

Selective detection of Cu²⁺ and Co²⁺ in aqueous media: Asymmetric chemosensors, crystal structure and spectroscopic studies

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abstract

Two new azo-azomethine receptors, H₂L¹ and H₂L², containing hydrazine, naphthalene and different electron withdrawing groups, Cl and NO₂, have been designed and synthesized for qualitative and quantitative detection of Cu²⁺ and Co²⁺ in aqueous media. The crystal structure of H₂L¹ is reported. The H₂L¹ was used as a chemosensor for selective detection of trace amount of Cu²⁺ in aqueous media. H₂L² was also applied to naked-eye distinction of Cu²⁺ and Co²⁺ from other transition metal ions in aqueous media. Detection limit of Cu²⁺ is 1.13 μM and 1.26 μM, in water, for H₂L¹ and H₂L², respectively, which are lower than the World Health Organization (WHO) recommended level. The binuclear Cu²⁺ and Co²⁺ complexes of the receptors have been also prepared and characterized using spectroscopic methods and MALDI-TOF mass analysis. Furthermore, the binding stoichiometry between the receptors upon the addition Cu²⁺ and Co²⁺ has been investigated using Job's plot. Moreover, the fluorescence emission spectra of the receptors and their metal complexes are also reported.

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1. Introduction

Heretofore, many techniques were used for detection of metal ions such as atomic absorption spectrometry, flow injection, fluorescence, electrochemical and voltammetry which are very complicated, drowsy sample preparations and required expensive instrumentation [1–3]. In the recent years, design and development of colorimetric chemosensors for specific and also naked eye detection of various transition metal ions are increasingly attended [4–6]. Among transition metal ions, cobalt plays important roles in biological systems [7]. It is vital trace element of vitamin B12 and very necessary for fatty acid metabolism [8]. However, cobalt is also acutely toxic in excess dosage and even long-time contact at a low level could cause harmful communicable diseases [9]. By the same token, copper plays a critical role in many environmental, fundamental physiological processes, biological and chemical systems [10]. Anyway, under overloading conditions copper is closely connected with neurodegenerative diseases [11]. Therefore, the demand for rapid detection of copper and cobalt ions, at lower concentration, has significant applications in environment and biological systems.

So far, a great number of receptors have been designed and suggested for selective detection of Cu²⁺ and Co²⁺ ions in organic media [12–15]. Consequently, in the recent years much attention has been paid to design of new chemosensors for recognizing and suitable monitoring of Cu²⁺ and Co²⁺ ions, with high sensitivity and low cost, in

aqueous media [16–18]. However azo-azomethine cations sensors are scarcely reported.

Accordingly, we have developed design and synthesis of two new asymmetric azo-azomethine receptors, H₂L¹ and H₂L², by condensation reaction of azo-coupled salicylaldehyde derivatives with 1-(hydrazonomethyl)naphthalene-2-ol (Scheme 1), for colorimetric detection of Cu²⁺ and Co²⁺ ions in aqueous media. The crystal structure of H₂L¹ was determined by single-crystal X-ray diffraction. H₂L¹ contains azo phenol and naphthalene-2-ol moieties serving as sensing units to selective detection of Cu²⁺, below than 1.13 μM, in aqueous media. On the other hand, H₂L² is able to recognize Cu²⁺ and Co²⁺ in aqueous media below than 1.26 μM and 2.45 μM, respectively. The binuclear Copper(II) and Cobalt(II) complexes of H₂L¹ and H₂L² were also prepared. The MALDI-TOF mass analysis of the complexes indicated that the stoichiometry, in solid state, was found to be 1:1. Furthermore, Job's method was used to define the stoichiometry of complexes in THF/Tris-HCl buffer (9:1). Moreover, the ability of the receptors towards Cu²⁺ and Co²⁺ has been investigated qualitatively. The fluorescence emission spectra of H₂L¹ and H₂L² in THF/Tris-HCl buffer (9:1, v/v) were also studied during titration with Cu²⁺ and Co²⁺ ions.

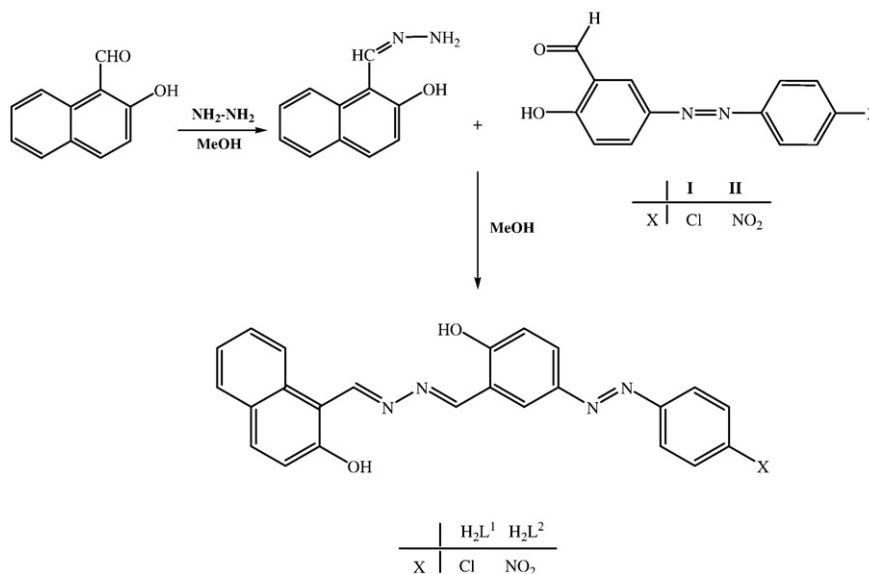
2. Experimental

2.1. Materials

All of the reagents and solvents involved in synthesis were of analytically grade and used as received without further purification. All

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Scheme 1. Synthesis of receptors H_2L^1 and H_2L^2 .

chemicals were purchased from Sigma-Aldrich and Merck. 1-(Hydrazonomethyl)naphthalene-2-ol and azo-coupled salicylaldehyde precursor, I and II, were prepared according to the well-known literature procedure [19–21].

2.2. Instrumentation

The structure of H_2L^1 and H_2L^2 was confirmed by 1H NMR spectra, recorded on Bruker AV 300 MHz spectrometers. FT-IR spectra were recorded, as pressed KBr discs, using Thermo scientific AVATAR 330 spectrophotometer in the region of 400–4000 cm^{-1} . Electronic spectral measurements were carried out using Optizen 3220 UV spectrophotometer in the range of 200–900 nm. Fluorescence measures were taken in a NanoLog TM-Horiba JobinYvon iHR320 spectrophotometer. Irradiation of the samples was taken with an ASAHIMAX 303 Xenon lamp. C.H.N. analyses were done at the CCiT-UB and Vario EL III elemental analyser. Positive and negative ion ESI analyses and MALDI-TOF were collected at the Unitat d'Espectrometria de Masses (SSR) of the University of Barcelona.

