



Aggoun Djouhra, Ourari Ali, Ruiz-Rosas Ramiro, Morallon Emilia

PII: S1386-1425(17)30389-X
 DOI: doi: [10.1016/j.saa.2017.05.022](https://doi.org/10.1016/j.saa.2017.05.022)
 Reference: SAA 15164

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received date: 26 December 2016
Revised date: 6 May 2017
Accepted date: 9 May 2017

Please cite this article as: Aggoun Djouhra, Ourari Ali, Ruiz-Rosas Ramiro, Morallon Emilia , A selective naked-eye chemosensor derived from 2-methoxybenzylamine and 2,3-dihydroxybenzaldehyde - synthesis, spectral characterization and electrochemistry of its bis-bidentates Schiff bases metal complexes, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2017), doi: [10.1016/j.saa.2017.05.022](https://doi.org/10.1016/j.saa.2017.05.022)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

A Selective Naked-Eye Chemosensor Derived From 2-Methoxybenzylamine and 2,3-Dihydroxybenzaldehyde - Synthesis, Spectral Characterization and Electrochemistry of its Bis-Bidentates Schiff bases Metal complexes

AGGOUN Djouhra^{1,2*}, OURARI Ali¹, RUIZ-ROSAS Ramiro³, MORALLON Emilia⁴

¹Laboratoire d'Electrochimie, d'Ingénierie Moléculaire et de Catalyse Redox (LEIMCR), Faculté de Technologie, Université Ferhat ABBAS de Sétif-1, Sétif 19000- Algeria.

²Département de chimie, faculté des sciences, Université Ferhat ABBAS de Sétif-1, Sétif 19000- Algeria,

³Departamento de Química Inorgánica, Instituto Universitario de Materiales, Universidad de Alicante, Ap. 99. E-03080 Alicante, Spain.

⁴Departamento de Química Física, Instituto Universitario de Materiales, Universidad de Alicante, Ap. 99. E-03080 Alicante, Spain.

Abstract

A new colorimetric receptor **HL**, acting as a bidentate Schiff base ligand, has been synthesized by condensation of 2-methoxybenzylamine on 2,3-dihydroxybenzaldehyde in a methanolic solution. Interestingly, this chelating agent can selectively detect **Cu²⁺**, **Co²⁺**, **Fe²⁺** and **Fe³⁺** ions with a simple and an easy-to-make, well defined naked-eye visible color changes in two different solvents like acetonitrile and methanol. This bidentate ligand coordinates three metal ions of Co(II), Cu(II) and Fe(II) via nitrogen and oxygen atoms. The molecular structures of the synthesized compounds were elucidated by various physicochemical properties such as the elemental analysis, FT-IR, ¹HNMR, UV-Vis and the Mass spectrometry. The resulting general formulae [M(L)₂·H₂O] (M(II) = Cu, Fe, Co) are proposed as mononuclear complexes. The solvatochromism properties of these compounds were studied with their absorption spectra using different solvents as methanol (**MeOH**), acetonitrile (**AN**), tetrahydrofuran (**THF**), dimethylformamid (**DMF**), dimethylsulfoxid (**DMSO**) and dichloromethane (**DC**). The Electrochemical behavior of copper complex was explored in DMF solutions by cyclic voltammetry (**CV**) with two working electrodes: glassy carbon (**GC**) and platinum electrode (**Pt**). This study reveals that copper complex shows successively two redox systems as **Cu^{III/II}** and **Cu^{III/I}**. The **Fe^{III/II}** and **Co^{III/I}** redox systems have also been studied in DMF and DMSO media.

Keywords: N,O donors; Spectral studies; Colorimetric sensor; Solvatochromic behavior; Transition metal complexes; Cyclic voltammetry.

- Corresponding author. Tel: +213.697.78.81.45; E-mail addresses: aggoun81@yahoo.fr
- (Dj. AGGOUN).

1. Introduction

The Schiff base ligands proved to be an important class of the chelating agents as far as the coordination chemistry is concerned, and this is mainly due to their easy synthesis, electronic properties and the tendency to form stable complexes with most of the transition metals [1-4]. These properties attract a large number of applications like those involved in the analytical chemistry field [5]. They can even serve as electrochemical catalysts [6] either in homogeneous or heterogeneous catalysis for alkanes oxidation, alkenes epoxidation [7], sensors [8] and corrosions inhibitors [9] as well.

Colorimetric sensors have attracted much attention to allow a “naked-eye” detection in an uncomplicated and an inexpensive manner so as to offer qualitative and quantitative information. During the last couple of decades, there have been numerous works which focused on the design and the synthesis of the artificial receptors based on this kind of Schiff base chelates [10]. The aim was to detect selectively and efficiently diverse cations or anions [11,12]. In fact, the colorimetric chemosensors of cations can be generated basically through the right combination of a receptor and a chromophore. Consequently, these chemosensors have been widely investigated for their fundamental role in environmental, analytical and biological applications [13-15]. As a consequence, the designing and the synthesizing chemosensors that can detect certain metal ions such as the bivalent ones : Ni^{2+} , Cu^{2+} , Mg^{2+} , Hg^{2+} , Mn^{2+} , Co^{2+} [16-21], or the trivalent cations such as Fe^{3+} , Mn^{3+} and Al^{3+} [22,23] with high selectivity and sensitivity were induced by most studies in the literature. This research attracts both university and industry researchers.

The coordination chemistry of metal(II) complexes via the use of the bidentate Schiff base ligands has been thoroughly investigated during the last years, especially in the oxidation reactions [24]. It has always been a subject of considerable attention due to its various properties. A large number of copper complexes with such ligands has been prepared and characterized for their involvement in several applications [25].

Therefore, in the present work, we report the synthesis and isolation of novel mononuclear metal(II) complexes that were derived from a bidentate Schiff base ligand. These compounds have been characterized by ^1H NMR, FT-IR, a Mass spectrometry, an Elemental analysis and an UV-Vis spectrophotometry. Moreover, the colorimetric sensing characteristics of the corresponding

synthesized receptor (**HL**) were investigated through the use of an UV–Vis absorption spectrophotometry in organic solutions at the expense of the presence of different metal ions such as Co^{2+} and Cu^{2+} , Fe^{3+} and Fe^{2+} . Furthermore, the cyclic voltammetric behavior has also been reported and discussed using two different working electrodes in two different media. The synthetic route of the Schiff base precursor (**HL**) and its Cu(II), Fe(II) and Co(II) Schiff base complexes is outlined in the following **Scheme 1**.

«Insert Scheme 1»

2. Experimental

2.1. Physicochemical characterization

All solvents and chemicals are of reagent grade and were used as received. The solutions of metal ions were prepared from their salts $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, FeCl_3 , CdCl_2 , $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , $\text{Al}(\text{NO}_3)_3$, BaCl_2 , CaCl_2 , LiCl , KCl , NaCl , PbCl_2 .

The ^1H NMR spectra were recorded on a Bruker AC300 Y 400 at 25 °C using tetramethylsilane (TMS) as an internal reference. All chemical shifts ^1H are given in ppm using deuterated DMSO- d_6 as solvent. While the FT-IR spectra were recorded on a Perkin Elmer 1000-FT-IR Spectrometer using KBr disks and electronic spectra (UV–Vis) were obtained with a Unicam UV-300 Spectrophotometer having 1 cm path length cell. The Elemental analysis was performed using a (C, N, H, S) LECO analyser (Micro TruSpec model). As for the experimental description of mass spectrometry, we have employed a HPLC Agilent 1100 series coupled to UV-Vis and MS with ionic trap detector (Agilent model 1100 Series LC/MSD Trap SL).

The Cyclic voltammetry was performed on Voltalab 40, Potentiostat–Galvanostat equipment. All measurements were carried out in a 5cm³ Metrohm single compartment cell with three conventional electrodes. The employed working electrodes are GC (3 mm) or Pt (2 mm). They were polished with a diamond paste and thoroughly rinsed with large amounts of acetone and finally with acetonitrile. The counter electrode was a platinum (Pt) wire and the potentials refer to the Saturated Calomel Electrode (SCE). DMF and DMSO solutions were used with 10^{−3} M of Schiff base metal complexes and their ionic strength was maintained at 10^{−1} M with tetra-*n*-butylammonium perchlorate (TBAP).

2.2. Synthesis of the Schiff base receptor ligand (HL)

138 mg of 2,3-dihydroxybenzaldehyde (1 mmol) were dissolved in methanol (10 mL) and stirred at a room temperature. Then, this solution was added drop-wise to 10 mL of methanol containing 137 mg (1 mmol) of 2-methoxybenzylamine. This mixture is held under stirring until it turns into yellow color which indicates that the Schiff base is formed. The solution was stirred again for 2 hours at a room temperature producing a yellow to an orange colored precipitate. The obtained precipitate was filtered off, washed with cold methanol and diethylether, and then dried under vacuum. The expected compound **HL** was obtained with yield of 90%.

HL: $^1\text{H NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 8.85 and 13.75 (s, 2H, O-H), 8.59 (s, 1H, N=CH), 6.50–7.50 (m, 7H, Ar-H), 4.76 (s, 2H, Ph-CH₂), 3.83 (s, 3H, methoxy O-CH₃). $\text{C}_{15}\text{H}_{15}\text{NO}_3$ (**HL**): calcd. C 70.02, H 5.88, N 5.44; found C 69.82, H 5.55, N 5.45. **FT-IR** (KBr pellet, cm^{-1}): 3350–3650 (br, O-H, phenolic), 2800–3100 (w, C-H aliphatic and aromatic), 1644 (s, C=N), 1240 (m, C-O). (**MS-LC**): (m/z) 257.2 ($[\text{HL}]^+$).

