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Scientific paper

Optical Response of Two Azo Ligands Containing Salicyaldimine-based Ligand as Side Chains Towards Some Divalent Metal Ions and Their Antioxidant Behavior

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Abstract

According to applicability of azo-azomethine compounds in chemical sensors and biological activities, two receptors: 1,2-[1-(3-imino-4-hydroxophenylazobenzene)]-4-nitrobenzene (**1**) and 1,2-[1-(3-imino-4-hydroxophenylazo-4-nitrobenzene)]-4-nitrobenzene (**2**) are investigated for detection of nickel, cobalt, copper, lead, mercury, zinc and cadmium divalent metal ions by UV-vis spectroscopy. With the addition of all metal ions to the DMSO solution of ligands, the peaks at 558 and 549 nm increase in intensity with hypsochromic or bathochromic shifts except Zn^{2+} ions and **2**, while the peaks at 388 and 391 nm dramatically decrease in intensity. In both cases, the largest shift is observed after addition of copper ions. In solution, both receptors produce a cation blue shift from 558 and 549 nm to 503 and 497 nm with the sensible color change of solutions from purple-red to orange. Therefore, both compounds can highly recognize copper ions in DMSO solution. In the next step, Benesi-Hildebrand plot and Job's method are used for determination of binding constant (K_a) and stoichiometry of formed complexes, respectively. Also, the investigation of solvent effect in the UV-vis spectra of ligands shows that the generation of hydrazine and enaminone tautomers increases in highly polar solvents such as DMF and DMSO. Finally, the antioxidant activity of ligands is studied by DPPH method. The results show that NO_2 withdrawing groups in 1,2-[1-(3-imino-4-hydroxophenylazo-4-nitrobenzene)]-4-nitrobenzene probably affect keto–enol equilibrium. As a result, this ligand reduces free radicals to non-reactive species by donating hydrogen.

Keywords: Azo-Azomethine ligands; UV-vis spectroscopy; Optical response; DPPH method; Molecular receptors

1. Introduction

Schiff bases are common organic compounds which can be easily synthesized. Among Schiff base derivatives, azo dyes are very important. Azo-azomethine compounds contain both azo and imine units. These compounds are produced by condensation of an azo dye containing aldehyde groups with primary amines.[1] Schiff bases and azo dyes have found applications in several fields such as medicinal, pharmaceutical and coordination chemistry. Some biological activities such as antifungal, antibacterial, antitumor, pesiticidal, antiviral and anti-inflammatory has been known for Schiff-bases[2–7] and azo compounds.[8–11] Because of the excellent donor properties of azo groups they are extensively used in coordination chemistry.[12–14] Additionally, azomethine compounds can be used as chemosensors for metal ions and anions. They bind as ligands to cations or interact with anions and therefore change color of the solution or maxima of absorbance band.[15–18]

Copper ions are important in metabolic processes, but in excess they can cause the imbalance of homeostasis leading to severe diseases such as Alzheimer's, Parkinson's, Mekne's, and Wilson's diseases.[19,20] Also copper ions are one of the materials that pollute environment and produce some problems in industry. Cobalt ions are dangerous pollutants. Cobalt can irritate respiratory system and cause lung diseases.[21] Therefore, the development of simple and selective chemosensors for copper and cobalt ions is necessary.[22,23] Previously, we reported easy methods for designing low cost sensors based on azo- azomethine ligands for recognition of copper and cobalt ions.[24,25] In progress, here we report synthesis, characterization and optical response of one new azo-salicyaldimine based ligand **1** (1,2-[1-(3-imino-4-hydroxophenylazobenzene)]-4-ni-

trobenzene) for detection of copper, lead, mercury, cobalt, nickel, cadmium and zinc divalent metal ions by spectrophotometry technique. Then, the response of azo-azomethine groups of compound **1** is compared with compound **2** (1,2-[1-(3-imino-4-hydroxophenylazo-4-nitrobenzene)] -4-nitrobenzene). Moreover, the antioxidant activity of both ligands is investigated against DPPH method.

2. Experimental

2. 1. General

1-(3-formyl-4-hydroxophenylazo)-4-nitrobenzene) and 1-(3-formyl-4- hydroxophenylazobenzene) were prepared according to previous methods.[1,26] Elemental analyses were performed on ElementarVario ELIII. IR spectra were recorded on a FT-IR Spectrometer Bruker Tensor 27 in the region 4000–400 cm^{-1} using KBr pellets. Electronic absorption spectra in the UV–vis region were obtained with T 60 UV/vis Spectrometer PG Instruments Ltd. NMR spectra were obtained on Bruker Avance 400 in DMSO with $SiMe_4$ as internal standard at room temperature.

2. 2. Synthesis of Ligands

2. 2. 1. 1, 2-[1-(3-imino-4-hydroxophenylazobenzene)]-4-nitrobenzene (1)

1-(3-formyl-4-hydroxophenylazobenzene) (1.84 mmol, 0.416 g) in ethanol (30 mL) was added drop wise over one hour to an ethanol solution (15 mL) of 4-nitro-1,2-diaminobenzene (0.920 mmol, 0.141 g), the color of solution changed quickly and brown precipitation appeared. After refluxing for 4h, the mixture was filtrated. The residue solid was washed with ethanol, recrystallized in CH_2Cl_2/C_2H_5OH and dried (red-brown powder). Yield (0.314 g, 60%). IR (KBr, cm^{-1}) 3363 (OH group), 1617 (–C=N– imine), 1519 and 1489 (–N=N– *cis* and *trans*), 1343 and 1313 (NO_2 group), 1273 (CO phenolic), 1150, 1106, 858, 747, 688, 643. ^{1}H NMR (400 MHz, DMSO-d_6): 12.60 (s, 2H, OH), 9.09 (s, 1H, ArH), 8.56 (s, 2H, –HC=N–), 8.41 (d, 4H, J = 8.69 Hz, ArH), 8.01–8.05 (m, 6H, ArH), 7.96 (d, 4H, J = 9.01 Hz, ArH), 7.20 (d, 1H, J = 8.90 Hz, ArH), 6.82 (d, 1H, J = 8.90 Hz, ArH), 6.76 (s, 2H, ArH), Elem. Anal. Calcd for $C_{32}H_{23}O_4N_7$: C, 67.48; H, 4.04; N, 17.22. Found: C, 67.27; H, 3.91; N, 17.40.