2.3. X-ray Crystal Structure Determination

Single-crystal diffraction data for H_2L^1 were collected on a Bruker APEXII SMART diffractometer at the Facultat de Química, Universitat de Barcelona, using a microfocus Molybdenum Ka radiation source. The structure was solved by direct method (SHELX-97) [22] and refined on F2 (SHELX-97). Crystallographic information file can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC 1514295, <http://www.ccdc.cam.ac.uk/>).

2.4. General Procedure for the Synthesis of Azo-azomethine Sensors, H_2L^1 , H_2L^2

A solution of 1-(hydrazonomethyl)naphthalene-2-ol (1 mmol) in MeOH (30 mL) was added to a stirring solution of azo-coupled precursors, (1 mmol) in MeOH (60 mL) during a period of 10 min at 50 °C. The mixture was heated in water bath over night at 60 °C and then filtered while hot. The obtained solid was washed with hot methanol (three times), diethyl ether and then dried in air (Scheme 1).

2.4.1. 1-(((5-((4-chlorophenyl)diazanyl)-2-hydroxybenzylidene)hydrazono)methyl)naphthalene-2-ol, H_2L^1

Yield: 69%, m. p. 268–269 °C. IR (KBr, cm^{-1}): 3447(\overline{OH}), 1624($C_{=N}$), 1579(phenol ring), 1470($N_{=N}$), 1281(\overline{NO}), 1187, 835 and 746. 1H NMR (300 MHz, DMSO- d_6 , ppm): δ 9.94(s, 1H), 9.18(s, 1H), 8.64(d, 1H, $J = 8.40$ Hz), 8.39(d, 1H, $J = 2.80$ Hz), 8.04(d, 1H, $J = 9.20$ Hz), 8.01(dd, 1H, $J = 8.80$ Hz and 2.8 Hz), 7.90(m, 3H), 7.65(d, 2H, $J = 8.80$ Hz), 7.62(t, 1H, $J = 7.20$ Hz), 7.45(t, 1H, $J = 7.20$ Hz), 7.28(d, 1H, $J = 9.20$ Hz), 7.22(d, 1H, $J = 8.80$ Hz). λ_{max} (nm) (ϵ ($M^{-1} cm^{-1}$)): 329 (38450) and 388 (40050) in THF. MS (ESI) $m/z = 429.11$ [$M + H$] $^+$.

2.4.2. 1-(((5-((4-nitrophenyl)diazanyl)-2-hydroxybenzylidene)hydrazono)methyl)naphthalene-2-ol, H_2L^2

Yield: 47% (0.56 g), m. p. 281–282 °C. IR (KBr, cm^{-1}): 3421(\overline{OH}), 1626 ($C_{=N}$), 1582 (phenol ring), 1517(NO_2), 1487($N_{=N}$), 1339(NO_2), 1282(\overline{NO}), 1109, 856 and 739. 1H NMR (300 MHz, DMSO- d_6 , ppm): δ 9.94(s, 1H), 9.18(s, 1H), 8.64(d, 1H, $J = 8.51$ Hz),

Table 1

Tentative assignments of some selected IR* frequencies (cm^{-1}) and UV–Vis data of the prepared azo-azomethine receptors, azo precursors and binuclear complexes.

Compounds	$\nu(\overline{NO})$	$\nu(C_{=O})$	$\nu(C_{=C})$	$\nu(C_{=N})$	$\nu(NO_2)$	$\nu(N_{=N})$	λ_{max} (nm) (ϵ ($M^{-1} cm^{-1}$))
I	1286	1668	1622	–	–	1477	246 (4500), 382 (12700), 551 (1850) in DMSO
II	1288	1666	1608	–	1525, 1346	1479	256 (6490), 410 (7850), 466 (9345) in DMSO
H_2L^1	1281	–	1579	1624	–	1470	329 (38450) and 388 (40050) in THF
H_2L^2	1282	–	1582	1626	1517, 1339	1487	340 (31250), 390 (36700) in THF
$[(CuL^1)_2]$	1315	–	1577	1614	–	1469	–
$[(CuL^2)_2]$	1369	–	–	1609	1522, 1339	1465	–
$[(CoL^1)_2]$	1300	–	1535	1601	–	1454	–
$[(CoL^2)_2]$	1353	–	–	1600	1517, 1339	1452	–

* KBr discs.

8.48(d, 1H, $J=2.01$ Hz), 8.43(d, 2H, $J=8.95$ Hz), 8.06 (m, 4H), 7.92(d, 1H, $J=8.0$ Hz), 7.61(t, 1H, $J=7.20$ Hz), 7.43(t, 1H, $J=7.20$ Hz), 7.26(m, 2H). λ_{\max} (nm)(ϵ ($M^{-1} \text{ cm}^{-1}$)): 340(31250) and 390(36700) in THF. MS (ESI) $m/z = 438.13$ [M - H]⁺.

2.5. General Procedure for Preparation of Metal Complexes

A solution of the ligand (1 mmol) in chloroform and acetonitrile (v/v, 40/60) (20 mL), at room temperature, was treated with $MCl_2 \cdot xH_2O$ (1 mmol, $M = Cu$ ($x = 2$), $M = Co$ ($x = 6$)) in CH_3CN (10 mL). Three equivalents of Et_3N were added to the mixture. The mixture was heated in water bath for 16 h at 70 °C. After this a precipitate was formed that collected by vacuum filtration, washed with CH_3CN and anhydrous diethyl ether. The resulted product was dried at room temperature.

2.5.1. [(CuL¹)₂]

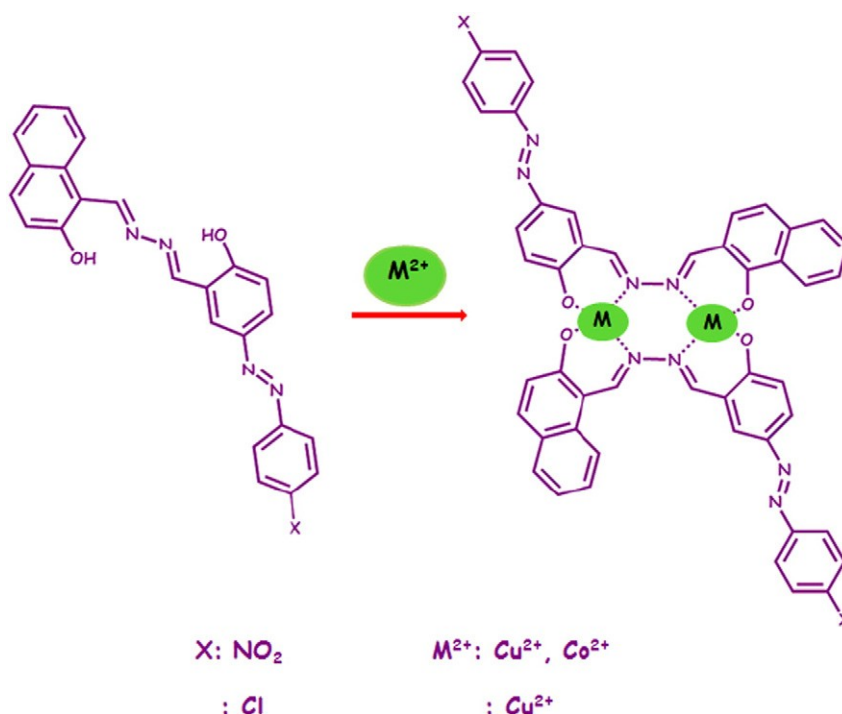
Yield: 45%. m.p. 263–265 °C. IR (KBr, cm^{-1}); 1614(C₋N), 1577(phenol ring), 1469(N₋N), 1315(C₋N=O), 1186, 833, 745, 676, and 530. Anal. Calcd. for [(C₄₈H₃₀Cl₂Cu₂N₈O₄). 2H₂O]: C, 56.80; N, 11.05; H, 3.38. Found: C, 57.34; N, 11.71; H, 3.63%. MW (C₄₈H₃₀Cl₂Cu₂N₈O₄) = 978.0, $m/z = 981.10$.