2.3. Synthesis of the cobalt(II)-, copper(II)- and iron(II)-Schiff base complexes

Cobalt(II), copper(II) and iron(II) complexes were prepared by the same method. To a hot solution of 1 mmol of the appropriate acetate metal salt in 10 mL of methanol was slowly added under stirring to a solution of 2 mmol of **HL** dissolved 10 mL of methanol. This mixture was heated to reflux with stirring for 4 hours. The resulting metal (II) complex was isolated by a simple addition of petroleum ether that led to the formation of precipitate which can easily be recovered by filtration. After that, this complex was washed with small portions of cold methanol, and then with diethylether. As a result, the novel bis-bidentate Schiff base metal(II) complexes with their general formulae $[\text{M}^{\text{II}}(\text{L})_2 \cdot \text{H}_2\text{O}]$ and yields ranging from 75 to 85% were obtained. (L= bidentate Schiff base ligand) (**Scheme 1**).

$\text{Co}^{\text{II}}(\text{L})_2 \cdot \text{H}_2\text{O}$: Anal. Calc. for $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_7\text{Co}$: C 61.21; H 5.13; N 4.75 Found: C 61.22; H 4.29; N 4.13 %. **FT-IR** (KBr pellet, cm^{-1}): 3300–3700 (br, O-H, phenolic), 2800–3120 (w, C-H aliphatic and aromatic), 1628 (s, C=N), 1248 (m, C-O), [510-650] (m, Co-O), [410-510] (m, Co-N). (**MS-LC**): (m/z) 569.4 ($[\text{CoL}_2]^+$).

$\text{Cu}^{\text{II}}(\text{L})_2 \cdot \text{H}_2\text{O}$: Anal. Calc. for $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_7\text{Cu}$: C 60.65; H 5.09; N 4.72 Found: C 60.81; H 4.61; N 4.26 %. **FT-IR** (KBr pellet, cm^{-1}): 3300–3700 (br, O-H, phenolic), 2840–3100 (w, C-H aliphatic

and aromatic), 1627 (s, C=N), 1248 (m, C–O), [510-610] (m, Cu–O), [405-490] (m, Cu–N). (**MS-LC**): (m/z) = 576.1 ($[\text{CuL}_2]^+$).

Fe^{II}(L)₂·H₂O: Anal. Calc. for **C₃₀H₃₀N₂O₇Fe**: C 61.45; H 5.16; N 4.78 Found: C 61.53; H 4.81; N 4.51 %. **FT-IR (KBr pellet, cm⁻¹)**: 3300–3700 (br, O–H, phenolic), 2820–3100 (w, C–H aliphatic and aromatic), 1635 (s, C=N), 1256 (m, C–O), [510-590] (m, Fe–O), [400-510] (m, Fe–N). (**MS-LC**): (m/z) 568.3 ($[\text{FeL}_2]^+$).

3. Results and discussion

3.1. Chemistry

- The Schiff base **HL** (**Scheme 1**) was prepared by refluxing of equimolar amounts of 2-methoxybenzylamine and 2,3-dihydroxybenzaldehyde in methanolic solution. The resulting chelate which could be involved in the UV-Vis studies requires the knowledge of its dissolving properties in diverse solvents. Its molecular structure was obviously established by using FT-IR, ¹H NMR, mass spectrometry and CHN analysis. Therefore, the synthesized Schiff base ligand appears as soluble in common organic solvents such as AN, DC, THF, DMF, DMSO and MeOH. This compound was further used in the complexation reaction via the use of the following metal acetate salts: Co(CH₃COO)₂·4H₂O, Cu(CH₃COO)₂·H₂O and Fe(CH₃COO)₂. The ligand **HL** with its metal(II) complexes, formed in solution, were isolated pure from methanol in very good yields and they are of various colors. All these compounds are carefully soluble in different organic solvents such as in DMF, MeOH, THF, DC, AN and DMSO except the cobalt(II) complex which is only soluble in DMF and DMSO solvents. The characterization of these complexes was performed by elemental analysis, FT-IR, UV–Vis, mass spectrometry and cyclic voltammetry technique. The microanalysis (CHN) was found to be in good agreement with the proposed molecular formulae.

3.2. Spectroscopic properties

➤ *FT-IR spectra*

The bonding modes of the coordinated ligand with the metal ions were discussed and elucidated by comparison of FT-IR spectrum of the ligand (**HL**) with its metal complexes. As a

consequence, the FT-IR spectrum of this ligand exhibits three characteristic absorption bands. The first one as a broad band centered at 3450 cm^{-1} that attributed to the ν (OH) stretching vibration as the main characteristic bands. A strong and sharp band is also observed at 1644 cm^{-1} , which is assigned to ν (C=N) azomethine groups, while the last one, appears as stronger band at 1247 cm^{-1} is attributed to the ν (C-O) (**Fig. S1**) [26]. The infrared spectra of the metal complexes of copper, cobalt and iron display vibration bands in the $1625\text{--}1628\text{ cm}^{-1}$ range and all of them were ascribed to the ν (C=N) stretching frequencies of the azomethine groups. These frequencies shifted to the lower energy when they are compared to those of **HL**. This shifting confirms that the ligand (**HL**) is coordinated to the metal ions. Inversely, this behavior was as well observed for the ν (C-O) vibration bands which shift to higher energy. This is essentially due to the strengthening of the electronic density of this bond from coordination process with metallic ions [29]. In addition, the appearance of new bands observed at around $420\text{--}490\text{ cm}^{-1}$ and $510\text{--}570\text{ cm}^{-1}$ are assigned to ν (M-N) [27] and ν (M-O) [28] respectively. These results are in good accordance with the involvement of the both heteroatoms like nitrogen and oxygen (NO) in the coordination process. The presence of some vibration bands with their weak intensities, between 3100 and 2800 cm^{-1} , suggests the presence of ν (C-H) stretching vibrations of both aliphatic and aromatic entities. The synthesized compounds show also other bands in the regions of $1460\text{--}1490$, $1010\text{--}1050$ and $720\text{--}750\text{ cm}^{-1}$, currently assigned to the aliphatic moieties (CH_2 and CH_3) and phenyl ring vibrations namely those of bending modes in or out of plane.

➤ *Mass spectrometry analysis*

The molecular formula of the investigated compounds were confirmed by chromatography HPLC, coupled with mass spectrometry technique (LC-MS). The Mass spectrum of **HL** exhibits a molecular ion peak at m/z 258.0 (**Fig. S2**) confirming its proposed molecular structure. The m/z ratio of peak 122.0 refers to the $[\text{C}_8\text{H}_9\text{O}]^+$ ion. As for mass spectrum of Co(II) complex showed a molecular ion peak with m/z ratio equal 569.3 (57.7%). This ion represents the molecular weight of the expected compound. This intermediate, continuing its fragmentation pathway, leads to the formation of another fragment for which the m/z ratio 122.0 (16.6%) corresponds to the $[\text{C}_8\text{H}_9\text{O}]^+$ ion. The ion $[\text{L}]^+$ with m/z 256.1 and relative abundance of 100%, observed in this spectrum, seems to be very stable corresponding to a base peak.

The $[\text{Cu}^{\text{II}}(\text{L})_2]$ complex displayed also its molecular peak as ratio m/z 576.0 confirming the proposed molecular structure of the copper complex. Since the same ligand (L^+) is coordinated to the both complexes cobalt and copper, their fragmentation process let appear a peak with m/z 258.1 (100%) behaving also as base peak for the fragmentation pathway of the copper complex. Similar

results were also observed in the mass spectrum of the iron complex with its molecular peak at m/z 568.1 (86.5%) and the base peak at m/z 258.1 (100%). The resulting entities with this complex generate as well another peak m/z 122.0 suggesting the existence of similarities in both fragmentation modes as above observed for copper and cobalt complexes (**Fig. S2**).

➤ *Electronic spectra*

The electronic spectra of **HL** and its metal complexes were recorded using freshly prepared **DMF** solutions with 10^{-5} M of solute (**Fig. 1**). The main results obtained on their spectra are given below:

- The UV–Vis spectrum of the free ligand (**HL**) showed four absorption bands in the UV region (250–450 nm). The first, with high intensity band is observed at 270 nm. This absorption band, according the literature [30], may be attributed to the π - π^* transitions for which molecular orbitals, particularly those of aromatic moieties were involved in the intraligand charge transfer. The second absorption band at 303 nm may be assigned to the π - π^* transitions of the azomethine group C=N while, the third band at 335 nm is attributable to the n - π^* transitions, involved in the promotion of the antibonding electrons of nitrogen atom (C=N) [31]. As the last band, located at 428 nm, it can be ascribed to the intermolecular charge transfer from the solvent molecules to the antibonding orbitals of the OH bond (n - σ^* transitions) belonging to the salicylaldehyde moiety. This band is currently observed in O-hydroxylated Schiff bases [32].
- For the UV–Vis spectrum of the cobalt complex, three bands were observed. The first and the second, appearing respectively at 282 and 320 nm, are attributed to the electronic transitions π - π^* and n - π^* of the ligand as reported in the literature [33]. Whereas the third, located at 472 nm, it corresponds to the “soret band” commonly assigned to the interactions ligand–metal (CTLM) [34] expressing the charge transfer between ligand (L^-) and Co(II) ion.
- As for the absorption bands of π - π^* (282 nm) and n - π^* (382 nm) above mentioned for the ligand (**HL**), they were also observed at higher wavelengths suggesting a bathochromic effect as above noted for copper complex. This characteristic may be considered as a confirmation for the coordination of copper ion to the nitrogen atom of the azomethine groups.
- Regarding the spectrum of iron complex, it displays its main bands between 300 and 550 nm. The more intense of them was seen at 318 nm. This absorption band, raised from the electronic transition involved in the conjugate system of the ligand, may be associated to the C=N linkages (n - π^*). The weak band at 450 nm can also be attributed to the Ligand-Metal Charge Transfer (LMCT) transitions [35].