2. 2. 2. 1,2-[1-(3-imino-4-hydroxophenylazo-4-nitrobenzene)]-4-nitrobenzene (2)

This ligand was prepared from condensation reaction between 1-(3-formyl-4-hydroxophenylazo-4-nitrobenzene) and 4-nitro-1,2-diaminobenzene in ethanol according to literature.[27] Yield (0.394 g, 65%). IR (KBr, cm^{-1}) 3364 (OH group), 1609 (–C=N– imine), 1520 and 1489 (–N=N– *cis* and *trans*), 1342 (NO_2 group), 1286 (CO phenolic), 1147, 1105, 1102, 857, 747, 688. ^{1}H NMR (400 MHz, DMSO-d_6): 12.60 (s, 2H, OH), 9.09 (s, 1H, ArH), 8.54 (s, 2H, –HC=N–), 8.41 (d, 4H, J = 8.05 Hz, ArH), 8.03 (d, 6H, J = 8.06 Hz, ArH), 7.95 (d, 2H, J = 9.1 Hz, ArH), 7.21 (d, 1H, J = 9.2 Hz, ArH), 6.81 (d, 1H, J = 9.2 Hz, ArH), 6.76 (s, 2H, ArH), Elem. Anal. Calcd for $C_{32}H_{21}O_8N_9$: C, 58.27; H, 3.19; N, 19.12. Found: C, 58.82; H, 2.91; N, 19.32.

2. 3. Measurement of Radical Scavenging Activity

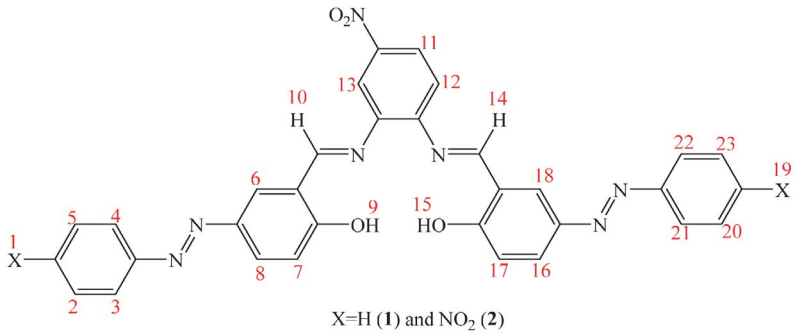
The ability of compounds **1** and **2** was investigated for removing free radicals by DPPH (1,1-diphenyl-2-picrylhydrazyl) using the method of litrature.[28] The solutions of **1** or **2** in DMSO with concentrations of 10 to 60μg/mL were added to a methanol solution of DPPH (0.1 mM). The mixtures were shaken seriously. Then the absorption of solutions was measured at λ = 517 nm after 10 minutes. Finally, the percentage of radical scavenging was determined by the following equation: (A_C is the absorbance of free DPPH and A_S is the absorbance of DPPH after reaction with **1** or **2**.)

$$RSA\% = 100\ (A_C - A_S)/A_C \quad (1)$$

3. Results and Discussion

3. 1. Synthesis and Characterization

Receptors **1** and **2** were synthesized from the condensation reaction of 1-(3-formyl-4-hydroxophenylazobenzene) or 1-(3-formyl-4-hydroxophenylazo-4-ni-



Scheme 1: Structures of azo-azomethine receptors

trobenzene) with 1,2-diamino-4-nitrobenzen benzene in ethanol and characterized by standard methods.

3. 1. 1. FT-IR and ^{1}H NMR Spectra

In the IR spectra of ligands, imine stretching vibration appears at 1617 cm^{-1} for **1** and 1609 cm^{-1} for **2**. The NO_2 symmetric and asymmetric stretching vibrations occur as sharp and strong bands at 1313 cm^{-1} and 1343 cm^{-1}. Moreover, the vibrations of (–N=N–) groups as *cis* and *trans* forms are present at 1519 cm^{-1} and 1489 cm^{-1} respectively.

The structure of **1** and **2** are fully characterized by ^{1}H NMR spectroscopy. The formation of imine group is established by the appearance of the signal at 8.56 ppm in **1** and 8.54 ppm in **2**, depending on the substituent attached to the imine nitrogen atom. The OH proton signals appear as one singlet at 12.64 in **1** and 12.61 ppm in **2**. The aromatic proton signals appear in the range of 6.76–9.09 ppm (Scheme 1 and Table 1).

An antioxidant acts *via* two mechanisms: one of them depends on the benzyl hydrogen atom and other follows the route of keto-enol form.[29] As shown in Fig. 1, compound **2** reveals high antioxidant activity against DPPH method (78% for 60 μg/mL), while compound **1** display low activity (less than 13% for 20 μg/mL). It seems that the possible mechanism for both compounds is the keto-enol route (Scheme 3). Several factors such as structure, temperature and solvent can affect the keto-enol equilibrium. The structure factors involve steric bulk, conjugation, electron-withdrawing/donating groups and resonance.[30] The structure of both compounds is similar (the only difference between two structures is the existence of NO_2 groups at the *para* position of azo units in **2**) (Scheme 1). These NO_2 withdrawing groups in compound **2** probably affect keto-enol equilibrium. As a result, ligand **2** reduces free radicals to non-reactive species by donating hydrogen.

Table 1: ^{1}HNMR chemical shifts of ligands **1** and **2**

Chemical shifts, δ TMS (ppm)	Assignments [a]	*J* (Hz)	Chemical shifts, δ TMS (ppm)	Assignments [a]	*J* (Hz)
	Compound 1			**Compound 2**	
12.64	[s, 2H] (9, 15)		12.61	[s, 2H] (9, 15)	
9.10	[s, 1H] (13)		9.09	[s, 1H] (13)	
8.56	[s, 2H] (10, 14)		8.54	[s, 2H] (10, 14)	
8.42	[d, 4H] (3, 4, 21, 22)	8.69	8.41	[d, 4H] (3, 4, 21, 22)	8.05
8.01–8.05	[m, 6H] (2, 5, 7, 17, 20, 23)		8.03	[d, 6H] (2, 5, 7, 17, 20,23)	8.06
7.96	[d, 4H] (1, 8, 16, 19)	9.01	7.95	[d, 2H] (8, 16)	9.01
7.20	[d, 1H] (12)	8.90	7.21	[d, 1H] (12)	9.20
6.82	[d, 1H] (11)	8.90	6.81	[d, 1H] (11)	9.20
6.76	[s, 2H] (6, 18)		6.76	[s, 2H] (6,18)	