2.5.2. [(CuL²)₂]

Yield: 70%. m.p. 294–295 °C. IR (KBr, cm^{-1}); 1609(C₋N), 1522(NO₂), 1465(N₋N), 1369(C₋N=O), 1339(NO₂), 1104, 852, 747 and 578. Anal. Calcd. for [C₄₈H₃₀N₁₀O₈Cu₂]. 6H₂O: C, 56.57; N, 13.75; H, 3.16. Found: C, 57.10; N, 13.76; H, 2.94%. MW (C₄₈H₃₀Cu₂N₁₀O₈) = 1000.01, $m/z = 1000.90$.

2.5.3. [(CoL¹)₂]

Yield: 67%. m.p. N 300 °C. IR (KBr, cm^{-1}); 1601(C₋N), 1535(phenol ring), 1454(N₋N), 1300(C₋N=O), 1111, 831 and 744. Anal. Calcd. for (C₄₈H₃₀Co₂Cl₂N₈O₄). 6H₂O: C, 53.43; N, 10.39; H, 3.93. Found: C, 53.13; N, 10.85; H, 3.72%.



Scheme 2. Proposed structure of binuclear complexes, [(MLⁿ)₂] (M = Cu, Co and n = 1, 2).

Table 2

Crystallographic and data collection parameters for receptor H₂L¹.

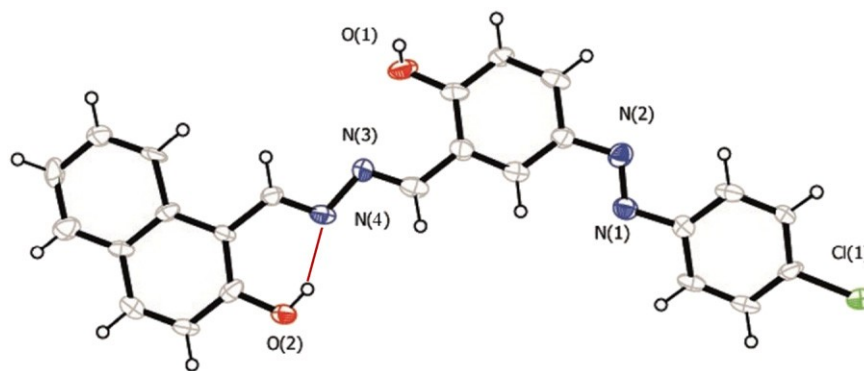
Molecular formula	C ₂₄ H ₁₇ ClN ₄ O ₂
Formula weight	428.10
Temperature, K	100(2)
Crystal system	Monoclinic
Space group	P2 ₁ /c
a, Å	8.8017(14)
b, Å	6.4862(17)
c, Å	34.581(7)
α °	90
β °	95.528(12)
γ °	90
V, Å ³	1965.0(7)
Z	4
Radiation	MoK α
Gof on F ²	1.074
Final R indexes [I N = 2 σ (I)]	R ₁ = 0.065, wR ₂ = 0.1839
Final R indexes [all data]	R ₁ = 0.158, wR ₂ = 0.1338
Formula weight	428.87
T _{min} , T _{max}	0.595, 0.745
Index ranges	-34 ≤ h ≤ 31 -6 ≤ k ≤ 4 -8 ≤ l ≤ 8
F(000)	888

2.5.4. [(CoL²)₂]

Yield: 71%. m.p. N 300 °C. IR (KBr, cm^{-1}); 1600(C₋N), 1517(NO₂), 1452(N₋N), 1353(C₋N=O), 1339(NO₂), 1100, 852 and 739. Anal. Calcd. for (C₄₈H₃₀Co₂N₁₀O₈). 6H₂O: C, 52.35; N, 12.72; H, 3.84. Found: C, 51.83; N, 12.33; H, 3.09%. MW (C₄₈H₃₀Co₂N₁₀O₈) = 992.10, $m/z = 991.90$.

3. Results and Discussion

Two new azo-azomethine receptors containing hydrazine and naphthalene active sites, 1-(3-formyl-4-hydroxyphenylazo)-4-chlorobenzene (H₂L¹) and 1-(3-formyl-4-hydroxyphenylazo)-4-nitrobenzene (H₂L²), have been designed and synthesized via condensation

Fig. 1. Crystal structure of the receptor H_2L^1 .

reaction of 1-(hydrazonomethyl)naphthalene-2-ol with azo-coupled salicylaldehyde precursors and in CH_3OH (Scheme 1). The receptors were characterized using standard spectroscopic techniques (Supporting materials). The total absence of $\nu(C=O)$ absorption band of azo-coupled salicylaldehyde precursors in the IR spectra of H_2L^1 and H_2L^2 together with the appearance of a new absorption band at 1624 cm^{-1} and 1626 cm^{-1} , respectively, obviously indicate that the Schiff-bases have formed, Table 1. Also, the infrared spectrum of H_2L^2 exhibits strong bands at 1339 and 1517 cm^{-1} assigned to the NO_2 group [23]. In the 1H NMR spectra of H_2L^1 and H_2L^2 , the $CH-N$ protons exhibit two singlet resonance at 9.94 and 9.18 ppm. The presence of a slightly broad and also a broad signal at ca. 12.90 ppm and ca.

11.80 ppm, assigned to the OH protons, as was confirmed by deuterium exchange when D_2O was added to $DMSO-d_6$ solution of H_2L^1 and H_2L^2 (Supporting materials). Furthermore, the molecular ion peaks observed at $m/z = 428.1$ and 438.1 confirm the formation of H_2L^1 and H_2L^2 , respectively.

H_2L^1 and H_2L^2 have been used to prepare binuclear Copper(II) and Cobalt(II) complexes, $[(ML)_2]$ ($M = Cu, Co$ and $n = 1.2$). All complexes have been characterized using FT-IR, UV-Vis spectroscopes, elemental analysis and MALDI-TOF mass analysis (Supporting materials).

