, Rb^+, Pb^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}) z UV-vis in fluorescenčnimi spektroskopskimi tehnikami. Rezultati spektroskopskih poskusov za rodaninsko azo barvilo 1a so pokazali odlično selektivnost za Cu^{2+} glede na ostale kovinske ione. Poleg tega smo izvedli protibakterijske študije rodaninskih azo barvil za nekatere izbrane bakterije po metodi razredčitve mikrogojišča. Dobljeni rezultati kažejo, da ima rodaninski ionofor 1a močno protibakterijsko aktivnost nasproti *S. aureus*.