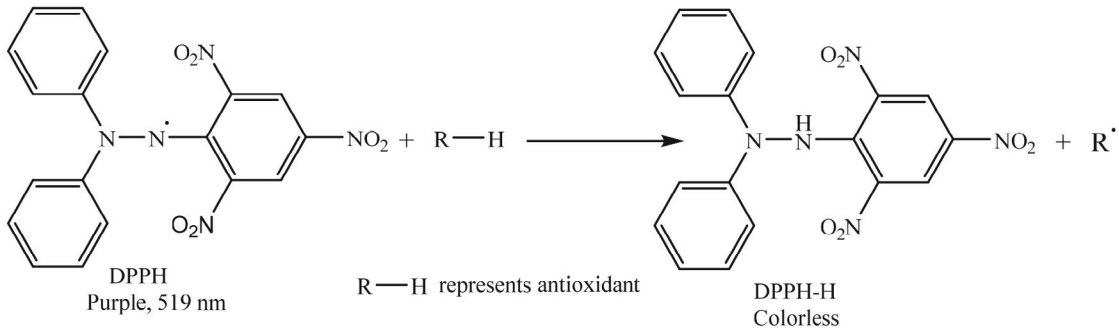
3. 2. Antioxidant Activity

The antioxidant activity of compounds **1** and **2** is investigated by DPPH radical scavenging method. In this method, radical DPPH reduces to its non-radical form in the presence of hydrogen-donating material that named antioxidant (Scheme 2).

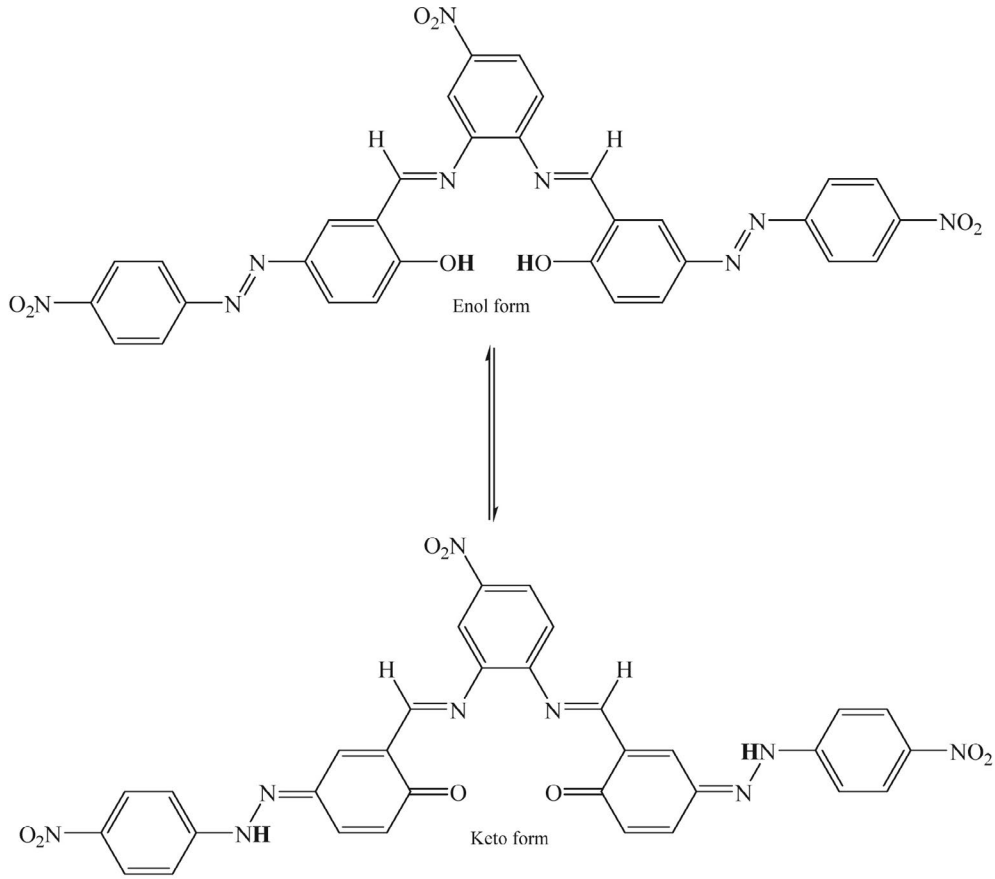
3. 3. UV-vis Spectroscopy Experiments

3. 3. 1. UV-vis Spectra of Ligands

Figs. 2 and 3 show the UV-vis spectra of receptors **1** and **2** in DMSO solution. Both compounds show one strong absorption band at λ = 278 nm corresponding to



Scheme 2: DPPH radical and its stable form (DPPH= 1,1-diphenyl-2-picrylhydrazyl)



Scheme 3. Suggested mechanism for 1,2-[1-(3-imino-4-hydroxophenylazo-4-nitrobenzene)]-4-nitrobenzene as antioxidant

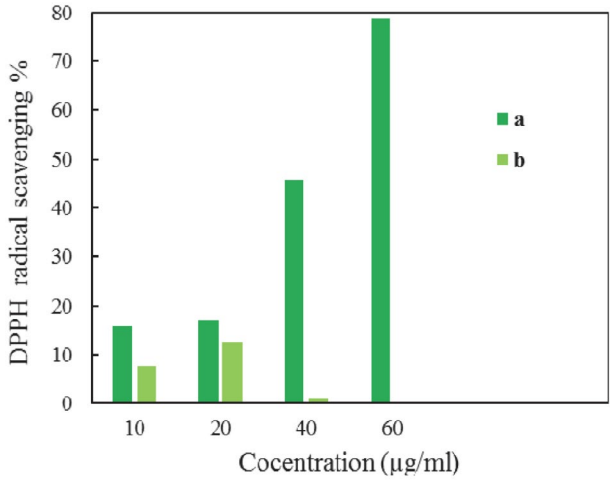


Fig. 1. Effects of 1,2-[1-(3-imino-4-hydroxophenylazo-4-nitrobenzene)]-4-nitrobenzene (**a**) and 1,2-[1-(3-imino-4-hydroxophenylazobenzene)]-4-nitrobenzene (**b**) against DPPH after 10 min