The $\nu(C-N)$ in the infrared spectra of complexes are red-shifted by $12-24\text{ cm}^{-1}$ from that of the free receptors. Notwithstanding, the $\nu(C=O)$ (phenolic) in IR spectra of the complexes are blue-shifted by

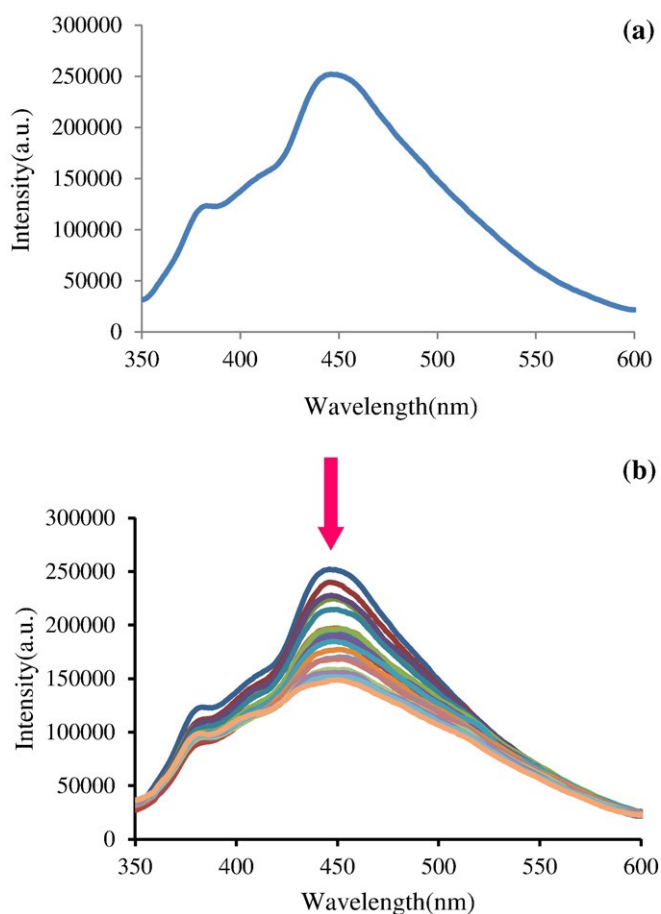


Fig. 2. (a) Fluorescence spectrum of H_2L^1 ($2 \times 10^{-5}\text{ mol L}^{-1}$) in THF/Tris-HCl buffer (9:1, v/v, pH = 7.0). (b) Fluorescence spectrum of H_2L^1 in the presence of different concentration of Cu^{2+} (0–4 equiv.) in THF/Tris-HCl buffer (9:1, v/v, pH = 7.0). The excitation wavelength: 340 nm and the emission wavelength: 443 nm .

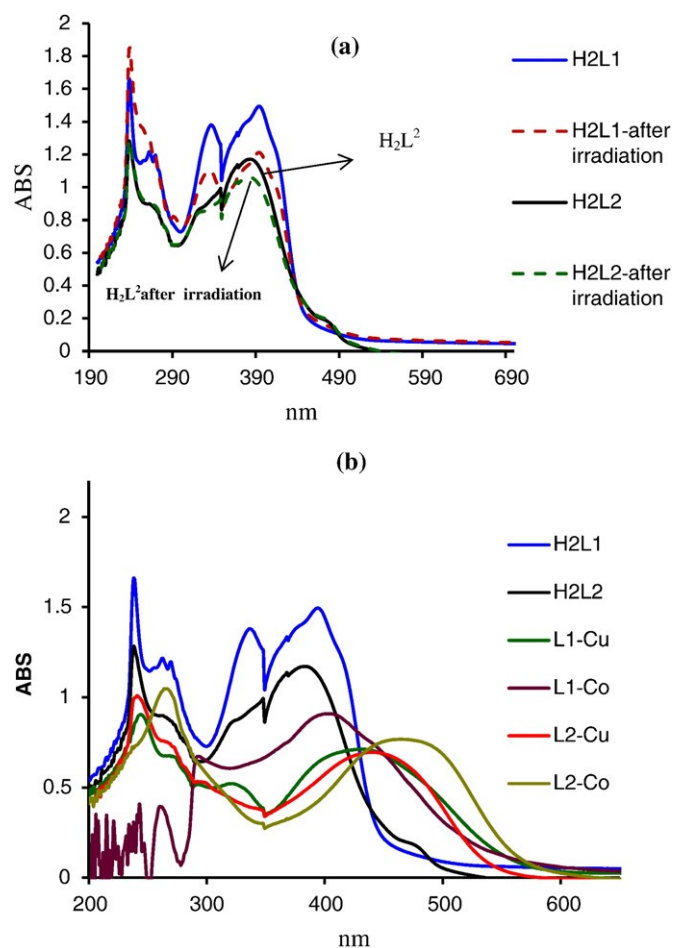


Fig. 3. (a) Electronic spectra of the receptors, H_2L^1 and H_2L^2 , in THF before and after irradiation with 435 and 425 nm radiation, respectively. (b) UV-Vis spectra of Cu^{2+} and Co^{2+} complexes of H_2L^1 and H_2L^2 .

33–80 cm^{-1} from that of the free receptors which is in agreement with the phenolato-O single bonded to metal ions. These can be ascribed to the withdrawal of electron density from the nitrogen atom owing to coordination. However, attempts to prepare suitable crystals of binuclear complexes were unsuccessful. The proposed structure of the prepared complexes is given in Scheme 2 which is also in accordance with data from the MALDI-TOF mass analysis (Supporting materials).

3.1. X-ray Crystal Structure

Suitable crystals for single-crystal X-ray diffraction were grown from concentrated acetonitrile solution by slow evaporation at room

temperature. Data collection and crystallographic parameters for H_2L^1 can be found in Table 2. The organic compound crystallizes in monoclinic the space group $P2_1/c$. The crystal structure is shown in Fig. 1. The crystal structure shows a delocalized organic compound that is nearly planar. The two $\text{N}=\text{N}$ bonds can be clearly distinguished due to the difference in bond distance. The azo double $\text{N1}_-\text{N2}$ bond has a bond distance of 1.261 Å, while the single bond $\text{N3}=\text{N4}$ has a bond distance of 1.417 Å, both in agreement with the expected value for the bond order. N3 and N4 are part of the two Schiff base units of the ligand and the C_-N distances are in agreement with a carbon-nitrogen double bond (1.274 and 1.282 Å respectively). The crystal structure of H_2L^1 is in agreement with the proposed structure for the ligand based on NMR, MS and IR.