«Insert Figure 1»

➤ *Solvatochromism*

The values of the wavelengths, their intensities with their shape depend on the molecular structure of the studied compound and the nature of the used solvent. These changes reflect the physical interactions between molecules of solute and solvent that modify the energy difference ($\Delta E = h\nu$) between an excited and ground states. Accordingly, the remarkable change of the UV-Vis absorption can be induced by using different solvents and therefore, this may be considered as a solvatochromism phenomenon. Consequently, in order to explore the solvatochromism properties for our ligand with its copper and iron complexes. Their UV-Vis spectra were recorded in diverse media by using different solvents as methanol, acetonitrile, tetrahydrofuran, dimethylformamid, dimethylsulfoxid and dichloromethane (**Fig. S3**). The main differences resulting in the absorption maxima for our receptor ligand in various solvents are imputable to the nature of chromophores associated to their different polarities as summarized in **Table S1**. So, it can be concluded that the increase of the polarity of solvents induces neat shifts of the band maxima to higher energies. This is a characteristic of a polar ground state compared to a non-polar excited state [36].

3.3. *Electrochemical properties*

The cyclic voltametric studies of the Co(II), Cu(II) and Fe(II) complexes were recorded in DMF and DMSO solutions containing 10^{-1} M of tetrabutylammonium perchlorate (TBAP) as supporting electrolyte and 10^{-3} M as metal complex concentration. All solutions were purged prealably by dinitrogen prior to experiment.

➤ *Copper complex*

Fig. S4 A shows the cyclic voltammogram of a copper complex recorded in the potential values ranging from -1.6 V to +1.4 V in DMF solution using glassy carbon electrode as working electrode and 100 mV/s as scan rate. The reduction waves, observed at -0.750 and -0.95 V vs. SCE, are due to the electroreduction of copper species [37]. The cyclic voltammogram, recorded in the same experimental conditions (**Figure S4 B**) in the range from -0.2 to -1.6 V, presents a well-defined redox couple that showed a reduction wave at -0.97 V associated to the oxidation wave observed at ca. -0.80 V. This response is presumably due to the reduction of Cu^{II} ions into the Cu^{I} species according a reversible electrochemical process [38]. This is clearly illustrated in **figure S4 A** where a well-defined redox system $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ with its half-wave potential $E_{1/2} = -0.257$ V/SCE. **Figure S4 A**

shows also a redox couple at $E_{1/2} = -0.27$ V exhibiting respectively two waves Cu(III) at 0.14 V and Cu(II) species at -0.39 V/SCE. The last peak observed at +0.79 V may probably be ascribed to the oxidation of the free hydroxyl groups (**Position 3**) of the ligand [39]. The electrochemical characteristics with other obtained results corroborate perfectly and are consistent with those reported in the literature for similar structures [40].

➤ *Effect of the scan rate*

The redox properties of the copper complex previously recorded with various scan rates (10-500 mVs⁻¹) were studied (See **Figure S4**). Therefore, the resulting voltammograms for the system Cu^{II}/Cu^I were recorded using glassy carbon electrode at different scan rates as early indicated. In this case, an increase of the intensities of i_{pa} , i_{pc} peaks with scan rates is observed in **figure S4 C**. Obviously, the peak-to-peak separation values (ΔE_p) increase as the scan rates increase. These electrochemical studies are in perfect agreement with a quasi-reversible process since; a linear relationship was evidenced from the both cathodic and anodic peak currents, plotted versus the square root of the scan rate ($v^{1/2}$, 10-500 mVs⁻¹). This behavior is typical for an electron transfer process controlled by diffusion.

The Cyclic voltammograms show a well-defined redox couple corresponding to the Cu^{III}/Cu^{II} redox system (**Figure S4 D and E**). The redox properties of this system were explored by varying the scan rate in the same range above mentioned (10-500 mVs⁻¹) by using two different working electrodes such as glassy carbon and platinum disk. Similarly, these voltammograms showed a continuous increase for both anodic and the cathodic (i_{pa} , i_{pc}) peak currents as the scan rate increase. In this case, it is clearly noticed that the (ΔE_p) peak-to-peak separation values are relatively far to reach 60 mV. Therefore, this suggested that this redox system is not Nernstian [41] since, its i_{pa}/i_{pc} ratios are systematically higher than unity. These results corroborate to the Cu^{III}/Cu^{II} redox couple which is in good accordance with a slow electrochemical process, governed by a diffusion regime [42].

➤ *Cobalt complex*

Fig. S4 displayed cyclic voltammogram of 1 mM solutions of cobalt complex [Co^{II}(L)₂] in DMF and DMSO solvents, recorded at different scan rates (25-400 mVs⁻¹) using glassy carbon electrode in the potential values ranging from -2.0 to -1.6 V and from -2.0 to -1.2 V vs. SCE, respectively. In these two potential ranges, reduction processes were observed indicating that Co(II) complex was reduced into Co(I) species [43]. As it can be seen, this electrochemical process seems

to be irreversible in DMF medium. This irreversibility is apparently imputable to the instability of the reduced species in the more cathodic potentials (**Fig. S5 A**). However, in the case of DMSO, the same redox system process becomes quasi-reversible ($\Delta E_p = 160$ mV) and the ratio i_{pa}/i_{pc} was found to be lower than the unity and equal to 0.6 (**Fig. S5 B**). In this case, a continuous increase of anodic and cathodic peak currents (i_{pa} , i_{pc}) was observed with increasing of the scan rate (25-400 mV/s⁻¹). Moreover, it can also be noted that peak-to-peak separation values are relatively far to be approached 60 mV. Therefore, this redox system Co^{II}/Co^I corresponds to one-electron charge transfer not Nernstian since, its i_{pa}/i_{pc} ratios are systematically lower than unity indicating a slow electrochemical process usually governed by a diffusion regime.

➤ *Iron complex*

The cyclic voltammograms of iron complex recorded in DMF and DMSO solutions using 100 mV.s⁻¹ as scan rate display a redox couple at $E_{1/2} = -0.11$ V and $+0.12$ V (vs. SCE), respectively [44]. This redox couple can be ascribed to the Fe^{III}/Fe^{II} system. The $\Delta E_p = (E_{pa} - E_{pc})$ value was found to be 160 mV for DMF and 115 mV for DMSO. The ratio i_{pa}/i_{pc} is equal 0.5 for DMF and 0.8 for DMSO. Additionally, the evolution of the anodic and cathodic current peaks of this complex at different scan rates going from 25 to 400 mVs⁻¹ have been analyzed as can be illustrated in (**Fig. S5 C and D**). The separation between E_p values increase as the scan rate increases suggesting that this redox system is not Nernstian but, it is a quasi-reversible system. Also, there is a linear relationship between the cathodic and anodic peaks currents and the square root of the scan rate ($v^{1/2}$). This behavior is typical for an electron transfer process controlled by diffusion.

3.4. Visual color change in presence of different metal cations

The visual color change of the ligand (HL) solutions (10⁻⁵ M). These solutions in AN and in MeOH were investigated in presence of various metal ions using 1:2 as molecular ratio: Na⁺, Fe²⁺, Al³⁺, K⁺, Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Li⁺, Ba²⁺, Ca²⁺ and Pb²⁺. At this stage, it seems worthy to note that the ligand solutions are yellowish in the both solvents. In the case of acetonitrile solutions, the addition of Na⁺, K⁺, Mn²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Li⁺, Ba²⁺, Ca²⁺ and Pb²⁺ do not cause color change. However, when Fe³⁺ and Al³⁺ ions were added, a colorless solution was immediately observed with the naked eye. As additional observations, a clear purple color is observed when the Fe²⁺ ions were added. Under similar conditions, the addition of Co²⁺ ions produces a blue color. If other ions are added to this solution as Cu²⁺ and Cr³⁺, it delivers dark yellow coloration that is easily distinguishable with the naked eye. When methanol is used as solvent in the same experimental

conditions, only the addition of Fe^{3+} and Fe^{2+} ions causes a color change going from yellow to olive color. However, the addition of all the rest of ions above indicated do not give any change in color.

➤ *UV-Vis spectral studies*

The chemosensor behavior of our receptor ligand **HL** (10^{-5} M) was investigated by monitoring the UV-Vis absorption experiments together with addition of various metal ions such as Na^+ , Fe^{2+} , Al^{3+} , K^+ , Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Li^+ , Ba^{2+} , Ca^{2+} and Pb^{2+} (10^{-5} M) in 1:2 molar ratio in the same experimental conditions using two main solvents AN and MeOH (See Figs. 2 and 4).

In an acetonitrile solution, The UV-Vis spectrum of the free ligand **HL** shows two absorption bands at 298 and 426 nm. The first is ascribed to π - π^* transitions while the second, is assignable to n - π^* transitions of the Schiff base moieties. When the metal ions as Fe^{3+} , Co^{2+} , Cu^{2+} and Fe^{2+} are separately added to the same solution, new absorption peaks appeared showing clearly the complexation of the ligand to the ions newly introduced as is concisely exposed below:

1. By adding 1.0 equiv. of Cu^{2+} to the probe **HL**, a new broad absorption band centered at 460 nm was observed, while the band centered at 426 nm in the case of the free ligand has disappeared. Finally, the band centered at 298 nm exhibits a slight shifting to lower intensities suggesting the presence of a hypochromic effect.
2. When 1.0 equiv. of Fe^{2+} and Fe^{3+} were added to the probe **HL**, a new broad absorption bands centered at 360 nm were also observed, while the bands centered at 426 nm disappeared. As the bands centered at 298 nm exhibit as well a slight shifting to the lower intensities inducing a hypochromic effect as early mentioned.
3. The addition of 1.0 equiv. Co^{2+} to the solution of **HL** is concerned, new wide absorption bands appearing as broads were observed. The first centered at 580 and the second at 680 nm. However other wide bands where the first is centered at 426 while the second at 298 nm exhibited a slight shifting as well to the lower intensities confirming always a hypochromic effect.

