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Recognition of hydrazone-containing benzimidazole derivative towards bismuth (III) ion studied by UV–vis spectromentry and DFT calculations

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ABSTRACT

A simple, selective and sensitive spectrophotometric method for the direct determination of trace amounts of Bi^{3+} in real samples was developed based on complexation reactions between Bi^{3+} and two benzyl-functionalized benzimidazolylidene ligands (L1 and L2). The important analytical parameters, such as pH, amounts of the regents, and their effects on UV–vis absorption properties of the studied systems were investigated. Under the optimum conditions, the absorbance of the Bi^{3+}-L complex obeys Beer's law in Bi^{3+} concentration range of 0.21–6.48 μg·mL^{-1} with the limit of detection of 95.51 and 55.80 μg·mL^{-1} for Bi^{3+}-L1 and Bi^{3+}-L2, respectively. The proposed method was successfully applied to the determination of Bi^{3+} content in water samples and stomach medicine samples. DFT calculations showed that L2 has higher selectivity towards Bi^{3+} than L1.

Keywords: Bi^{3+} ion detection; Benzyl-functionalized benzimidazolylidene derivative; Uv-vis spectrometry; DFT

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1. Introduction

Bismuth compounds are used in semiconductors, alloys and metallurgical additives, cosmetics, pigments, a few pharmaceuticals and etc [1]. Bismuth has low toxicity. As the use of bismuth has increased, it has been distributed in the environment increasing the chance of exposure of organisms. A number of toxic effects on humans have been attributed to bismuth compounds, such as nephropathy, osteoarthropathy, hepatitis, and neuropathology [1,2]. These cases underscore the necessity for methods to determine bismuth for pollution control.

Various techniques have been used in the past for the determination of Bi^{3+} ions at trace levels. These include inductively-coupled plasma atomic emission spectrometry (ICP-AES) [3–5], ICP-mass spectrometry (ICP-MS) [6,7], flame atomic absorption spectrometry (FAAS) [8,9], hydride generation atomic absorption spectrometry (HGAAS) [10,11], anodic stripping voltammetry [12,13] and etc. The techniques listed here have disadvantages, either the use of toxic mercury electrodes, tedious procedures for sample preparation, well-controlled experimental conditions or costly instrumentation. The identification and quantitative analysis of metal ions by ultraviolet–visible (UV-vis) spectroscopy have been proven to be an attractive technique [14,15], due to its simplicity, low cost and rapidity without requirement of any sophisticated instrumentation [16,17]. As a routine quantitative method, UV-vis spectrometry is widely applied to determine metal ions. In this area, emphasis is focused on the development of new molecules with special organic structures whose donor groups provide a suitable coordinating site, aiming at enhancing the selectivity of the method. Although there are many reports about the determination of metal ions using UV-vis spectrometry, relatively very few studies were carried out for Bi^{3+} ion [18].

Because nitrogen, sulphur and oxygen containing compounds can form selective and stable complexes with many metal ions, continuous interest has been focused on the design and synthesis of new functionalized compounds for specific application. In the present work we synthesized two benzyl-functionalized benzimidazolylidene

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ligands N´-(4-nitrobenzylidene)-1H-benzo[d]imidazole-2-carbohydrazide (L1) and N´-(4-hydroxy-3-methylbenzylidene)-1H-benzo[d]imidazole-2-carbohydrazide (L2), and investigated their UV-vis absorption characteristics. Such compounds were chosen because of their structural characteristics [19,20], such as semi-cavity of proper size, selective binding with metal ion, and high stability. They may act as analytical reagents for the microdetermination of metals cations [20]. On the other hand, there are some structural differences between the two proposed ligands. We expected that small structural changes can modify molecules properties and change selectivity towards selected cations. The results show that L1 and L2 can selectively recognize Bi^{3+} ion. The proposed method is sensitive and environment friendly. It requires no control of temperature and does not suffer from most of the potential interferences. The method was applied successfully to determine trace amounts of Bi^{3+} in real samples. Furthermore, density functional theory (DFT) calculations were used to compare the recognition ability of two ligands with Bi^{3+} ion.

2. Materials and methods

2.1. Reagents

Ligands L1 and L2 were synthesized according to the procedures described in the literature [21]. Other chemical reagents were of analytical grade. Nitrate and chloride salts of all metals were purchased from Shanghai Chemical Company (China) and used without further purification. Double distilled water was used throughout the experiments.