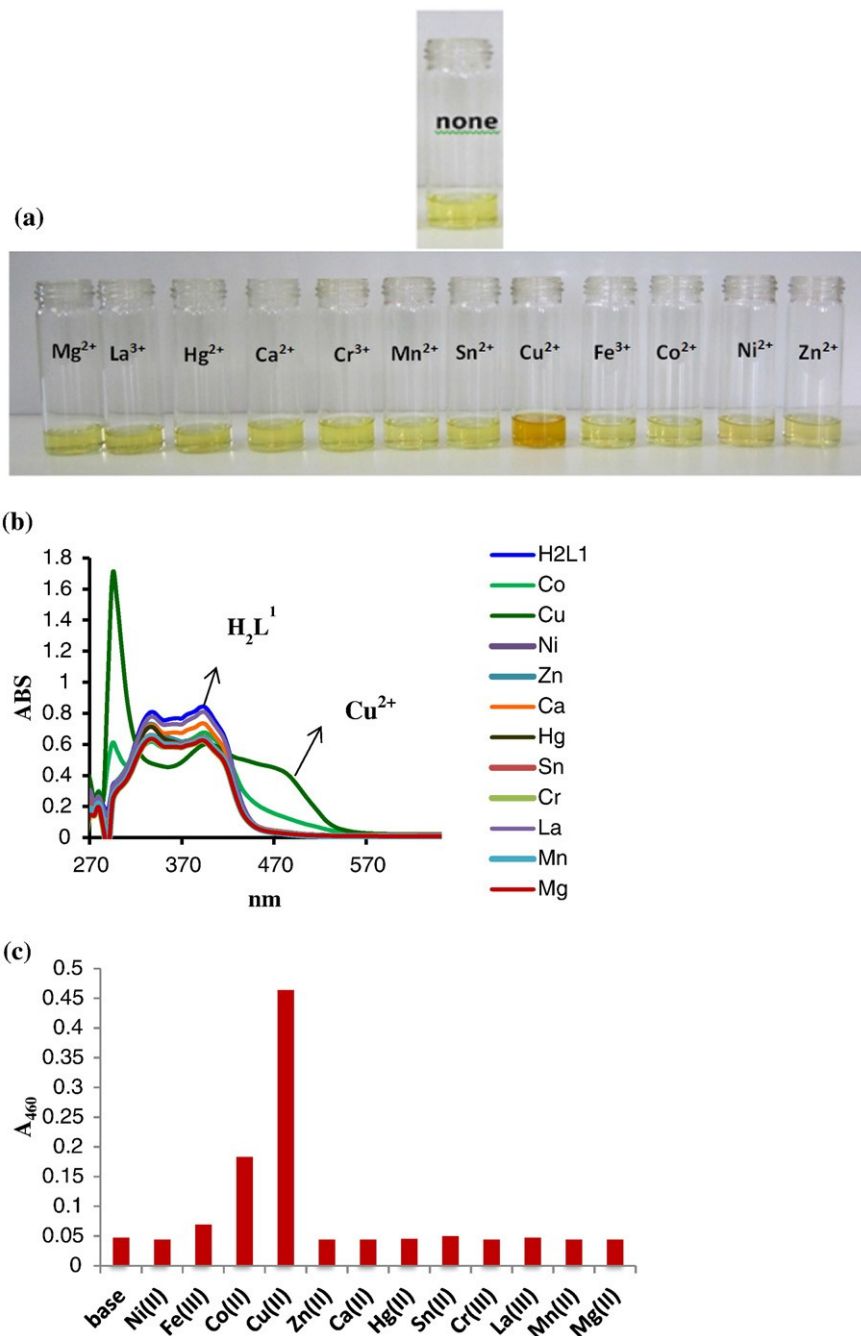


Fig. 4. (a) Color changes of sensor H_2L^1 in THF/Tris-HCl buffer (9:1, v/v, pH = 7.0) after addition of 10 equiv. of various metal ions. From left to right: Mg^{2+} , La^{3+} , Hg^{2+} , Ca^{2+} , Co^{2+} , Cr^{3+} , Mn^{2+} , Sn^{2+} , Cu^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Zn^{2+} . (b) UV-Vis absorption spectra of H_2L^1 (2×10^{-5} mol L^{-1} in THF/Tris-HCl buffer) in the presence of 10 equiv. of various metal ions. (c) Ratiometric absorbance changes (460 nm band) of UV-Vis spectrum of H_2L^1 in the presence of various metal ions.

3.2. Fluorescence Study of the Receptors

The fluorescence emission spectra of H_2L^1 and H_2L^2 (2×10^{-5} mol L^{-1}) in THF/Tris-HCl buffer (9:1, v/v, pH = 7.0) were studied during titration with Cu^{2+} and Co^{2+} ions. As shown in Fig. 2 the fluorescence emission of the free receptors appear at ca. 450 and ca. 550 nm, after emitted with 340 nm and 400 nm excitation wavelengths, for H_2L^1 and H_2L^2 , respectively (Supporting materials). The fluorescent titration showed that the emission bands intensity of the receptors reduced upon gradual addition of Cu^{2+} and Co^{2+} , indicating quenching phenomena during metal complex formation [24] (Supporting materials). Actually, delocalization of π electrons, redox-activity and

also electron energy transfer was changed after complex formation with Cu^{2+} and Co^{2+} ions [25].

3.3. Electronic Spectra of the Receptors and their Capability for Metal Ion Recognition

The electronic absorption spectra of the H_2L^1 and H_2L^2 , recorded in THF at room temperature, display mainly three bands. The first UV band located at 275–285 nm can be assigned to the moderate energy ($\pi \rightarrow \pi^*$) transition of the aromatic rings while the second band at ca. 340 nm is due to low energy ($\pi \rightarrow \pi^*$) transition involving the π -electrons of the chromophore groups. The band located at ca. 390 nm