From the detailed observations about the spectral changes, induced by the ions added to the solutions studied, the observed shift of the original absorption bands presented by the Schiff base to lower absorption values seems to indicate the involvement of imine ($\text{C}=\text{N}$) and phenoxy ($=\text{C}-\text{O}$) in the coordination with metal ions. These results show clearly that the Intra Molecular Charge Transfer (IMCT) processes are also involved during the complexation. With addition of other ions, the absorption bands of the Schiff base ligand show a negligible absorption change, except for Cr^{3+} ,

where its addition induced slight shifts in these bands. However, no new absorption band was observed in this case.

The binding ability of the ligand to coordinate metal ions depends on the size, the charge and the electronic configuration of the metal ion. The size, the charge and electron configuration of Cu(II), Fe(II), Fe(III) and Co(II) ions and the probe are very suitable to form a metal complex. These results imply that the probe **HL** develops an extraordinary selectivity towards these ions, and the experiments herein carried out demonstrate that this ligand could serve as a naked-eye probe for these ions, with the response time of color changes being measured in less than 3 seconds.

When adding various amounts of copper and cobalt ions to **HL**, the strong absorption band centered at 460 nm gradually increased. In the case of the cobalt ion, the main absorption bands at 580 and 680 nm progressively increased whereas the absorption bands at 426 of ligand decreased gradually with the increasing of Co(II) ion concentrations (**Fig. 3**). Color changes of chemosensor could be clearly observed via the successive addition of copper and cobalt ions (**Fig. 3**). The huge potential of **HL** ligand, as a copper chemosensor, is therefore demonstrated by a linear increase in the absorbance observed at 680 nm with Cu addition with its controlled amounts varying from 0.1 to 1 equivalent (See **Fig. 3**).

«Insert Figure 2»

«Insert Figure 3»

As for the methanolic solutions of these ions, we have examined the sensing ability of **HL** in the presence of the same variety of metal ions previously tested in acetonitrile. The receptor **HL** showed an instantaneous color change from yellow to olive in the successive presence of Fe^{2+} and Fe^{3+} (**Fig. 4**). In addition to the color change, the addition of Fe^{2+} and Fe^{3+} to **HL** caused significant hypsochromic shifts of the band centered at 425 nm to a lower wavelength (360 nm). However, other species such as Na^+ , Al^{3+} , K^+ , Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Li^+ , Ba^{2+} , Ca^{2+} and Pb^{2+} almost showed no change with the naked eye in the UV–Vis spectra under similar experimental conditions (**Fig. 4A**). When adding several amounts of Fe^{3+} ions were added to a methanol solution containing the ligand **HL**, a strong absorption band centered at 365 nm gradually increased, while the main absorption band 710 nm decreased progressively with an increase of the Fe^{3+} ions concentrations (**Fig. 5B**). Again, **HL** ligand is seen as a promising chemosensor for Fe^{3+} ions [45], as manifested by the linear relationship between the iron concentration and its absorbance at 365 nm

(see **Fig. 5C**). Color changes of chemosensor can be obviously observed with the gradual addition of Fe^{3+} ionic species (**Fig. 5A**).

«Insert Figure 4»

«Insert Figure 5»

Linear fitting of the titration profiles using Benesi-Hildebrand plot [46] results in a good linearity (correlation coefficient is over 0.96) (**Fig. 6**), which probably support the 2:1 binding stoichiometry complexation between **HL** with Co^{2+} and Fe^{3+} , and the binding constants are found to be $5.09 \times 10^7 \text{ M}^{-1}$, and $4.54 \times 10^7 \text{ M}^{-1}$, respectively.

«Insert Figure 6»

So we can concluded that all the absorption spectra demonstrate that our receptor **HL** has shown high selectivity and sensitivity for its responsiveness towards Cu^{2+} , Co^{2+} , Fe^{2+} and Fe^{3+} among various other metal ions. These results revealed the remarkable differences in UV-Vis spectra of our receptor **HL** with these metal cations. This is due to the introduction of high rigidity in its coordination sphere avoiding any other complexation.

4. Conclusion

Throughout this study, a new bidentate Schiff base ligand **HL** that is derived from the condensation of 2,3-dihydroxybenzaldehyde and alkylamine with its Co(II) , Cu(II) and Fe(II) complexes were prepared in a methanolic solution. These synthesized compounds were also characterized by fully physicochemical and spectroscopic methods such as the elemental analysis, FT-IR, ^1H NMR and the UV-Vis spectrophotometry. The electrochemical behavior of the copper complex was investigated via the cyclic voltammetry through the use of two different working electrode materials GC and Pt in DMF solutions. Two other complexes cobalt and iron were also studied in two different media like dimethylformamid and dimethylsulfoxide. Also, it was again demonstrated that the synthesized bidentate Schiff base ligand (**HL**) as simple chelate which is endowed with high performances conferring it better selectivity giving an efficient chemosensor able to coordinate a serial of metallic ions such as Cu^{2+} , Co^{2+} , Fe^{2+} and Fe^{3+} in two different media as

methanol and acetonitrile. As a result, it has been established that this sensor (**HL**) exhibits an excellent selectivity and good sensitivity towards some of these metal ions studied.

Acknowledgements

The authors would like to thank the Algerian Ministère de l'Enseignement Supérieur et de la Recherche Scientifique et la Direction générale de la Recherche and the Ministerio de Economía y Competitividad for their undeniable financial support (MAT2013-42007-P). RRR thanks The Spanish Ministry of Economy and Competitiveness (MINECO) for a “Juan de la Cierva” contract (JCI-2012-12664).

References

- [1] E.E. Shehata, M.S. Masoud, E.A. Khalil, A.M. Abdel-Gaber, Synthesis, spectral and electrochemical studies of some Schiff base N_2O_2 complexes, *J. Mol. Liq.* 194 (2014) 149–158.
- [2] A.H. Kianfar, S. Ramazani, R.H. Fath, M. Roushani, Synthesis, spectroscopy, electrochemistry and thermogravimetry of copper(II) tridentate Schiff base complexes, theoretical study of the structures of compounds and kinetic study of the tautomerism reactions by ab initio calculations, *Spectrochim. Acta A* 105 (2013) 374–382.
- [3] K.H. Kumar Naik, S. Selvaraj, N. Naik, Metal complexes of ONO donor Schiff base ligand as a new class of bioactive compounds; Synthesis, characterization and biological evolution, *Spectrochim. Acta A* 131 (2014) 599–605.
- [4] S. Chandra, S. Gautam, H.K. Rajor, R. Bhatia, Syntheses, spectroscopic characterization, thermal study, molecular modeling, and biological evaluation of novel Schiff's base benzilbis(5- amino-1,3,4-thiadiazole-2-thiol) with Ni(II), and Cu(II) metal complexes, *Spectrochim. Acta A* 137 (2015) 749–760.
- [5] C. Ji, D.G. Peters, Electrochemical reduction of benzyl iodide, benzal bromide, and benzalchlorobromide at carbon cathodes in the presence of nitric oxide in acetonitrile, *J. Electroanal. Chem.* 516 (2001) 39–49.
- [6] M. Najafi, M. Rahbar, M.A. Naseri, Cyclic voltammetry study of the electrocatalytic reduction of sevoflurane by a cobalt(III) Schiff base complex in the presence of oxygen, *J. Electroanal. Chem.* 655 (2011) 111–115.

- [7] S. Rayati, M. Koliaei, F. Ashouri, S. Mohebbi, A. Wojtczak, A. Kozakiewicz, Oxovanadium(IV) Schiff base complexes derived from 2,2'-dimethylpropanediamine: A homogeneous catalyst for cyclooctene and styrene oxidation, *Appl. Catal. A-Gen.* 346 (2008) 65–71.
- [8] W. Zhu, L. Yang, M. Fang, Z. Wu, Q. Zhang, F. Yin, Q. Huang, C. Li, Newcarbazole-based Schiff base: Colorimetric chemosensor for Fe^{3+} and fluorescent turn-on chemosensor for Fe^{3+} and Cr^{3+} , *J. Lumin.* 158 (2015) 38–43.
- [9] M. Mishra, K. Tiwari, A.K. Singh, V.P. Singh, Synthesis, structural and corrosion inhibition studies on Mn(II), Cu(II) and Zn(II) complexes with a Schiff base derived from 2-hydroxypropiophenone, *Polyhedron* 77 (2014) 57–65.
- [10] M. Saleem, C.H. Khang, M-Hwan. kim, K.H. Lee, Chromo/Fluorogenic Detection of Co^{2+} , Hg^{2+} and Cu^{2+} by the Simple Schiff Base Sensor, *J. Fluoresc.* 26 (2016) 11–22.
- [11] (A) G. Cui, Design and synthesis of a terbium(III) complex-based luminescent probe for time-gated luminescence detection of mercury(II) ions, *J. Fluorescence* 22 (2012) 261–7; (B) E.J. Songa, G.J. Parka, J.J. Leea, S. Leec, I. Nohc, Y. Kimd, S-J. Kimd, C. Kima, R.G. Harrison, A fluorescence sensor for Zn^{2+} that also acts as a visible sensor for Co^{2+} and Cu^{2+} , *Sensor. Actuat. B-Chem.* 213 (2015) 268–275.
- [12] (A) Q. Meng, Y. Wang, M. Yang, R. Zhang, R. Wang and Z. Zhang, A new fluorescent chemosensor for highly selective and sensitive detection of inorganic phosphate (Pi) in aqueous solution and living cells, *RSC Adv.* 5 (2015) 53189–53197; (B) R. Zhang, X. Yu, Y. Yin, Z. Ye, G. Wang, J. Yuan, Development of a heterobimetallic Ru(II)–Cu(II) complex for highly selective and sensitive luminescence sensing of sulfide anions, *Anal. Chim. Acta* 691 (2011) 83–88; (C) S. Ghosh, M.A. Alam, A. Ganguly, N. Guchhait, Amido-Schiff base derivatives as colorimetric fluoride sensor: Effect of nitro substitution on the sensitivity and color change, *Spectrochim. Acta A* 149 (2015) 869–874.
- [13] H.Y. Jo, S.A. Lee, Y.J. Na, G.J. Park, C. Kim, A colorimetric Schiff base chemosensor for CN^- by naked-eye in aqueous solution, *Inorg. Chem. Commun.* 54 (2015) 73–76.
- [14] Y. Yang, C-Yi. Gao, J. Liua and D. Dong, Recent developments in rhodamine salicylidene hydrazone chemosensors, *Anal. Methods* 8 (2016) 2863–2871.
- [15] M. Kose, G. Ceyhan, M. Tumer, I. Demirtas, I. Gonul, V. McKee, Monodentate Schiff base ligands: Their structural characterization, photoluminescence, anticancer, electrochemical and sensor properties, *Spectrochim. Acta A* 137 (2015) 477–485.
- [16] D. Peralta-Domínguez, M. Rodríguez, G. Ramos-Ortíz, J.L. Maldonado, M.A. Meneses-Nava, O. Barbosa-García, R. Santillan, N. Farfán, A Schiff base derivative from cinnamaldehyde for colorimetric detection of Ni^{2+} in water, *Sensor. Actuat. B-Chem.* 207 (2015) 511–517.