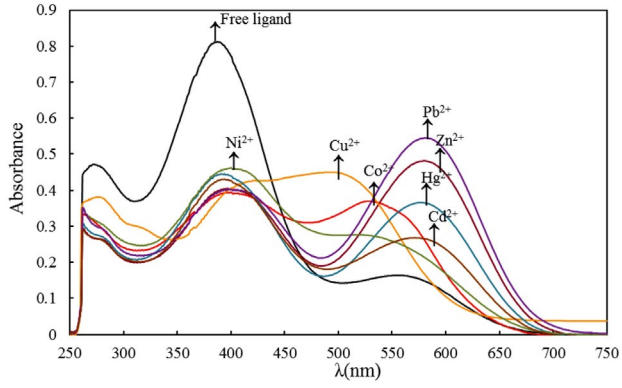


Fig. 2. UV–vis spectra of ligand **1** (0.02 mM) before and after adding a 0.02 mM concentration of various metal acetates in a DMSO solution

the π→π* transition of aromatic rings, one broad absorption band at λ = 388 nm for **1** and 391 nm for **2** attributable to the π→π* transition of azo groups and π→π* or n→π* transition of imine groups[31] and the strong and broad absorption band at λ = 558 nm for **1** and 549 nm for **2** corresponding to the n →π* transition of (–N=N) units.[32]

The UV-vis absorption spectra of azo Schiff-base ligands **1** and **2** in CH_2Cl_2, $CHCl_3$, CH_3OH and C_2H_5OH show main band at 364–382 nm which can be assigned to π→π* transition of azo groups. However, in DMSO and DMF solution, the first band that located at 388-391 nm, similar to other solvents, is because of π→π* transition of azo groups, while the second one which appeared at 549–558 nm can be assigned to an intramolecular charge transfer n→π* transition of azo-aromatic chromophore (Fig. 4).[33,34] In general, the absorption bands of **1** and **2** at 364–

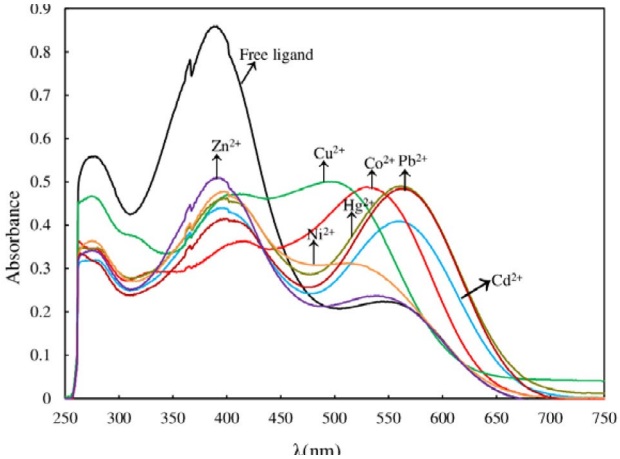


Fig. 3. UV–vis spectra of ligand **2** (0.01 mM) before and after adding a 0.01 mM concentration of various metal acetates in a DMSO solution.

391 nm show bathochromic shift with polarity change of solvents.[35,36] Also, the solvatochromism that exhibited by azo ligands may be to the effect of proton transfer or dipole moment changes in various solvents (in DMSO and DMF an additional absorption maximum is observed at 549–558 nm. This absorption is attributed to the existence of tautomeric form on highly polar solvents).[37,38]

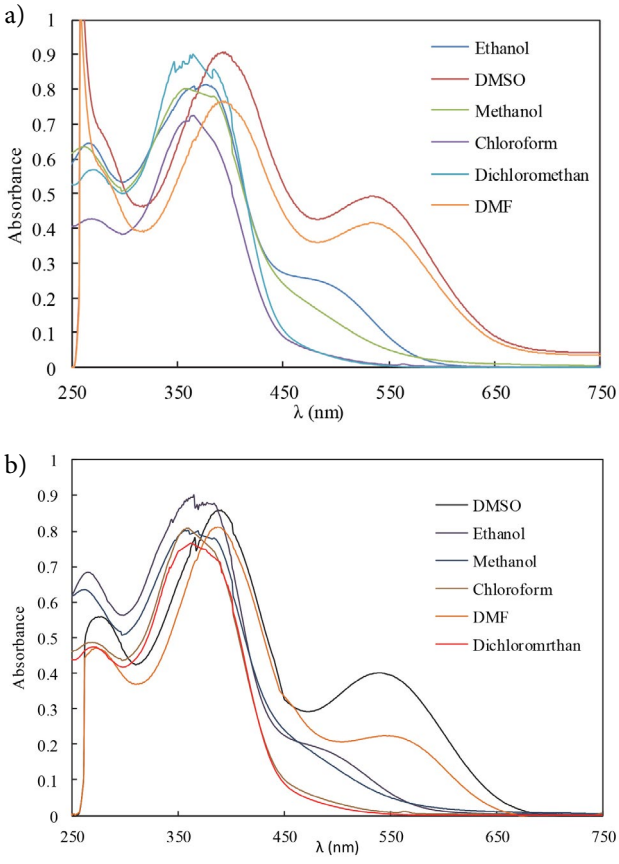


Fig. 4: UV-vis spectra of azo Schiff-bases **1** (a) and **2** (b) in various solvents (~10^{-4} M)

3. 3. 2. Cation Binding Studies

The optical response of **1** (2×10^{-5} mol L^{-1}) for Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, $Pb^{2+}$and Hg^{2+} as their acetate salts (2×10^{-5} mol L^{-1}) in DMSO is studied. As shown in Fig. 2, the broad bond at 558 nm rises in intensity after addition of Pb^{2+}, Zn^{2+}, Hg^{2+} and Cd^{2+} ions to the DMSO solution of **1** with a bathochromic shift (+29 nm). The intensity of the band at 558 nm increases as fellow: Pb^{2+}> Zn^{2+}> Hg^{2+} > Cd^{2+}. Upon the addition of Cu^{2+} and Co^{2+} ions to **1** the peak at 558 nm increases in intensity and shits to shorter wavelengths. The largest hypsochromic shift is seen after addition of copper ions (–55 nm) with the sensible color change of solution to orange. The peak at 388 nm shrinks in intensity with the addition of all studied cations. As shown in Fig. 2, no significant change is observed in the UV-vis spectrum of **1** after adding nickel ions.

The recognition ability of **2** (2×10^{-5} mol L^{-1}) for Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, $Pb^{2+}$and Hg^{2+} as acetate salts (2×10^{-5} mol L^{-1}) in DMSO is shown in Fig. 3. Upon addition of Pb^{2+}, Cd^{2+} and Hg^{2+} ions to **2**, the peak at 549 nm increases in intensity with a bathochromic shift (almost +20 nm). Addition of Cu^{2+}, $Co^{2+}$and Ni^{2+} ions to the DMSO solution of **2** exhibits significant increase in peak intensity at 549 nm with a hypsochromic shift. Similarity to **1**, the largest blue shift is obtained after addition of Cu^{2+} ions (–52 nm). As expected, addition of all metal ions to **2** shows decrease in peak intensity at 391 nm. It is notable that no significant change is observed in the UV-vis spectra of **2** after addition of Zn^{2+} ions.