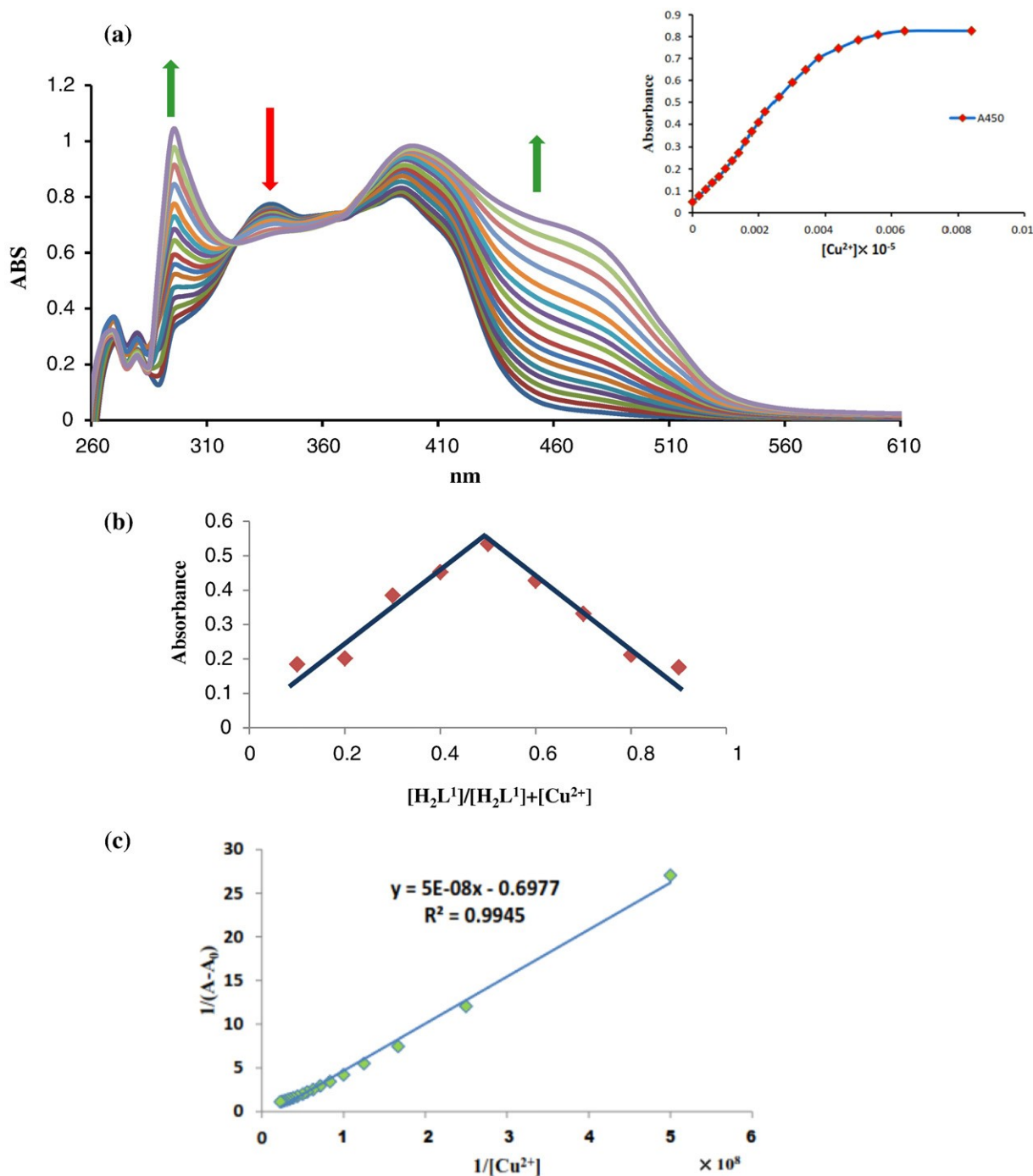


Fig. 5. (a) UV-Vis spectra of H_2L^1 (2×10^{-5} mol L^{-1}) in THF/Tris-HCl buffer (9:1, v/v, pH = 7.0) upon the addition of increasing amounts of Cu^{2+} ion (0–4 equiv.). (b) Benesi-Hildebrand plot of receptor H_2L^1 binding with Cu^{2+} associated with absorbance change at 450 nm. (c) Job's plot of H_2L^2 with Cu^{2+} .

corresponding to the charge transfer transitions involving whole molecules of the prepared receptors [26]. The absorption changes of electronic spectra of the receptor solution upon photo irradiation were examined at room temperature. Upon this, a solution ($2 \times 10^{-5} \text{ mol L}^{-1}$ in THF) of H_2L^1 and H_2L^2 were irradiated with 435 and 425 nm radiation. As shown in Fig. 3(a), interconversion between *cis* and *trans* isomers and also changes in position of the bands should not occur in H_2L^1 and H_2L^2 under this condition [27].

In the other hand, when the receptors coordinated to Cu^{2+} and Co^{2+} , the 335 nm and 395 nm bands mixed, collapsed and bathochromic shifted to 410–420 nm and 450–480 nm for metal complexes of H_2L^1 and H_2L^2 , respectively, Fig. 3(b).

The sensing ability of H_2L^1 towards various metal cations (Co^{2+} , Ni^{2+} , Cu^{2+} , Hg^{2+} , Ca^{2+} , Zn^{2+} , Sn^{2+} , Cr^{3+} , La^{3+} , Mn^{2+} and Mg^{2+} as their chloride salts), has been investigated qualitatively by visual examination of the cation-induced color changes of the receptor in THF/Tris-HCl buffer (9:1, v/v, pH = 7.0). Upon the addition of 10 equiv. of cations, in water, to the solution of H_2L^1 ($2 \times 10^{-5} \text{ mol L}^{-1}$) only in the presence of Cu^{2+} , a vivid color change was observed drastically, Fig. 4(a). However, in the presence of other cations no obvious color changes were observed. Furthermore, to provide fundamental insights about sensing ability of H_2L^1 , the cation recognition behavior of the current receptor

was explored using UV–Vis spectroscopy upon the addition of 10 equiv. of various cations to H_2L^1 , Fig. 4(b). A distinct change was observed in the spectral pattern of free receptor in the presence of Cu^{2+} . In the other word, the addition of Cu^{2+} to H_2L^1 gave a bathochromic shift to ca. 450 nm Fig. 4(c). while other cations induced negligible spectral changes.

Moreover, in order to get quantitative insights into H_2L^1 -Cu interaction, sensing mechanism and also study of absorption spectra changes, the spectrophotometric titration experiment was carried out. For this purpose, absorption spectra changes were probed after gradually addition of different concentrations of Cu^{2+} (0–4 equiv.) to a solution of H_2L^1 ($2 \times 10^{-5} \text{ mol L}^{-1}$) in THF/Tris-HCl buffer (9:1, v/v, pH = 7.0). As shown in Fig. 5(a), the addition of Cu^{2+} caused gradual decrease in intensity of the band at 340 nm, and increase in intensity of the band at ca. 290 and a new absorption band, attributed to the charge transfer (CT), was formed simultaneously at ca. 450 nm. Two isosbestic points were observed at 325 and 375 nm which the later point is not clear, may be due to long reaction time [28].

Plotting of $1/(A - A_0)$, which A and A_0 are the absorbance of H_2L^1 in the presence and absence of Cu^{2+} , versus $1/[\text{Cu}^{2+}]$ showed a linear relationship, Fig. 5(b), which indicates that H_2L^1 bound with Cu^{2+} in a 1:1 binding stoichiometry. The 1:1 stoichiometry