Standard stock solutions of ligand (1.0×10^{-3} M) and metal ions salt (1.0×10^{-4} M) were prepared with CH_3OH for the investigation of the interactions between ligands and metal cations by spectrophotometric method. Working solutions were prepared by appropriate dilution of the stock solutions. The pH of metal salt solution was adjusted by dilute HNO_3 solution.

2.2. Apparatus

The UV-vis spectroscopy measurements were carried out in a spectrophotometer (Model HP Agilent 8453) with a matched pair of quartz cells of 1 cm optical path length. pH values were measured using a pH meter of model pHS-3C (Shanghai Leici Instrument Factory) with a combined glass-calomel electrode of sensitivity (±0.01) pH units.

2.3. General procedure for UV-vis titrations

UV-vis absorbance study was performed as following procedure: (i) Mixture solutions of appropriate amounts of 1×10^{-4} M Bi^{3+} and 0.65 mL 1×10^{-3} M ligand were obtained in 10 mL volumetric flask. The pH of the solution was 3.4. (ii) The mixture solutions were put in an ultrasonic bath for 10 min, and then placed in room temperature for 4 h to reach coordination equilibrium. (iii) The adsorption spectra scanning (190–450 nm) of mixture solutions were measured by UV-vis spectrometer.

3. Results and discussion

3.1. UV–visible studies

To clarify the interactions of ligands with different metal ions, the UV-vis absorption spectrum of two liagnds in CH_3OH were studied. It can be seen from Fig. 1 that two ligands are characterized by two strong bands at about 205 and 330 nm. Various metal ions such as K^+, Na^+, Mn^{2+}, Ni^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Ag^+, Cu^{2+}, Mg^{2+}, Hg^{2+}, Zn^{2+}, Pb^{2+}, Bi^{3+}, Fe^{3+} and Cr^{3+} were used to measure the selectivity of ligands. As seen from Fig. 1, other metal ions had little or no influence on the UV-vis absorption spectrum of two ligands except Bi^{3+} ions. Upon addition of equal mole Bi^{3+} ions, the absorbance at 205 nm shows a significant increase accompanied by a 4 nm red shift, while the other absorption peak at 330 nm shows an increase in intensity and a 6 nm red shift. The spectral change may be attributed to the changes of conjugated system of ligand molecules. Trivalent bismuth ion

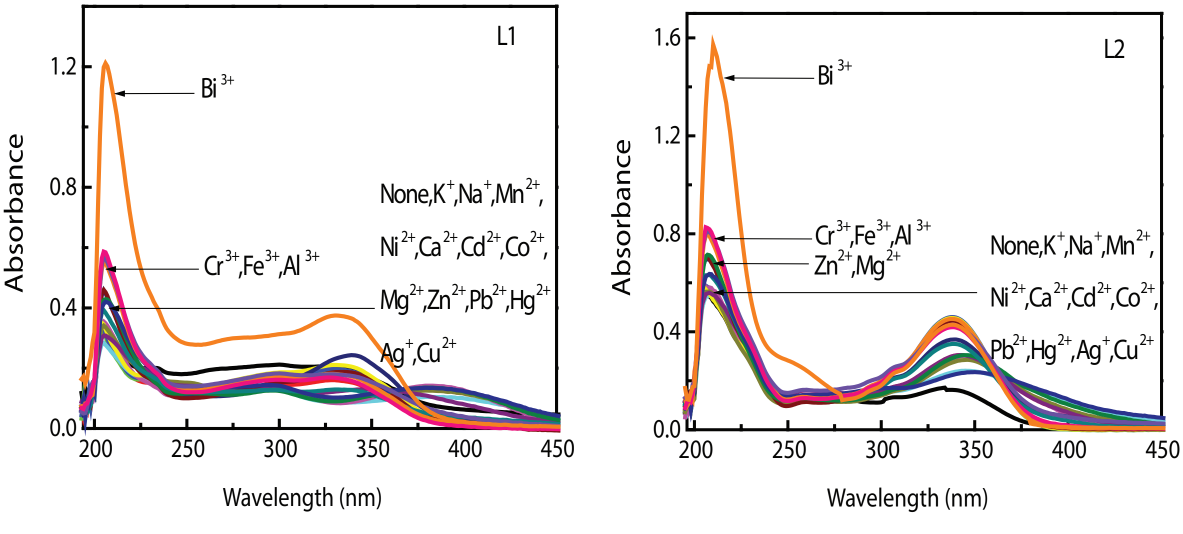

Fig. 1. UV-vis absorption spectra of ligand upon addition of different metal ions in CH_3OH solutions.

was connected with the nitrogen and oxygen atoms, and formed a coordination bond. Therefore, as the conjugated system increased, the maximum absorbance of Bi^{3+}-L complex was shifted to longer wavelength. This finding suggests a binding of ligand with Bi^{3+} ion.

