UV-vis spectroscopic characterization of heterocyclic azines as colorimetric chemosensors for metal ion detection

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Abstract: Thienyl, pirrolyl and furyl azine derivatives **L1-L3** were obtained in excellent yields (93-98%) using a simple methodology that allows their synthesis and purification in higher yields, compared to previous methods. The photophysical properties of compounds **L1-L3** were studied by UV-vis spectroscopy in acetonitrile. Spectrophotometric titrations of receptors **L1-L3** in the same solvent, in the presence of several cations such as Cd(II), Co(II), Cr(III), Cu(II), Fe(II), Fe(III), Hg(II), Ni(II), Pb(II), Pd(II) and Zn(II) revealed that they could be used as colorimetric chemosensors for Hg(II), Cu(II), Cr(III) and Fe(III).

Keywords: Azines; Heterocycles, Colorimetric chemosensors; Metal ion detection.

1. Introduction

The development of colorimetric chemosensors is an area in great expansion due to the simplicity of assay and lower cost compared with others sensing methods. Sensing devices for the analysis of toxic or heavy metal ions play an important role in clinical toxicology, environmental, bioorganic chemistry, bioremediation, and waste management [1]. Until now, most of the chemosensors developed involve laborious and expensive procedures and there is an interest in strategies for single step synthesis, optimizing the efficiency of the chemical reaction and avoiding time-consuming processes of separation and purification. Therefore, the development of small molecule-based colorimetric chemosensors with simple synthetic and isolation procedures has received much attention in the last decade [2].

The current interest in azine derivatives arises from their wide range of applications in diverse areas such as material and environmental sciences, biomedical, analytical, supramolecular chemistry and catalysis. Additionally, azine ligands bearing N, O and S heteroatoms in their structure should exhibit improved coordination ability [3]. Following our previous work [4], azine ligands functionalized with heterocycles such as thiophene **L1**, pyrrole **L2** and furan **L3**, were used in a cation chemosensory study in acetonitrile solutions.

2. Experimental

2.1. General procedure for the synthesis of ligands L1-L3

To a solution of aldehyde (2.0 mmol) in 10 mL of ethanol, was added hydrazine hydrate (1.0 mmol) and the reaction mixture was heated under reflux for 5 h. The mixture was concentrated at reduced pressure, which induced precipitation of a solid. The solid product formed was separated by filtration, purified by crystallization from ethanol and then dried under vacuum.

1,2-bis((1H-Thiophene-2-yl)methylene)hydrazine (**L1**) was obtained as a brown solid (0.431 g, 98%). Mp: 153.0–154.7 ºC (136–138 ºC [5a]). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 7.11–7.14 (m, 2H, 2 x H-4), 7.42–7.44 (m, 2H, 2 x H-5), 7.48–7.50 (m, 2H, 2 x H-3), 8.79 (s, 2H, 2 x *N*=C*H*) ppm.

1,2-bis((1H-Pyrrol-2-yl)methylene)hydrazine (**L2**) was obtained as a dark yellow solid (0.349 g, 94%). Mp: 163.4–164.9 ºC (186–187 °C [5b]). IR (KBr) ν 3212 (NH), 1633 (C=N), 1540, 1407, 1294, 1132, 1028, 953, 881, 810 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 6.16–6.19 (m, 2H, 2 x H-4), 6.58–6.60 (m, 2H, 2 x H-5), 6.96–6.98 (m, 2H, 2 x H-3), 8.37 (s, 2H, 2 x *N*=C*H*), 11.54 (s, 2H, 2 x N*H*) ppm. ^{13}C NMR (75.4 MHz, DMSO-d_6) δ = 109.66 (2 x C4), 114.79 (2 x C5), 123.21 (2 x C3), 127.32 (2 x C2), 150.54 (2 x N=*C*H) ppm.

1,2-bis(Furan-2-ylmethylene)hydrazine (**L3**) was obtained as a brown solid (0.350 g, 93%). Mp: 121.0–123.0 ºC (134–136ºC [5c]). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 6.54–6.55 (m, 2H, 2 x H-4), 6.90 (dd, 2H, *J* = 3.2 and 0.4 Hz, 2 x H-3), 7.60 (d, *J* = 1.6 Hz, 2H, 2 x H-5), 8.53 (s, 2H, 2 x *N*=C*H*) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$) δ = 112.26 (2 x C4), 116.76 (2 x C3), 145.79 (2 x C5), 149.42 (2 x C2), 150.94 (2 x N=*C*H) ppm.