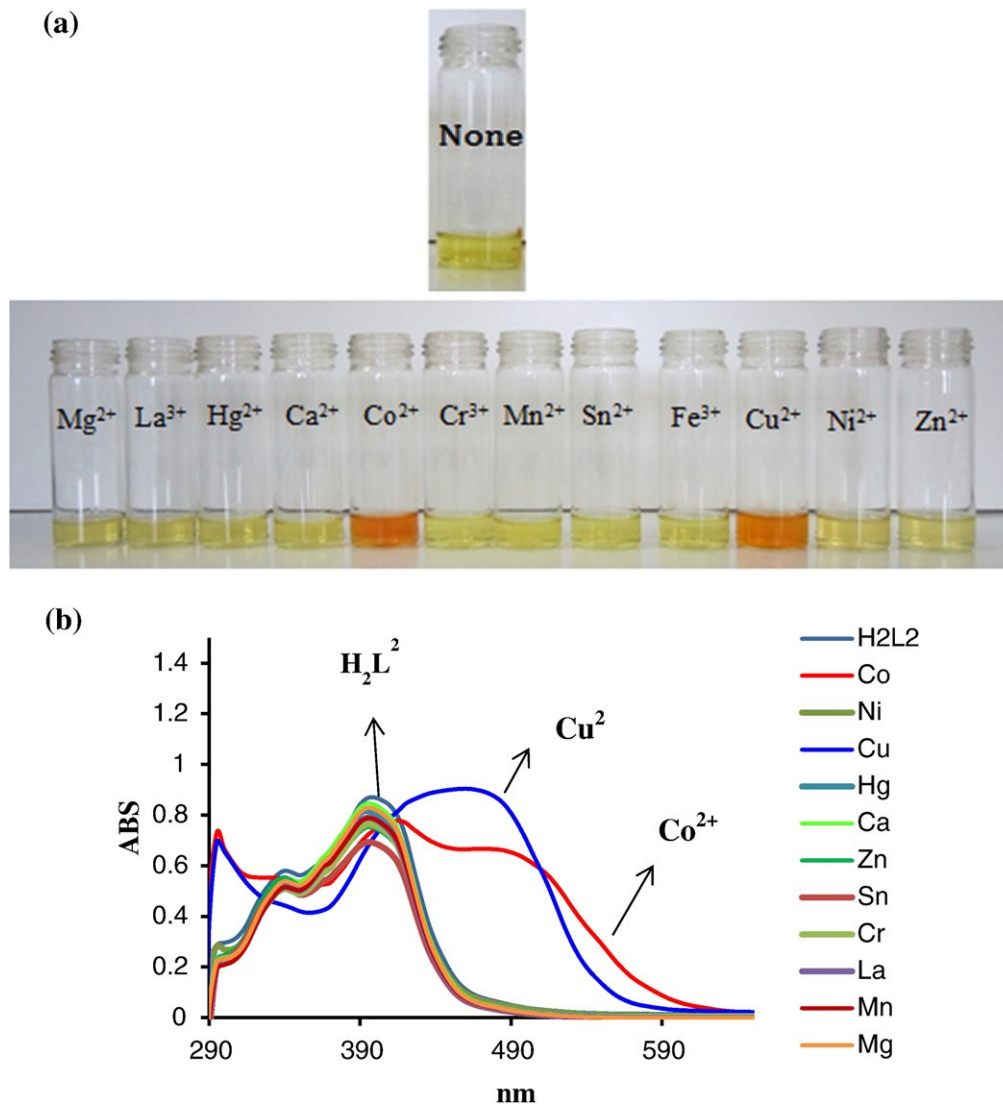


Fig. 6. (a) Color changes of sensor H_2L^2 ($2 \times 10^{-5} \text{ mol L}^{-1}$ in THF/Tris-HCl buffer (9:1, v/v, pH = 7.0)) after addition of 10 equiv. of various cations. From left to right: Mg^{2+} , La^{3+} , Hg^{2+} , Ca^{2+} , Co^{2+} , Cr^{3+} , Mn^{2+} , Sn^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} and Zn^{2+} . (b) UV–Vis spectra of H_2L^2 ($2 \times 10^{-5} \text{ mol L}^{-1}$ in THF/Tris-HCl buffer (9:1, v/v)) in the presence of 10 equiv. of various metal ions.

was also accepted by Job's plot, Fig. 5(c). The binding constant, K_a , as obtained from Benesi-Hildebrand eq. [29], is $1.42 \times 10^7 \text{ M}^{-1}$. The detection limit of H_2L^1 for Cu^{2+} ion was calculated from the UV-Vis titration experiment using the formula $(3\delta/\kappa)$ is $1.13 \times 10^{-6} \text{ mol L}^{-1}$. δ represents the standard deviation of the 15 blank the receptor solution, κ represents the value of slope obtained from the plot of graph as shown in the Fig. S17 (ESI). Remarkably, LOD value is lower than the World Health Organization (WHO) recommended level (below $30 \mu\text{M}$) for safe drinking water [30].

The cation sensing capability of H_2L^2 was also checked. As an initial experiment, the color changes of H_2L^2 , in THF/Tris-HCl buffer, upon the addition of 10 equiv. of various metal cations were tested. As

shown in Fig. 6(a), a remarkable color change was observed from light yellow to orange in the presence of Cu^{2+} and Co^{2+} . To validate these initial qualitative studies, UV-Vis absorption experiments were also executed upon the addition of 10 equiv. of chloride salts of various metal cations to H_2L^2 solution. A distinct change was observed in the spectral pattern of free H_2L^2 in the presence of Cu^{2+} and Co^{2+} whereas the spectral changes in the presence of other cations were negligible, Fig. 6(b).

Moreover, in order to get better understanding about the sensing mechanism of H_2L^2 , the changes in absorption spectra were probed after gradual addition of different concentrations of Cu^{2+} (0–4 equiv.) and Co^{2+} (0–6 equiv.) to a solution of H_2L^2 ($2 \times 10^{-5} \text{ mol L}^{-1}$) in THF/Tris-HCl buffer (9:1, v/v). As shown in Fig. 7(a) intensity of the