In order to further illuminate the interaction between the ligands and metal ions, the relative reduction in the absorbance ($(A–A_0)/A_0$) was calculated. As shown in Fig. 2, among the tested metal ions, Bi^{3+} addition caused the largest relative reduction in the absorbance. Therefore, it can be concluded that L1 and L2 possess the excellent selectivity in binding with Bi^{3+}. This finding indicates that two ligands could be used for the detection of Bi^{3+}.

The stoichiometry of L1 and L2 binding with Bi^{3+} was determined by Job's-plot method [22], and the results are shown in Fig. 3. The UV-vis absorbance was measured at 205 nm and the absorbance difference was plotted as a function of Bi^{3+} mole fraction by keeping the total concentration of Bi^{3+} and ligand at 5×10^{-5} M in CH_3OH solution. It is interesting to observe the maximum absorbance at the molar fraction of 0.5, indicating a 1:1 stoichiometry complexation between ligands and Bi^{3+} ions.

Benesi-Hildebrand (B-H) method [23] is a widely used approach for determining the binding stoichiometry and equilibrium constants of non-covalent binding interactions, particularly for 1:1 and 1:2 binding stoichiometry. The association constant, K_a of the ligand with Bi^{3+} was calculated using the Benesi-Hildebrand equation.

$$1/(A–A_0) = 1/(K_a(A_{max}–A_0)[M^{Z+}]^n) + 1/(A_{max}–A_0) \quad (1)$$

where A_0 is the absorbance before metal ion addition, A is the absorbance after metal ion addition, A_{max} is the absorbance after adding an excess amount of metal ions. It can be seen from Fig. 4 that there is a linear relationship between $1/(A–A_0)$ and $1/[Bi^{3+}]$ with the linear correlation coefficients of 0.9992 and 0.9995 for Bi^{3+}-L1 and Bi^{3+}-L2, respectively. The excellent linear relationship further indicates a 1:1 stoichiometric binding between ligand and Bi^{3+}. From the slope and the intercept values, the K_a values were determined to

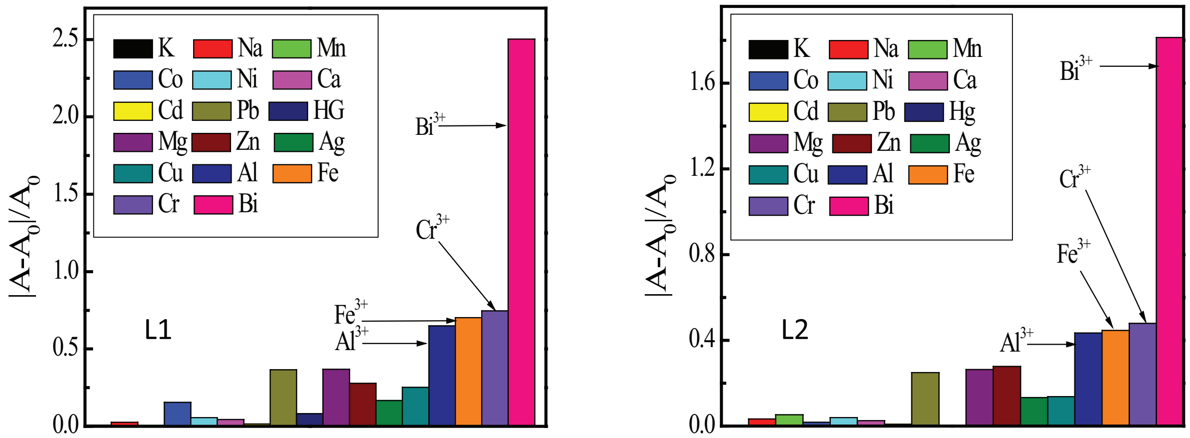

Fig. 2. Relative reduction in UV-vis absorbance at λ_{max} (205 nm) of L1 and L2 upon addition of different metal ions, where A_0 was the absorbance of the original solution, A was the absorbance at its λ_{max} (205 nm) after metal ions addition.