- [17] X. Wang, T. Xu, H. Duan, Schiff base fluorescence probes for Cu^{2+} based on imidazole and benzimidazole, *Sensor. Actuat. B-Chem.* 214 (2015) 138–143.
- [18] S. Devaraj, Y-k. Tsui, C-Y. Chiang, Y-P. Yen, A new dual functional sensor: Highly selective colorimetric chemosensor for Fe^{3+} and fluorescent sensor for Mg^{2+} , *Spectrochim. Acta A* 96 (2012) 594–599.
- [19] L.D. Chebrolu, S. Thurakkal, H.S. Balaramana, R. Danaboyina, Selective and dual naked eye detection of Cu^{2+} and Hg^{2+} ions using a simple quinoline–carbaldehyde chemosensor, *Sensor. Actuat. B-Chem.* 204 (2014) 480–488.
- [20] N. Roy, A. Dutta, P. Mondal, P.C. Paul, T.S. Singh, A new turn-on fluorescent chemosensor based on sensitive Schiff base for Mn^{2+} ion, *J. Lumin.* 165 (2015) 167–173.
- [21] S.Y. Lee, J.J. Lee, K.H. Bok, S.Y. Kim, C. Kim, Highly selective and sensitive colorimetric chemosensor for detection of Co^{2+} in a near perfect aqueous solution, *RSC Adv.* 6 (2016) 28081–28088.
- [22] G.R. You, G.J. Park, S.A. Lee, K.Y. Ryu, C. Kim, Chelate-type Schiff base acting as a colorimetric sensor for iron in aqueous solution, *Sensor. Actuat. B-Chem.* 215 (2015) 188–195.
- [23] L. Chun-jiao, Y. Zheng-yin, F. Long, J. Xiu-long, A. Jun-mei, C. Xiao-ying, W. Bao-dui, Novel optical selective chromone Schiff base chemosensor for Al^{3+} ion, *J. Lumin.* 158 (2015) 172–175.
- [24] (A) H. Wang, D. Zhang, Y. Chen, Z-H. Ni, L. Tian, J. Jiang, Synthesis, crystal structures, and magnetic properties of new tetranuclear Cu(II) complexes of bis-bidentate Schiff-base ligands, *Inorg. Chim. Acta* 362 (2009) 4972–4976; (B) R. Bikas, Hassan H. Monfared, T. Lis, M. Siczek, Synthesis, structural characterization and electrochemical studies of an ionic cobalt complex derived from a tridentate hydrazone Schiff base and azide ligands, *Inorg. Chem. Commun.* 15 (2012) 151–155; (C) L.P. Nitha, R. Aswathy, N.E. Mathews, B.S. kumari, K. Mohanan, Synthesis, spectroscopic characterisation, DNA cleavage, superoxidase dismutase activity and antibacterial properties of some transition metal complexes of a novel bidentate Schiff base derived from isatin and 2-aminopyrimidine, *Spectrochim. Acta A* 118 (2014) 154–161.
- [25] A. Mukherjee, R. Chakrabarty, S.W. Ng, G.K. Patra, The syntheses, characterizations, X-ray crystal structures and properties of Cu(I) complexes of a bis-bidentate schiff base ligand, *Inorg. Chim. Acta* 363 (2010) 1707–1712.
- [26] O.A.M. Ali, S.M. El-Medani, D.A. Ahmed, D.A. Nassar, Synthesis, characterization, fluorescence and catalytic activity of some new complexes of unsymmetrical Schiff base of 2-pyridine carboxaldehyde with 2,6-diaminopyridine, *Spectrochim. Acta A* 144 (2015) 99–106.
- [27] P. Tyagi, S. Chandra, B.S. Saraswat, D. Yadav, Design, spectral characterization, thermal, DFT studies and anticancer cell line activities of Co(II) , Ni(II) and Cu(II) complexes of Schiff bases

- derived from 4-amino-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol, *Spectrochim. Acta A* 145 (2015) 155–164.
- [28] A. Ourari, D. Aggoun, L. Ouahab, A novel copper(II)-Schiff base complex containing pyrrole ring: Synthesis, characterization and its modified electrodes applied in oxidation of aliphatic alcohols, *Inorg. Chem. Commun.* 33 (2013) 118–124.
- [29] H. Keypour, M. Shayesteh, M. Rezaeivala, F. Chalabian, Y. Elerman, O. Buyukgungor, Synthesis, spectral characterization, structural investigation and antimicrobial studies of mononuclear Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) complexes of a new potentially hexadentate N₂O₄ Schiff base ligand derived from salicylaldehyde, *J. Mol. Struct.* 1032 (2013) 62–68.
- [30] Y-T. Liu, G-D. Lian, D-W. Yin, B-J. Su, Synthesis, characterization and biological activity of ferrocene-based Schiff base ligands and their metal (II) complexes, *Spectrochim. Acta A* 100 (2013) 131–137.
- [31] P.S. Hariharan, S.P. Anthony, Substitutional group dependent colori/fluorimetric sensing of Mn²⁺, Fe³⁺ and Zn²⁺ ions by simple Schiff base chemosensor, *Spectrochim. Acta A* 136 (2015) 1658–1665.
- [32] A.A. Soliman, Effect of solvents on the electronic absorption spectra of some salicylidene thio schiff bases, *Spectrochim. Acta A* 53 (1997) 509-515.
- [33] A.B.P. Lever, *Inorganic electronic spectroscopy*, 2nd edn. (Elsevier, London, 1992).
- [34] C. Rimington, Spectral-absorption coefficients of some porphyrins in the Soret-band region, *Biochem. J.* 75 (1960) 620-3.
- [35] Z. Chen, Y. Wu, D. Gu, F. Gan, Spectroscopic, and Thermal Studies of Some New Binuclear Transition Metal(II) Complexes With Hydrazone Ligands Containing Acetoacetanilide and Isoxazole, *Spectrochim. Acta A* 68 (3) (2007) 918–926.
- [36] S.D. Cummings, R. Eisenberg, Tuning the excited-state properties of platinum(II) diiminedithiolate complexes, *J. Am. Chem. Soc.* 118 (1996) 1949-1960.
- [37] S.A. Hosseini-Yazdi, A. Mirzaahmadi, P. Samadzadeh-Aghdam, A.A. Khandar, G. Mahmoudi, W.S. Kassel, W.G. Dougherty, Synthesis, characterization, X-ray structure, spectroscopic and electrochemical studies of copper and zinc complexes with two new polydentate ligands, *Inorg. Chim. Acta* 414 (2014) 115–120.
- [38] M.H. Habibi, M. Mikhak, Synthesis, spectral, photolysis and electrochemical studies of mononuclear copper(II) complex with a new asymmetric tetradentate ligand: Application as copper nanoparticle precursor, *Spectrochim. Acta A* 96 (2012) 501–505.
- [39] A. Simić, D. Manojlović, D. Šegan and M. Todorović, Electrochemical Behavior and Antioxidant and Prooxidant Activity of Natural Phenolics, *Molecules* 12 (2007) 2327-2340.

- [40] A.H. Kianfar, S. Ramazani, R.H. Fath, M. Roushani, Synthesis, spectroscopy, electrochemistry and thermogravimetry of copper(II) tridentate Schiff base complexes, theoretical study of the structures of compounds and kinetic study of the tautomerism reactions by ab initio calculations, *Spectrochim. Acta A* 105 (2013) 374-382.
- [41] J.T. Lundquist, J.R. and R.S. Nicholson, Theory of the potential step-linear scan electrolysis method with a comparison of rate constants determined electrochemically and by classical methods, *J. Electroanal. Chem.* 16 (1968) 445-456.
- [42] C.S. Martina, C. Gouveia-Caridade, F.N. Crespilho, C.J.L. Constantino, C.M.A. Brett, Nickel-N,N'-bis(salicylidene)-1,3-propanediamine (Ni-Salpn) film-modified electrodes. Influence of electrodeposition conditions and of electrode material on electrochemical behaviour in aqueous solution, *Electrochim. Acta* 178 (2015) 80-91.
- [43] A. Ourari, S. Messali, B. Bouzerafa, Y. Ouennoughi, D. Aggoun, M.S. Mubarak, L.M. Strawsine, D.G. Peters, Synthesis, characterization, and electrochemical behavior of a cobalt(II) salen-like complex, *Polyhedron* 97 (2015) 197-201.
- [44] A. Pui, M. Teodor, M-O. Apostu, A. Gref, Synthesis and Characterization of New Fe(II) Schiff Bases Complexes. *Buletinul I.P.I. Iasi*, 3-4 (2000) 41-46.
- [45] H. Jia, X. Gao, Y. Shi, N. Sayyadi, Z. Zhang, Q. Zhao, Q. Meng, R. Zhang, Fluorescence detection of Fe³⁺ ions in aqueous solution and living cells based on a high selectivity and sensitivity chemosensor, *Spectrochim. Acta A* 149 (2015) 674-681.
- [46] H.A. Benesi, J.H. Hildebrand, A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons, *J. Am. Chem. Soc.* 71 (1949) 2703-2707.