In both cases, the changing in the UV-vis Spectra can be explained that: there is likely a fine balance between enol and keton forms of ligands in DMSO solution and the complexion of ligands with metal ions probably affect it. In additional, decreasing of n→π* transition of imine groups in intensity shows nitrogen atoms of imine units coordinate to the metal ion center.[39–41]

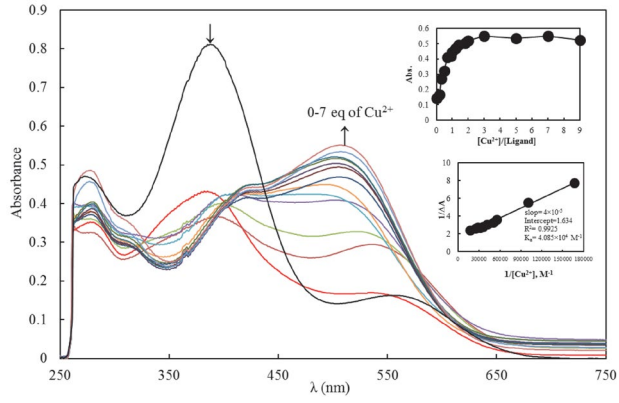


Fig. 5. Changes in the UV–vis spectra of **1** (0.020 mM) upon titration by $Cu(CH_3COO)_2$ in a DMSO solution, where the concentration of $Cu(CH_3COO)_2$ varies from 0.004–0.14 mM. Insets: above: Absorption at selected wavelength versus equivalents of cation added, down; Benesi–Hildebrand plot of the receptor with Cu^{2+} ion.

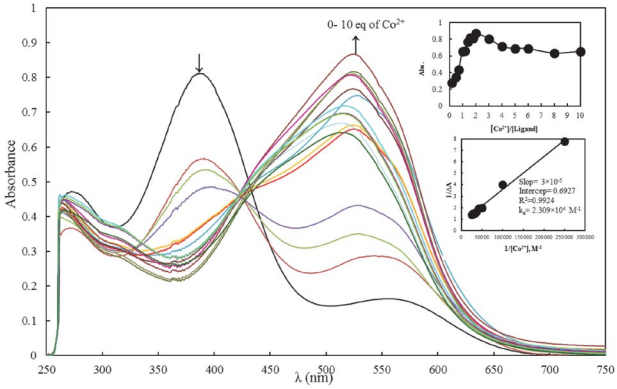


Fig. 6. Changes in the UV–vis spectra of **1** upon titration by $Co(CH_3COO)_2$ in a DMSO solution, where the concentration of $Co(CH_3COO)_2$ varies from 0.004–0.2 mM. Insets: above: Absorption at selected wavelength versus equivalents of cation added, down; Benesi–Hildebrand plot of the receptor with Co^{2+} ion.

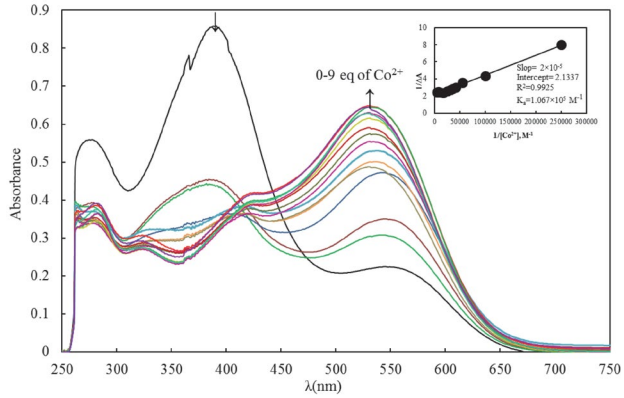


Fig. 8. Changes in the UV–vis spectra of **2** (0.020 mM) upon titration by $Co(CH_3COO)_2$ in a DMSO solution, where the concentration of $Co(CH_3COO)_2$ varies from 0.004–0.18 mM. Inset: Benesi–Hildebrand plot of the receptor with Co^{2+} ion.

2. 3. 3. Titrations with UV-vis Spectroscopy

Upon gradual addition of Cu^{2+} ions to DMSO solution of **1**, the absorption at 558 nm gradually increases in intensity with hypsochromic shift to 503 nm and the peak at 388 nm strongly decreases in intensity (Fig. 5). Similarity to **1**, with the progressive addition of Cu^{2+} ions to **2**, the peak at 549 nm shifts to 497 nm and increases in intensity, while the peak at 391 nm dramatically decreases and finally disappears (Fig. 7). In both case, the color solution change from purple-red to orange after addition of copper ions.

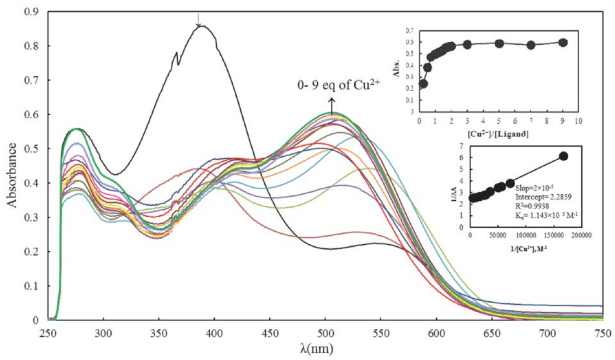


Fig. 7. Changes in the UV–vis spectra of 2 (0.020 mM) upon titration by $Cu(CH_3COO)_2$ in a DMSO solution, where the concentration of $Cu(CH_3COO)_2$ varies from 0.004–0.18 mM. Insets: above: absorption at selected wavelength versus equivalents of cation added, down; Benesi–Hildebrand plot of the receptor with Cu^{2+} ion.

Upon successive addition of Co^{2+} to **1**, a hypsochromic shift is observed from 558 to 525 nm. The peak at 525 nm rises with the gradual addition of cobalt ions to **1**. The peak at 388 nm dramatically decreases in intensity and disappears after extra addition of Co^{2+} ions (Fig. 6). Finally, upon incremental addition of Co^{2+} to **2**, n→π* transition shifts from 549 nm to 537 nm. The peak at 537 nm gradually increases in intensity while the peak at 391 nm decreases in intensity (Fig. 8).

The Job's plot results show a 1:1 binding stoichiometry for **1** and **2** with Cu^{2+}. (the proposed structure of **1** and **2** with Cu^{2+} is shown in Scheme 4) while the 2:1 binding stoichiometry for **1** and **2** with Co^{2+} is determined by Job's plot experiments (Fig. 9).