2.2. Spectrophotometric titrations and chemosensing studies of azines L1-L3

Solutions of azines **L1-L3** (10^{-5} M) and of the cations under study (10^{-3}–10^{-2} M) were prepared in UV-grade acetonitrile (in the form of hexahydrated tetrafluorborate salts for Cu(II), Co(II), Ni(II) and Pd(II), and perchlorate salts for Cd(II), Cr(III), Zn(II), Hg(II), Fe(II) and Fe(III)) and the titration was performed by the sequential addition of equivalents of metal ion to the azine derivative solution, in a 10 mm path length quartz cuvette and absorption spectra were measured.

3. Results and discussion

3.1. Synthesis

The ligands **L1-L3** were prepared in high yield by the simple and straightforward Schiff's base condensation by refluxing hydrazine hydrate with the heterocyclic aldehydes in ethanol for 5 h.

Purification of the crude solids by recrystallization from ethanol gave the pure heterocyclic ligands in excellent yields (93–98 %). Preparation of compounds **L1-L3** through this simple synthetic methodology allows their synthesis in higher yields compared to earlier methods [5]. The ligands were characterized through the usual spectroscopic techniques.

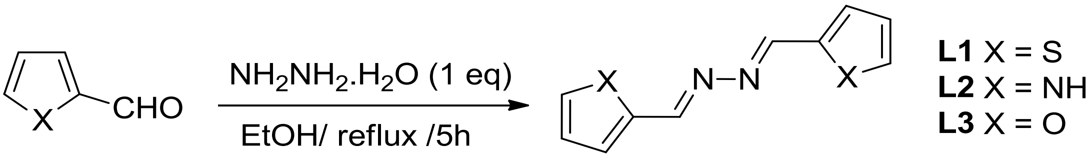

Table 1. Yields, ^{1}H NMR and UV-vis data of azines **L1-L3**.

Azine	**Yield (%)**	**δ_H C*H*=N (ppm)**	**UV-vis** [d]	
			λ_{max} (nm)	**log ε**
L1	98	8.79[a]	337	4.50
L2	94	8.37[b]	352	4.54
L3	93	8.49[c]	331	4.59

[a] at 300 MHz, $CDCl_3$. [b] at 300 MHz, DMSO-d_6. [c] at 400 MHz, DMSO-d_6. [d] in acetonitrile.

The absorption spectra of compounds **L1-L3** were obtained in acetonitrile solutions (Table 1) showing broad and intense absorptions in the visible region from 331 to 352 nm. The position of this band is strongly influenced by the different donating electronic strength of the heterocycle (thiophene, pyrrole or furan) linked to the azine moiety. Substitution of furan (**L3**) by pyrrole (**L2**) in the azine system results in a bathochromic shift (21 nm) in the UV-Vis spectra due to the stronger electron-donating ability of pyrrole compared to that of thiophene (Table 1).

3.2. Spectrophotometric titrations of compounds L1-L3 in the presence of metal ions in acetonitrile solutions

The ligands **L1-L3** were evaluated as chemosensors for metal ion detection by spectrophotometric titrations, in the presence of cations such as Cd(II), Co(II), Cr(III), Cu(II), Fe(II), Fe(III), Hg(II), Ni(II), Pb(II), Pd(II) and Zn(II) in acetonitrile solutions. A preliminary study with 10 equiv of the metal ions revealed that compounds **L1** and **L3** showed selectivity to Cr(III), Cu(II) and Fe(III) with a distinct colour change from colourless to yellow. On the other hand, receptor **L2** exhibit a lower selectivity in the presence of the same cations showing a colour change from colourless to yellow in the presence of Cr(III), Cu(II), Fe(III), Hg(II), Pb(II), and Pd(II) (Figures 1 and 2).