List of captions

Scheme

Scheme 1. Preparation of Schiff base ligand and its metal complexes.

Figures

Fig. 1. Electronic spectra of the Schiff base ligand **HL** and its metal complexes at 25 °C in DMF medium.

Fig. 2 (A) UV–Vis absorption response of probe **HL** (10^{-5} M) in AN upon addition of various metal ions with color change. **(B)** Absorbance of **HL** at 360 nm with various metal ions.

Fig. 3 (A) Absorption spectral changes in a acetonitrile solution containing 10^{-5} M of probe **HL** ligand after successive addition of amounts of Cu^{2+} (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 equiv.) with color change. Inset: Absorption at 460 nm versus the number of equiv. of Cu^{+2} added; **(B)** Absorption spectral changes in a acetonitrile solution containing 10^{-5} M of probe **HL** ligand after successive addition of amounts of Co^{2+} (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 equiv.) with color change. Inset: Absorption at 680 nm versus the number of equiv. of Co^{+2} added.

Fig. 4 (A) UV–Vis absorption response in a methanolic solution containing 10^{-5} M of probe **HL** ligand upon addition of various metal ions with color change. **(B)** Absorbance of **HL** at 360 nm with various metal ions.

Fig. 5 (A) Visual colour changes induced by the addition of different Fe^{3+} concentrations in a methanolic solution containing 10^{-5} M of **HL** ligand. **(B)** Absorption spectral changes of **HL** after addition of increasing amounts of Fe^{3+} . **(C)** Absorption at 365 nm versus the number of equiv. of Fe^{3+} added.

Fig. 6 Benesi–Hildebrand fit for **(A)** HL-Co^{2+} (at 680 nm) and **(B)** HL-Fe^{3+} (at 365 nm).