In the next step, 1:1 association constants of **1** and **2** with Cu^{2+} are determined on the Benesi-Hildebrand plots[42] at λ = 503 and 497 nm, respectively (Figs. 5 and 7). Correspondingly, assuming a 2:1 (**1** or **2**: cobalt ion) complex, the binding constants (K_a) are also calculated using the Benesi-Hildebrand method (Figs. 6 and 8). The resulting values are summarized in Tables 3 and 4. As shown, the ability of both receptors for recognition of Cu^{2+} metal ion is similar while the tendency of **1** for detection of Co^{2+} ion is higher than **2**.

Table 2: UV-vis spectra data upon titration of compound **1** with cations in DMSO

Ligand + cation	Ligand, λ_{max} (nm)	Complex, λ_{max} (nm)	Hypsochromic shift, $\Delta\lambda_{max}$ (nm)	K_a (M^{-1})
Ligand-Cu^{2+}	558	503	−55	4.085×10^4
Ligand-Co^{2+}	558	525	−33	2.309×10^4

Table 3: UV-vis spectra data upon titration of compound **2** with cations in DMSO

Ligand + cation	Ligand, λ_{max} (nm)	Complex, λ_{max} (nm)	Hypsochromic shift, $\Delta\lambda_{max}$ (nm)	K_a (M^{-1})
Ligand-Cu^{2+}	549	497	−52	1.143×10^5
Ligand-Co^{2+}	549	537	−12	1.067×10^5

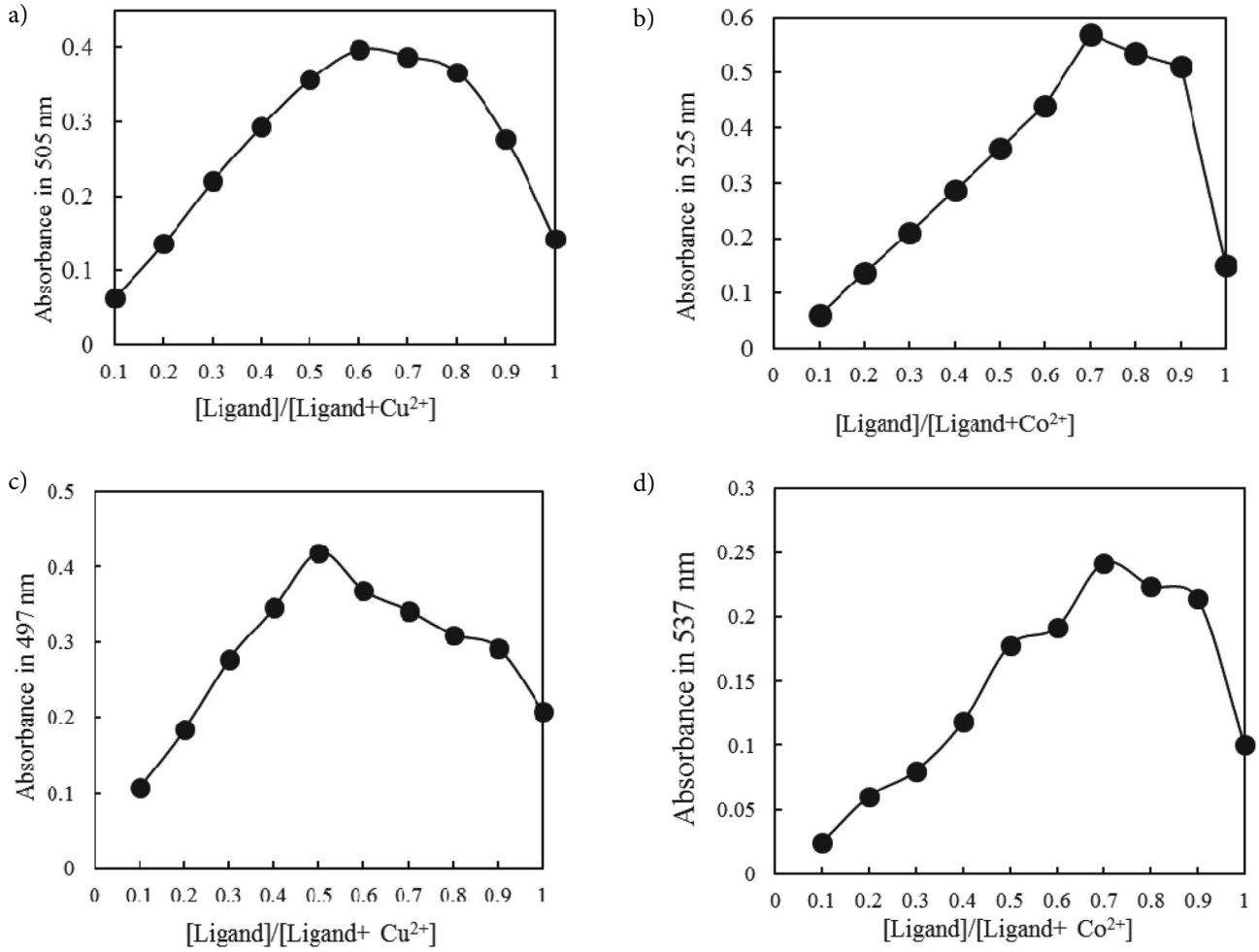
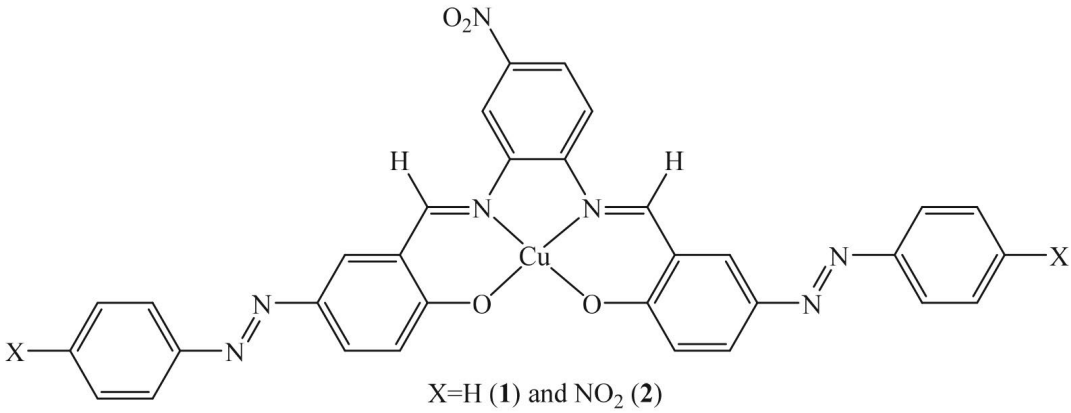


Fig. 9. Job plots for ligand **1** with Cu^{2+} (a) and Co^{2+}(b) and ligand **2** with Cu^{2+} (c) and Co^{2+} (d), where the absorptions are plotted against the mole fractions of ligands at an invariant total concentration of 2×10^{-5} M in DMSO.