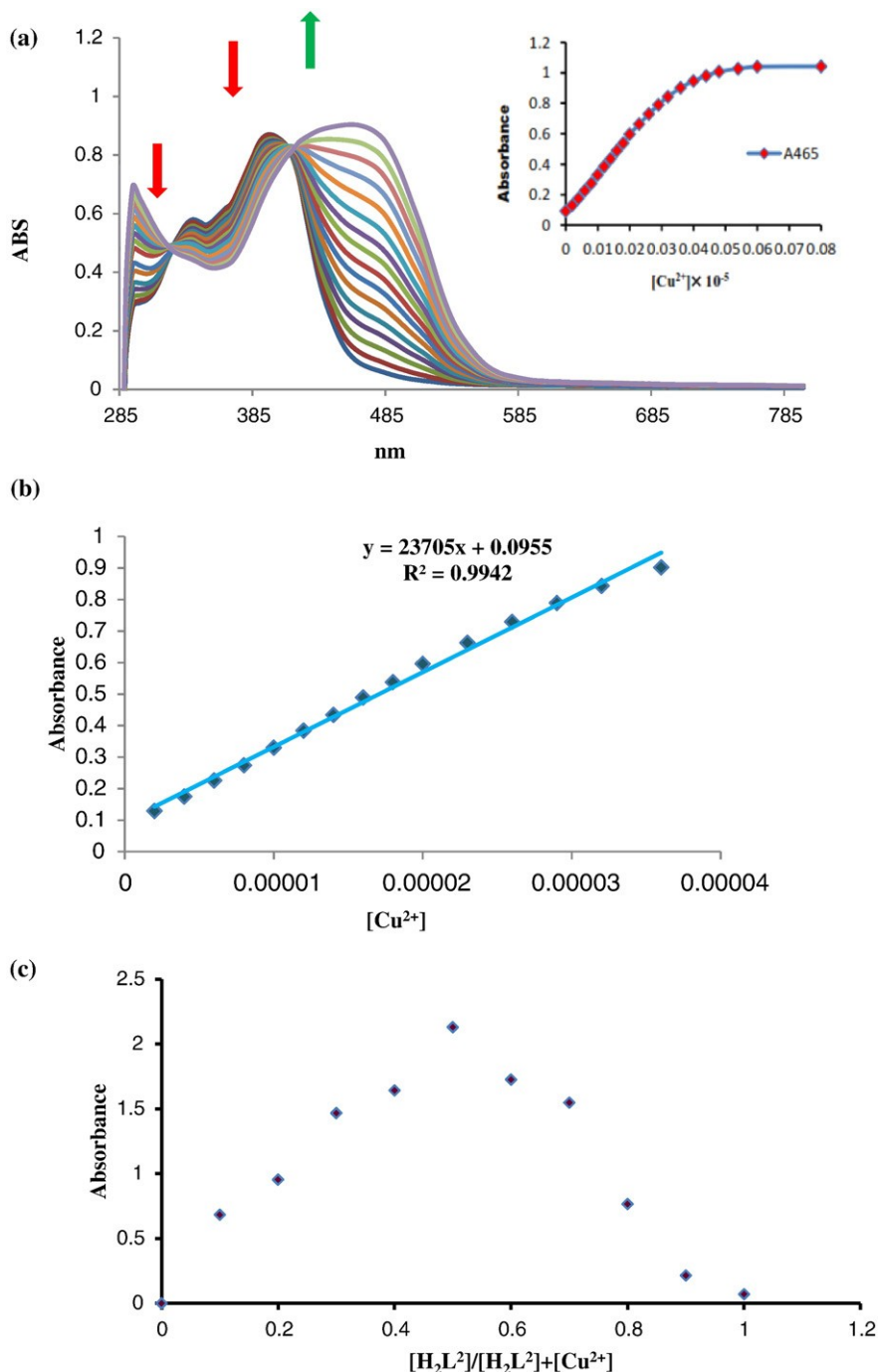


Fig. 7. (a) UV-Vis spectra of H_2L^2 ($2 \times 10^{-5} \text{ mol L}^{-1}$) in THF/Tris-HCl buffer (9:1, v/v), upon the addition of increasing amounts of Cu^{2+} ion (0–4 equiv.). (b) Plot for determination of LOD for Cu^{2+} in the presence of H_2L^2 (c) Job's plot of H_2L^2 with Cu^{2+} .

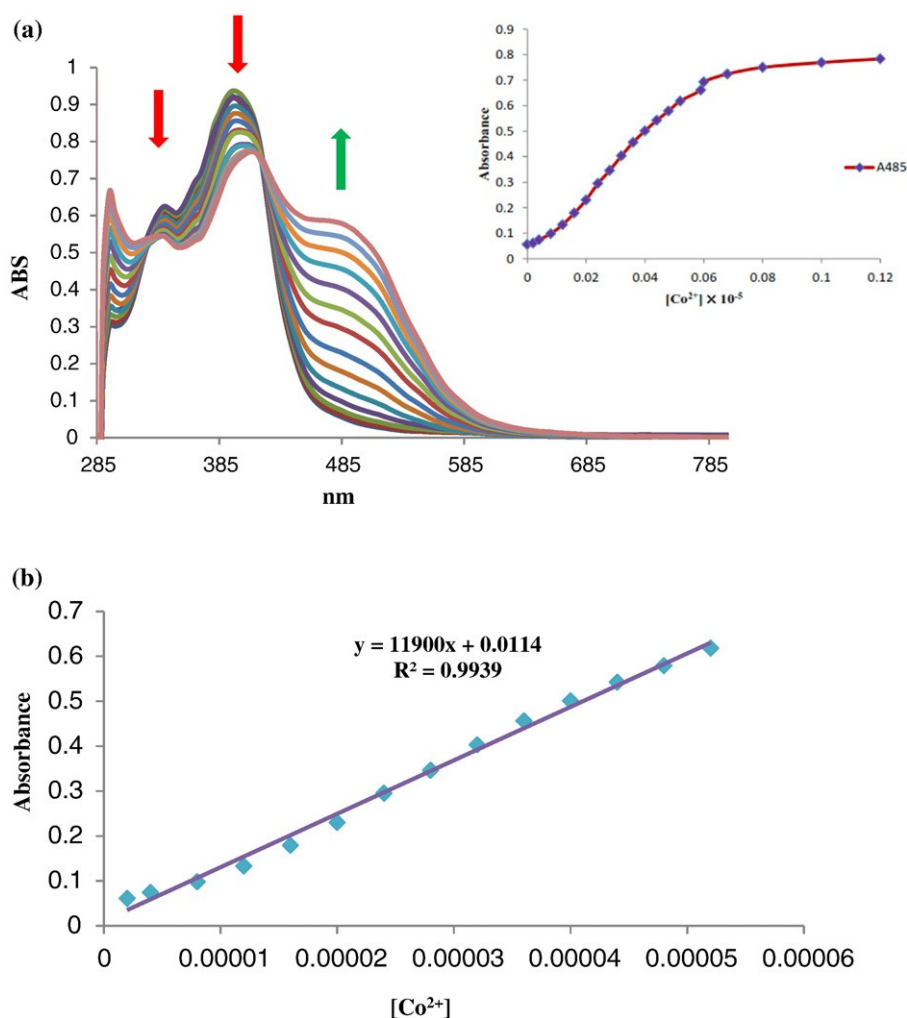


Fig. 8. (a) Changes of UV-Vis spectrum of H_2L^2 (2×10^{-5} mol L^{-1}) in THF/Tris-HCl buffer (9:1, v/v) upon the addition of increasing amounts of Co^{2+} ion (0–10 equiv.) (b) Plot for determination of LOD for Co^{2+} in the presence of H_2L^2 .

band at 340 nm, after addition of Cu^{2+} , decreased gradually and simultaneously a new strong absorption band, attributed to the charge transfer (CT), was formed at ca. 460 nm representative interaction between Cu^{2+} and H_2L^2 .

To investigate the stoichiometry between H_2L^2 and Cu^{2+} ion, both Benesi–Hildebrand plot [29] and Job's plot experiments were carried out. The result indicated that H_2L^2 bound with Cu^{2+} in a 1:1 binding stoichiometry, Fig. 7(a). The binding constant, K_a , between H_2L^2 and Cu^{2+} ion was 2.105×10^7 M^{-1} (Supporting materials). The detection limit of Cu^{2+} in aqueous solution was defined to be 1.26×10^{-6} mol L^{-1} , Fig. 7(b).

Upon the addition of Co^{2+} to the H_2L^2 in THF/Tris-HCl buffer (9:1, v/v), a new band appeared at ca. 485 nm, attributed to the charge transfer (CT), and band at 400 nm slightly decreased and red-shifted of about 15 nm, Fig. 8(a). The Benesi–Hildebrand and also Job's experiments were carried out which indicate that H_2L^2 bound with Co^{2+} in a 1:1 binding stoichiometry. The binding constant, K_a , between H_2L^2 and Co^{2+} ion was 4.580×10^6 M^{-1} (Supporting materials). The detection limit of Co^{2+} ion in aqueous solution was defined to be 2.45×10^{-6} mol L^{-1} , Fig. 8(b).

4. Conclusion

In summary, we have prepared two new asymmetric azo-azomethine receptors, H_2L^1 and H_2L^2 . The receptors have been

thoroughly characterized using spectroscopic techniques. The crystal structure of H_2L^1 is also reported. H_2L^1 and H_2L^2 were applied to visual detection of Cu^{2+} and Co^{2+} , with high selectivity and sensitivity, in aqueous media. The Cu^{2+} sensing, by H_2L^1 , as well as Cu^{2+} and Co^{2+} sensing, by H_2L^2 , with high value of binding constants and 1:1 binding stoichiometry are also supported by UV-Vis. Detection limits of Cu^{2+} and Co^{2+} in aqueous media are lower than the World Health Organization (WHO) recommended level for safe drinking water. Furthermore, the binuclear Copper(II) and Cobalt(II) complexes of the receptors have been prepared and characterized using spectroscopic methods and MALDI-TOF mass analysis.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.saa.2017.02.017>.

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