Scheme 1

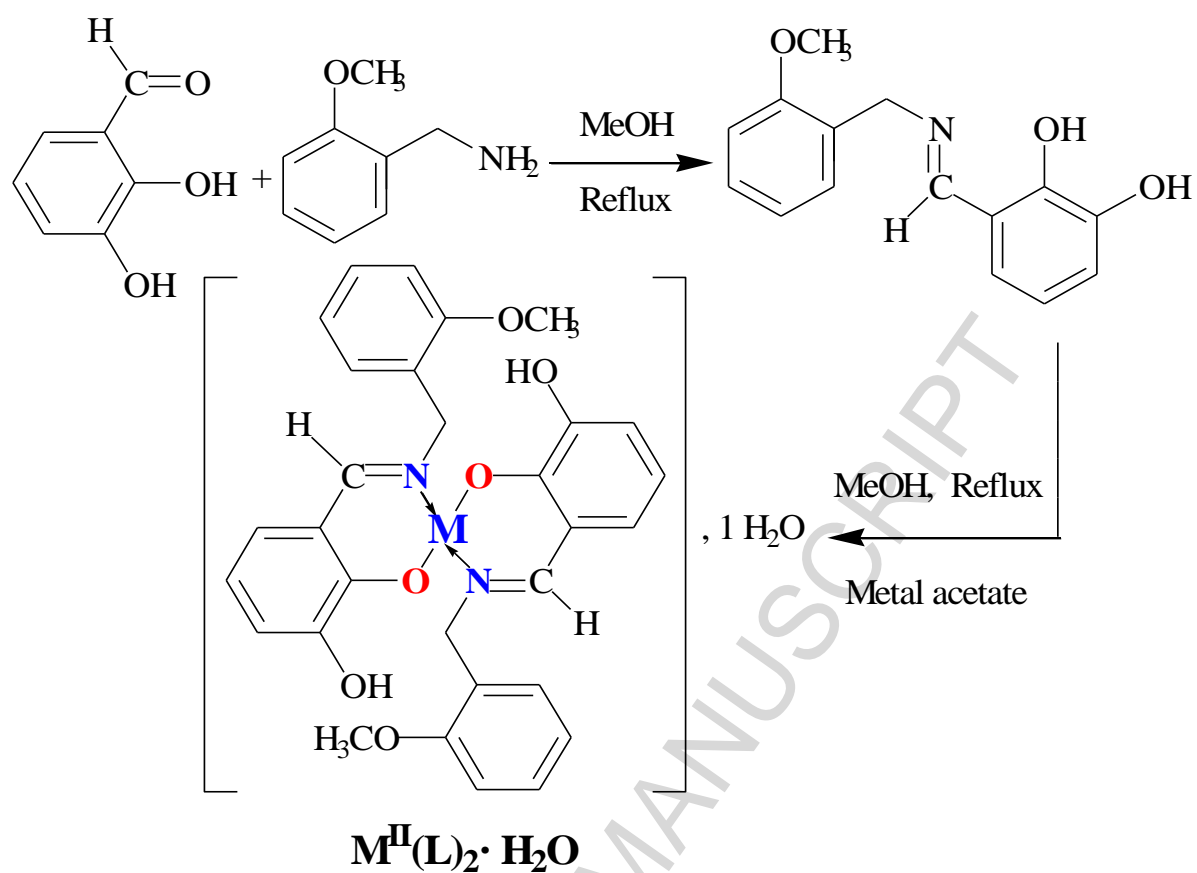


Figure 1

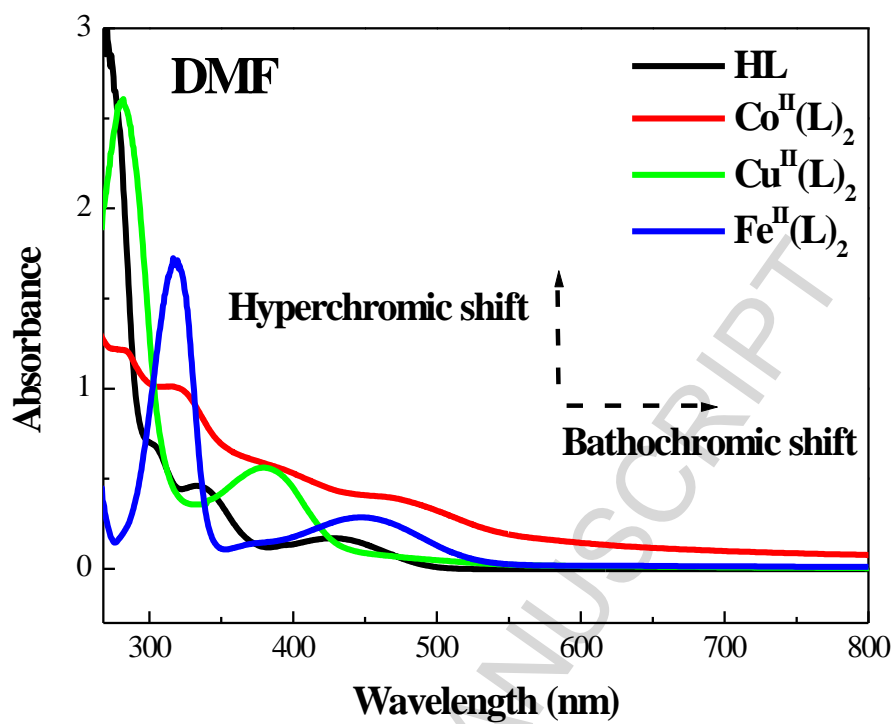


Figure 2

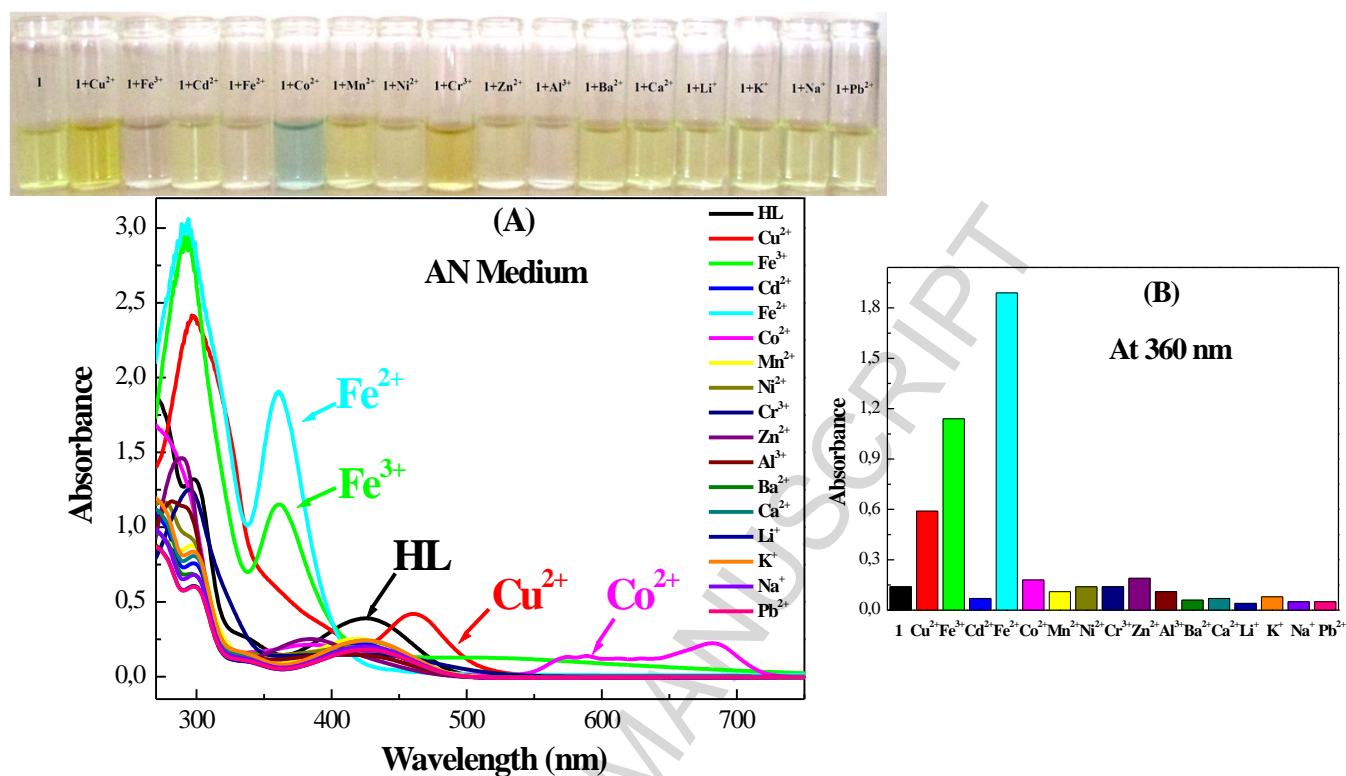
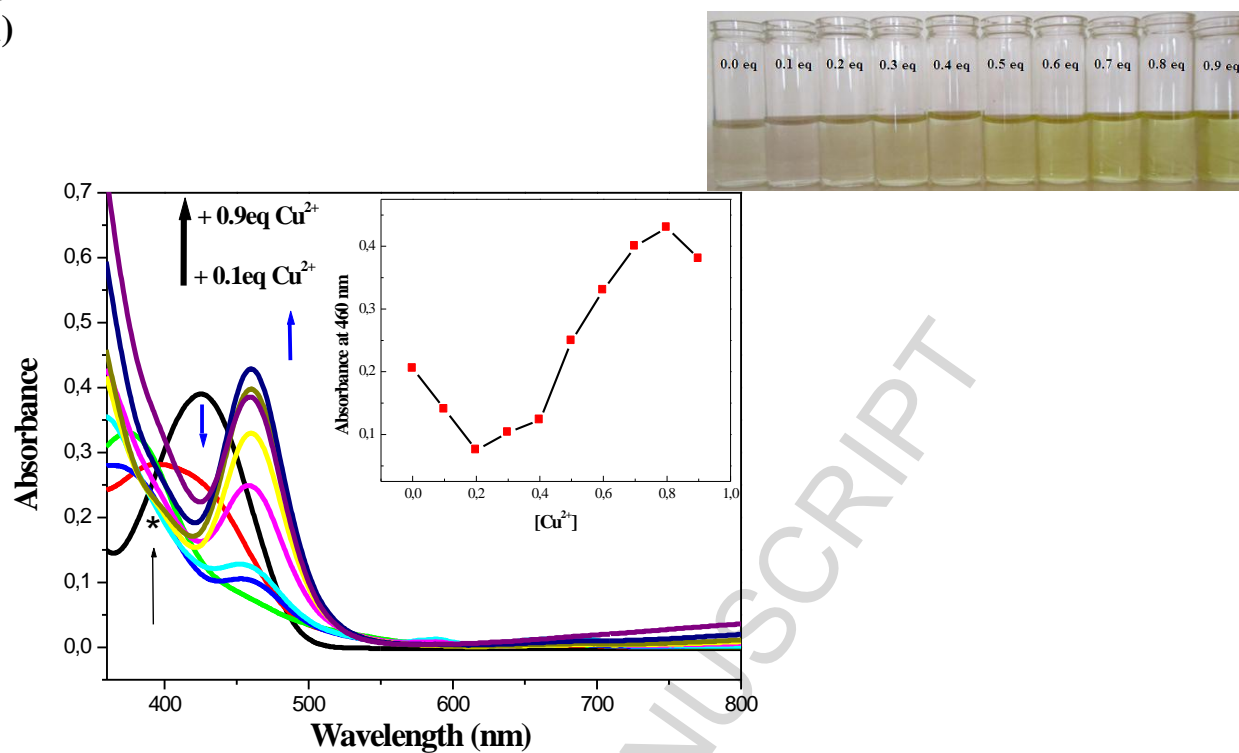


Figure 3

(A)



(B)