Scheme 4. Suggested structure for ligands with Cu^{2+}

4. Conclusion

At first new azo-azomethin derivative **1** was synthesized and characterized with some standard methods. Then the optical response of azo units of the synthesized compound was investigated for detection of some divalent metal ions by spectrophotometry technique. In the next step, the results of cation recognition by 1,2-[1-(3-imino-4-hydroxophenylazobenzene)]-4-nitrobenzene (**1**) was compared with 1,2-[1-(3-imino-4-hydroxophenylazo-4-nitrobenzene)]-4-nitrobenzene (**2**) (the only difference of

between two structures is the existence of nitro groups at the *para* positions of azo units in **2**). Study revealed the ability of both receptors for recognition of Cu^{2+} metal ion to be similar while the tendency of **1** for detection of Co^{2+} ion is higher than **2** (the binding constant of **1** with copper and cobalt ions is larger than **2**). Also, the investigation of solvent effect in the UV-vis spectra shows that the generation of hydrazine and enaminone tautomers increase in highly polar solvents such as DMF and DMSO. Moreover, the investigation of antioxidant activity of ligands with DPPH method indicates NO_2 withdrawing groups in compound **2** probably affect keto–enol equilibrium. As a result, ligand **2** strongly reduced free radicals to non-reactive species while compound **1** showed low activity.

5. Appendix

FT-IR and ^{1}H NMR spectra of compounds **1** and **2** are available in Appendix.

6. Acknowledgments

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7. References

1. H. Dincalp, F. Toker, I. Durucasu, N. Avcibasi, S. Icli, *Dyes Pig.* **2007**, *75*, 11–24. **DOI:**10.1016/j.dyepig.2006.05.015
2. E. Gungor, S. Celen, D. Azaz, H. Kara, *Spectrochim. Acta A.* **2012**, *94*, 216–221. **DOI:**10.1016/j.saa.2012.03.034
3. S. A. Hudson, P. M. Maitlis, *Chem. Rev*. **1993**, *93*, 861–885. **DOI:**10.1021/cr00019a002
4. A. Halve, A Goyal, *Orient. J. Chem*. **2001**, *12*, 87–88.
5. E. H. Saffa, D. M. Etaiw, E. A. Abd**,** H. A. E. Z. Eman, A. A. Elham, *Spectrochim. Acta A*. **2011**, *79*, 1331–1337. **DOI:**10.1016/j.saa.2011.04.064
6. V. E. Kuzmin , V. P. Lozitsky, G. L. Kamalov, R. N. Lozitskaya, A. I. Zheltvay, A. S. Fedtchouk , D. N. Kryzhanovsky, *Acta Biochim. Pol.* **2000**, *47*, 867–875.
7. G. Ceyhan, M. Kose, M. Tumer, I. Demirtas, A. S. Yağlioğlu, V. McKee, *J. Lumin*. **2013**, *143*, 623–634. **DOI:**10.1016/j.jlumin.2013.06.002
8. M. Sarigul, P. Deveci, M. Kose, U. Arslan, T. H. Dagi, M. Kurtoglu, *J. Mol. Struct*. **2015**, *1096*, 64–73. **DOI:**10.1016/j.molstruc.2015.04.043
9. D. Mahata, S. M. Mandal, R. Bharti, V. K. Gupta, M. Mandal, A. Nag, G. B. Nando, *Int. J. Biol. Macromol.* **2014**, *69*, 5–11. **DOI:**10.1016/j.ijbiomac.2014.05.017
10. S. N. Pandeya, D. Sriram, G. Nath, E. DeClercq, *Eur. J. Pharm. Sci.* **1999**, *9*, 25–31. **DOI:**10.1016/S0928-0987(99)00038-X
11. D. Das, N. Sahu, S. Mondal, S, Roy, P. Dutta, S. Gupta, T. K. Mondal, C. Sinha, *Polyhedron***, 2015**, *99*, 77–86. **DOI:**10.1016/j.poly.2015.06.027
12. M. Sarigul, A. Sari, M. Kose, V. McKee, M. Elmastas, I. Demirtas, M. Kurtoglu, *Inorg. Chim. Acta*. **2016**, *444*, 166–175. **DOI:**10.1016/j.ica.2016.01.042
13. C. Anitha, C. D. Sheela, P. Tharmaraj, S. Sumathi, *Spectrochim. Acta A*. **2012**, *96*, 493–500. **DOI:**10.1016/j.saa.2012.05.053
14. M. Al-Noaimi, A. Hammoudeh, M. El-khateeb, F. F. Awwadi, D. Taher, A. Mansi, O. S. Abdel-Rahman, *Inorg. Chim. Acta.* **2017**, *454*, 222–228. **DOI:**10.1016/j.ica.2016.04.029
15. V. Reena, S. Suganya, S. Velmathi, *J. Fluor. Chem*. **2013**, *153*, 89–95. **DOI:**10.1016/j.jfluchem.2013.05.010
16. A. K. Mahapatra, S. K. Manna, P. Sahoo, *Talanta***, 2011**, *85*, 2673–2680. **DOI:**10.1016/j.talanta.2011.08.040
17. M. Orojloo, S. Amani, *Talanta***, 2016***, 159*, 292–299. **DOI:**10.1016/j.talanta.2016.06.042
18. N. Kaur, S. Kumar, *Tetrahedron*, **2011***, 67*, 9233–9264. **DOI:**10.1016/j.tet.2011.09.003
19. E. L. Que, D. W. Domaille, C. Chang, *J. Chem. Rev*. **2008**, *108*, 1517–1549. **DOI:**10.1021/cr078203u
20. D. Pramanik, C. Ghosh, S. G. Dey, *J. Am. Chem. Soc*. **2011**, *133*, 15545–15552. **DOI:**10.1021/ja204628b
21. A. Shahat, M. Awual, M. Naushad, *Chem. Eng. J*. **2015**, *271,* 155–163. **DOI:**10.1016/j.cej.2015.02.097
22. J. Cheng, L. Yang, X. Zeng, H. D. Zhao, D. Tian, *Sens. Actuators B*. **2016***, 237*, 495–500. **DOI:**10.1016/j.snb.2016.06.106
23. G. Wang, H. Chen, Y. Chen, N. Fu, *Sens. Actuators B*. **2016***, 233*, 550–558. **DOI:**10.1016/j.snb.2016.04.119
24. B. Shaabani, Z. Shaghaghi, A. A. Khandar, *Spectrochim. Acta A*. **2012**, *98*, 81–85. **DOI:**10.1016/j.saa.2012.07.097
25. Z. Shaghaghi, *Spectrochim. Acta A*. **2014**, *131*, 67–71. **DOI:**10.1016/j.saa.2014.04.026
26. A. A. Khandar, Z. Rezvani, *Polyhedron* **1999**, *18*, 129–133. **DOI:**10.1016/S0277-5387(98)00275-7
27. K. Hamidian, M. Irandoust, E. Rafiee, M. Joshaghani, *Z. Naturforsch*. **2012**, *57b*, 159–164.
28. G. Dehghan, Z. Khoshkam, *Food Chem***. 2012**, *131*, 422–426. **DOI:**10.1016/j.foodchem.2011.08.074
29. A. A. H. Kadhum, A. A. Al-Amiery, A. Y. Musa, A. B. Mohamad, *Int. J. Mol. Sci*. **2011**, *12*, 5747–5761. **DOI:**10.3390/ijms12095747
30. K. T. Smith, S. C. Young, G. W. DeBlasio, C. S. Hamann, *J. Chem. Educ*. **2016**, *93*, 790–794. **DOI:**10.1021/acs.jchemed.5b00170
31. A. Arab Ahmadi, S. Amani, *Molecules***, 2012**, *17*, 6434–6448. **DOI:**10.3390/molecules17066434
32. H. Galen, G. Hennrich, J. D. Mendoza, P. Prados, *Eur. J. Org. Chem*. **2010**, 1249–1297. **DOI:**10.1002/ejoc.200901394
33. A. Kakanejadifard, F. Azarbani, A. Zabardasti, A. Rezayat, M. Ghasemian, S. Kakanejadifard, *Spectrochim. Acta A*. **2013**, *114*, 404–409. **DOI:**10.1016/j.saa.2013.05.027
34. M. Ghasemian, A. Kakanejadifard, F. Azarbani, A. Zabardasti, S. Kakanejadifard. *Spectrochim. Acta A*. **2014**, *124*, 153–158. **DOI:**10.1016/j.saa.2014.01.005
35. G. Kurtoglu, B. Avar, H. Zengin, M. Kose, K. Sayin, M. Kurtoglu, *J. Mol. Liquids* **2014**, *200*, 105–114.