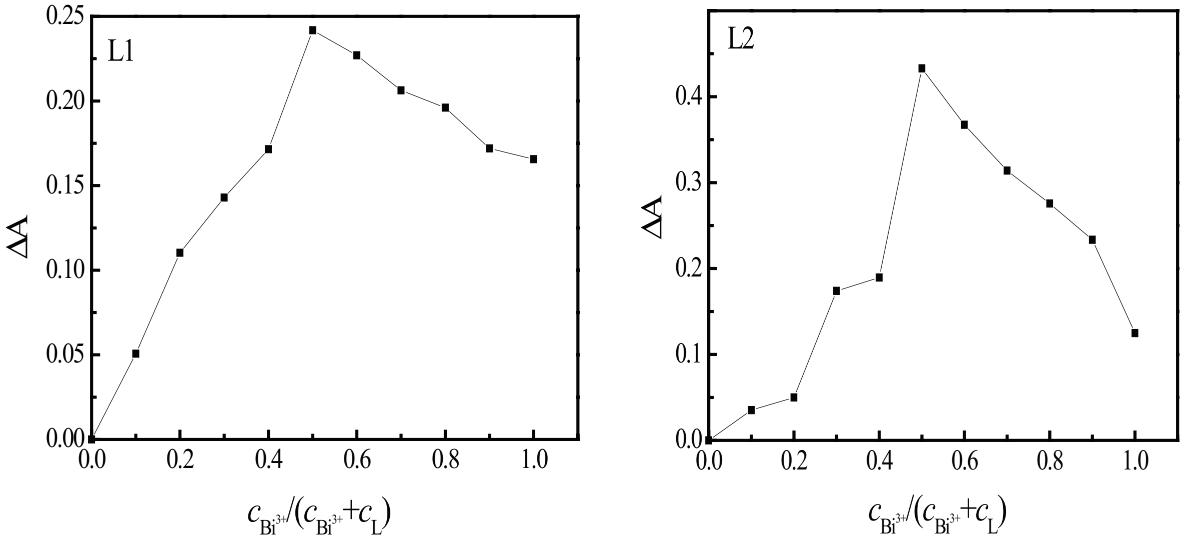

Fig. 3. Job's plot as a function of Bi^{3+}: L mole fraction at a total concentration of 5×10^{-5} M in CH_3OH solutions.

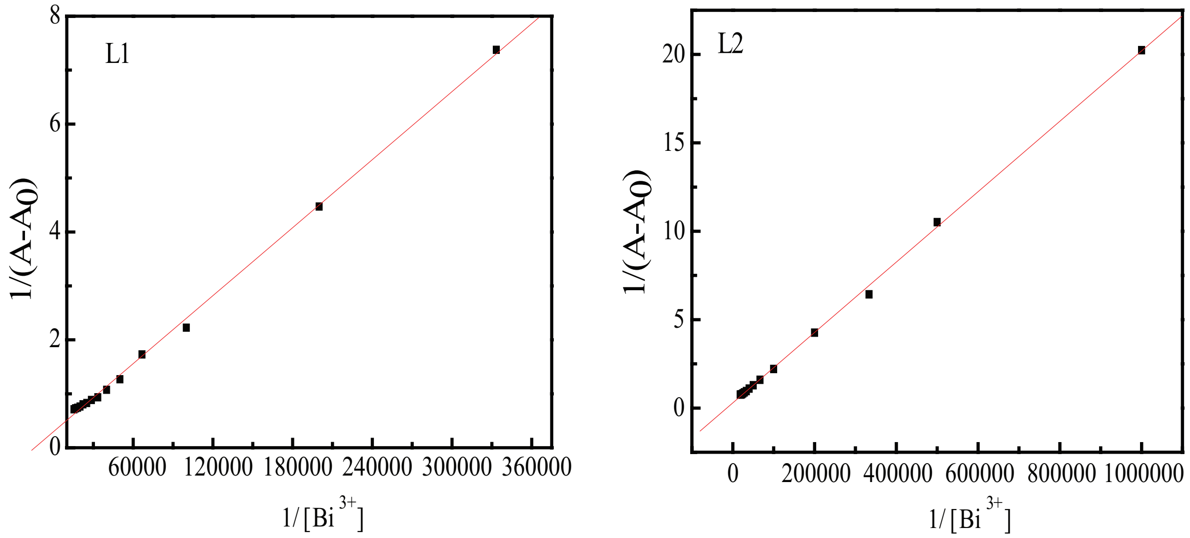

Fig. 4. Changes in UV-vis spectrum with addition of different amounts of Bi^{3+} in CH_3OH.