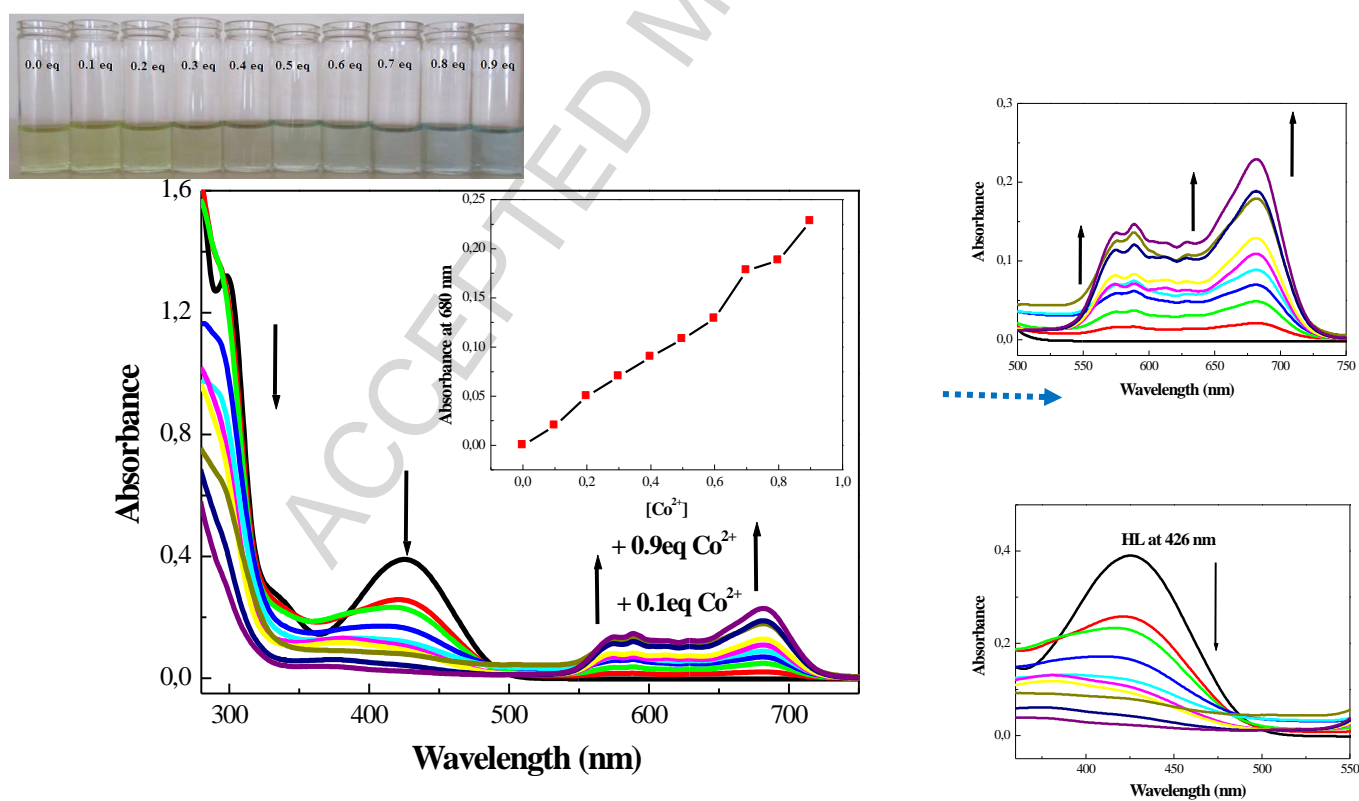


Figure 4

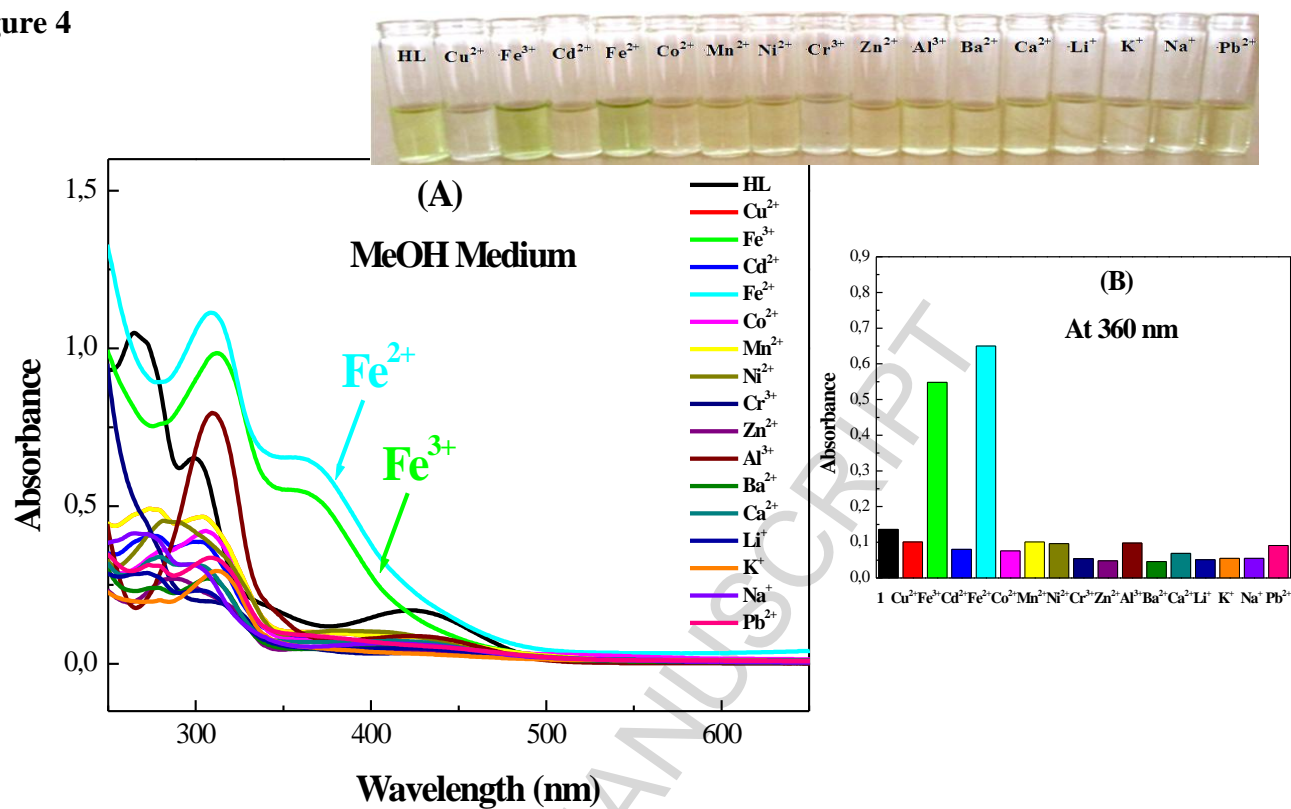


Figure 5

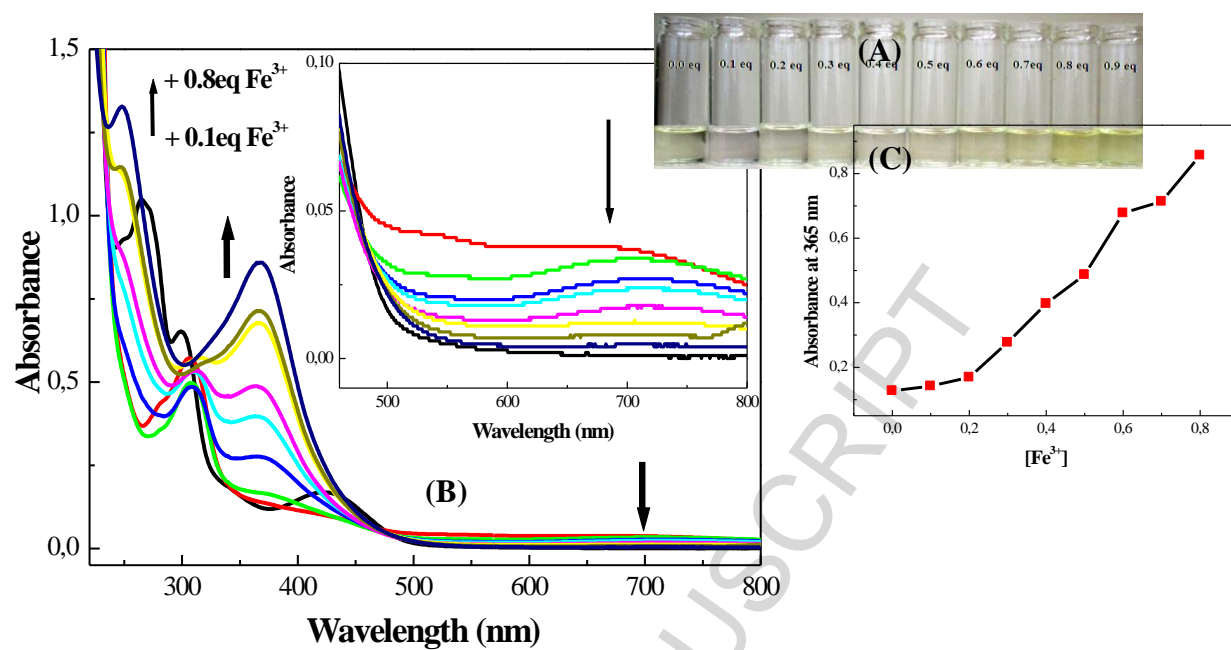
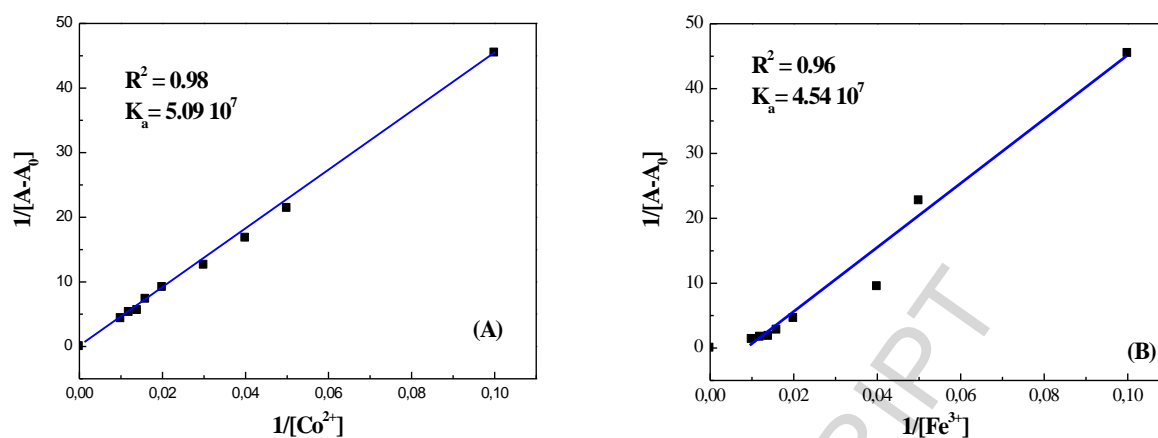
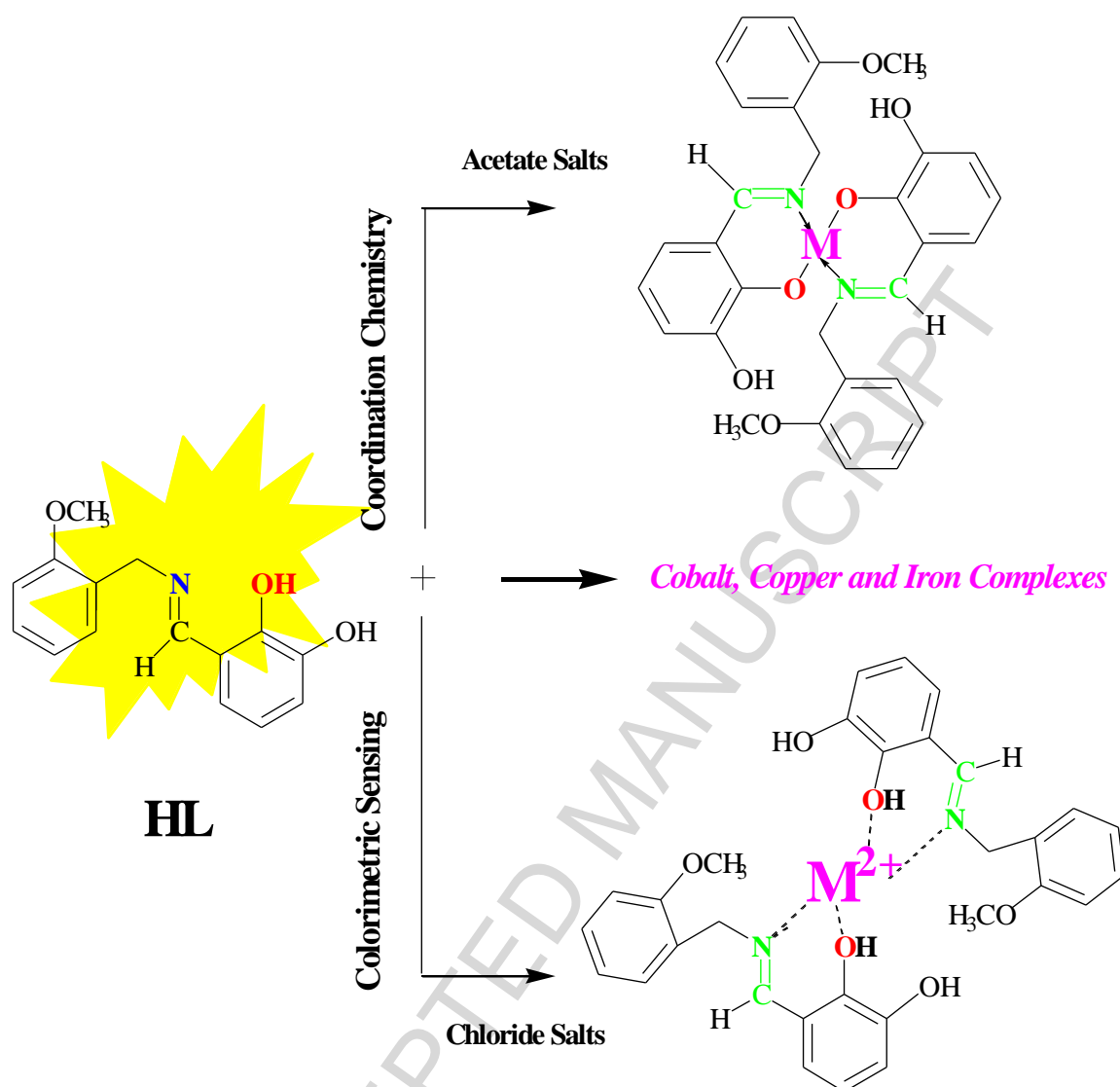


Figure 6



GRAPHICAL ABSTRACT



Highlights

- Bidentate Schiff base ligand with its metal complexes.
- UV-Vis, FT-IR, elemental analysis, Mass spectrometry and cyclic voltammetry.
- The solvatochromism properties for the ligand with its copper and iron complexes.
- A simple and an easy-to-make colorimetric chemosensor.

ACCEPTED MANUSCRIPT