DOI:10.1016/j.molliq.2014.10.012
36. M. Ghasemiana, A. Kakanejadifarda, F. Azarbani, A. Zabardasti, S. Shirali, Z. Saki, S. Kakanejadifard, *Spectrochim. Acta A*. **2015**, *138*, 643–647. **DOI:**10.1016/j.saa.2014.11.048
37. H. Khanmohammadi, M. Pass, K. Rezaeian, G. Talei, *J. Mol. Struct*. **2014**, *1072*, 232–237. **DOI:**10.1016/j.molstruc.2014.05.014
38. H. Khanmohammadi, A. Abdollahi, *Dyes Pigm*. **2012**, *94*, 163–168. **DOI:**10.1016/j.dyepig.2011.12.013
39. T. H. Kim, S. H. Kim, L. V. Tan, Y. G. Seo, S. Y. Park, H. Kim, J. S. Kim, *Talanta***, 2007**, *71*, 1294–1297. **DOI:**10.1016/j.talanta.2006.06.035
40. Y. Dong, T. H. Kim, H. J. Kim, M. H. Lee, S. Y. Lee, R. K. Mahajan, H. Kim, J. S. Kim, *J. Electroanal. Chem*. **2009**, *628*, 119–124. **DOI:**10.1016/j.jelechem.2009.01.015
41. T. H. Kim, S. H. Kim, L. Y. Tan, Y. Dong, H. Kim, J. S. Kim, *Talanta*, **2008**, *74,* 1654–1658. **DOI:**10.1016/j.talanta.2007.10.033
42. T. L. Kao, C. C. Wang, Y. T. Pan, Y. J. Shiao, J. Y. Yen, C. M. Shu, G. H. Lee, S. M. Peng, W. S. Chung, *J. Org. Chem*. **2005**, *70*, 2912–2920. **DOI:**10.1021/jo047880a

Povzetek

Glede na uporabo azo-azometinov v kemijskih senzorjih in zaradi njihove biološke aktivnosti smo raziskovali dva receptorja, 1,2-[1-(3-imino-4-hidroksofenilazobenzen)]-4-nitrobenzen (**1**) in 1,2-[1-(3-imino-4-hidroksofenilazo-4-nitrobenzen)]-4-nitrobenzen (**2**) za detekcijo nikljevih, kobaltovih, bakrovih, svinčevih, živosrebrovih, cinkovih in kadmijevih dvovalentnih ionov z UV-vis spektroskopijo. Z dodatkom kovinskih ionov v raztopino ligandov v DMSO se vrhovom pri 558 in 549 nm poveča intenziteta s hipokromnim ali batokromnim premikom, razen v primeru Zn^{2+} iona in **2**, medtem ko se vrhovom pri 388 in 391 nm znatno zmanjša intenziteta. V obeh primerih se po dodatku bakrovih ionov pojavi največji premik. V raztopinah oba receptorja povzročita premik vrhov pri 558 in 549 nm na 503 in 497 nm z zaznavno barvno spremembo raztopin od vijolično-rdeče do oranžne barve. Obe spojini zelo dobro zaznavata bakrove ione v raztopini DMSO. V naslednjem koraku smo uporabili Benesi-Hildebrandove diagrame in Jobovo metodo za določanje konstant stabilnosti (K_a) in stehiometrije nastalih kompleksov. Proučevanje vpliva topil na UV-vis spektre ligandov kaže, da je pri polarnih topilih, kot sta DMF in DMSO, večji delež hidrazinskega in enaminonskega tautomera. Nadalje smo določili antioksidativno aktivnost ligandov z metodo DPPH. Rezultati kažejo, da NO_2 elektronakceptorske skupine na 1,2-[1-(3-imino-4-hidroksofenilazo-4-nitrobenzen)]-4-nitrobenzenu verjetno vplivajo na keto-enol ravnotežje. Rezultat tega je, da ligand pretvori proste radikale v nereaktivne zvrsti z doniranjem vodika.