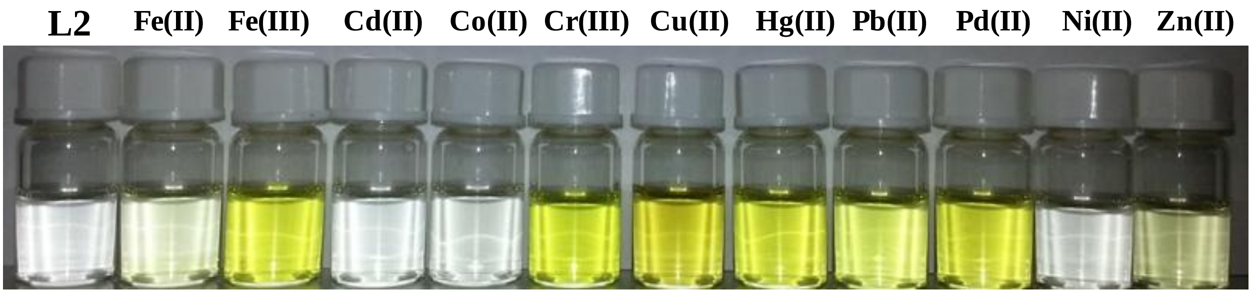

Figure 1. Colour changes of compound **L2** (10^{-5} M in ACN) in the presence of 10 equiv. of Fe(II), Fe(III), Cd(II), Co(II), Cr(III), Cu(II), Hg(II), Pb(II), Pd(II), Ni(II) and Zn(II).

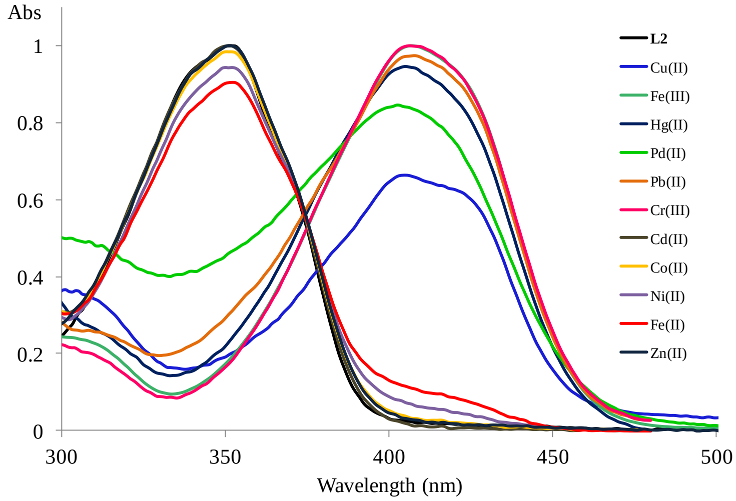

Figure 2. Normalised absorption of compound **L2** (10^{-5} M) in ACN in the presence of 10 equiv. of metal ions.

Spectrophotometric titrations of compound **L2** in ACN (10^{-5} M) with Cr(III), Cu(II), Fe(III), Hg(II), Pb(II), and Pd(II) revealed a trend in the UV-vis spectra: the intensity of the longest wavelength absorption band at 352 nm decreased progressively upon addition of the metal ion, with the simultaneous growth of a new red-shifted absorption band located between 402 and 408 nm (Figure 3). The number of necessary metal equivalents of Cu(II) to achieve a plateau was 0.6 equivalents for compound **L2** and more than 100 equivalents for compounds **L1** and **L3**.

The interaction between **L2** with other metals, such as Cr(III) or Fe(III) revealed similar results comparatively to the other ligands. While **L2** needed 0.5 equivalents of Cr(III) and Fe(III) to achieve the plateau, ligands **L1** and **L3** required approximately 6 and 2 equivalents, respectively. The enhanced chelating ability of ligand **L2** could be explained having in mind the stronger donor electronic nature of pyrrole, bearing a NH group, compared to thiophene or furan.

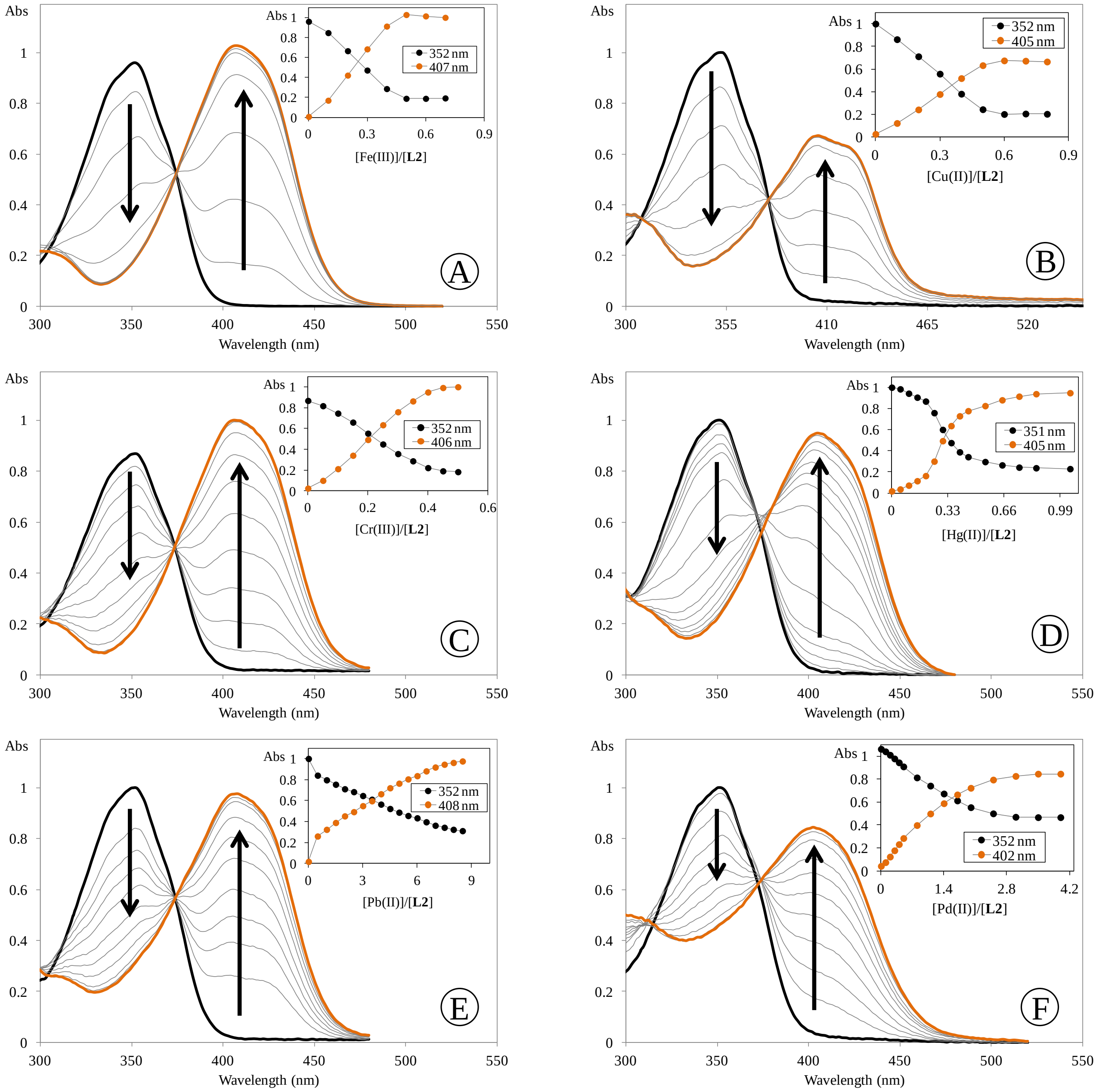

Figure 3. UV-vis spectral changes of compound **L2** in ACN (10^{-5} M) with the addition of increasing amounts of Fe(III) (**A**), Cu(II) (**B**), Cr(III) (**C**), Hg(II) (**D**), Pb(II) (**E**) and Pd(II) (**F**) solutions. The black line represents the free ligand and the orange line corresponds to the metal complex.

4. Conclusions

Heterocyclic azines **L1-L3** were synthesized in excellent yields through a simple synthetic procedure and a simple purification methodology and completely characterised. The photophysical properties of all compounds were studied by UV-vis spectroscopy in acetonitrile solution. The ability of **L1-L3** as colorimetric chemosensors was studied in acetonitrile through spectrophotometric titrations of all receptors with various cations. Higher sensitivity was observed for Cu(II) (0.4-0.6 equivalents) with a straightforward naked-eye detection from colourless to yellow with ligand **L2**.

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