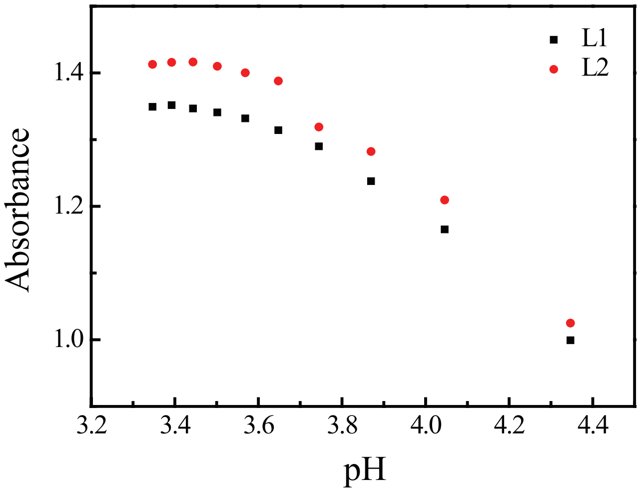

Fig. 5. The variation of the absorbance of the Bi^{3+}-L complex vs. pH at 205 nm. $[Bi^{3+}] = 1.0 \times 10^{-5}$ M, $[L] = 1.0 \times 10^{-5}$ M, blank reagent.

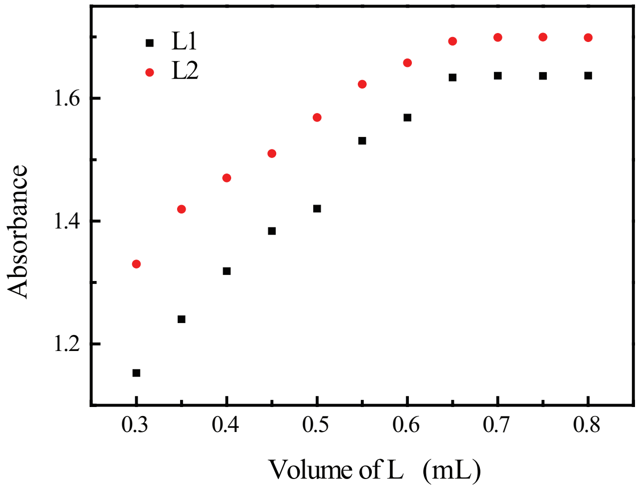

Fig. 6. Effect of the volume of 1.0×10^{-3} M ligand on complex with Bi^{3+} (1.0×10^{-5} M).

be 1.42×10^4 and 1.47×10^4 L · mol^{-1} for Bi^{3+}-L1 and Bi^{3+}-L2, respectively.

The effect of pH was investigated over the pH range of 3.3–4.4 by the addition of 1.5 mM nitric acid in 10 ml mixed solution. The results are shown in Fig 5. From the results, it is observed that the complex exhibits maximum absorbance in the pH range of 3.3–3.6. The reason was possibly that the complete chelation required a proper acidity. In more alkaline media the absorbance reduced because of complex hydrolysis and hydroxide formation. Thus, all samples discussed in the following section were prepared around pH = 3.4.

The effect of reagent concentration on the absorbance of the complex was investigated by varying the reagent concentration at constant Bi^{3+} concentration (1.0×10^{-5} M). It is clear from Fig. 6 that the maximum absorbance was attained with 0.65 mL of 1.0×10^{-3} M ligand and above this volume up to 0.8 mL the absorbance remained unchanged. Therefore, 0.65 mL of 1.0×10^{-3} M ligand was used in all further measurements for Bi^{3+}.

A working curve was constructed at optimum conditions by conducting a set of similar experiment at various concentration of Bi^{3+} and respective results are depicted in Fig. 7. The linear ranges (Table 1) of absorbance as a function of Bi^{3+} concentration i.e. obeyance to Beer's law, provide a satisfactory measure of the sensitivity of the method. Under the optimum conditions, the absorbance of both Bi^{3+}-L complexs obeys Beer's law in Bi^{3+} concentration range of 0.21–6.48 μg·mL^{-1}. The limit of detection (LOD) was estimated using normalize response of UV-vis absorbance calibration value $(A_{min}-A)/(A_{min}-A_{max})$ as a function of $\log[Bi^{3+}]$ [24,25]. As shown in Fig. 8, the lowest detectable limit (LOD) for Bi^{3+} using this method was 95.51 and 55.80 μg·mL^{-1}, respectively. Beer's law range, molar absorptivity,

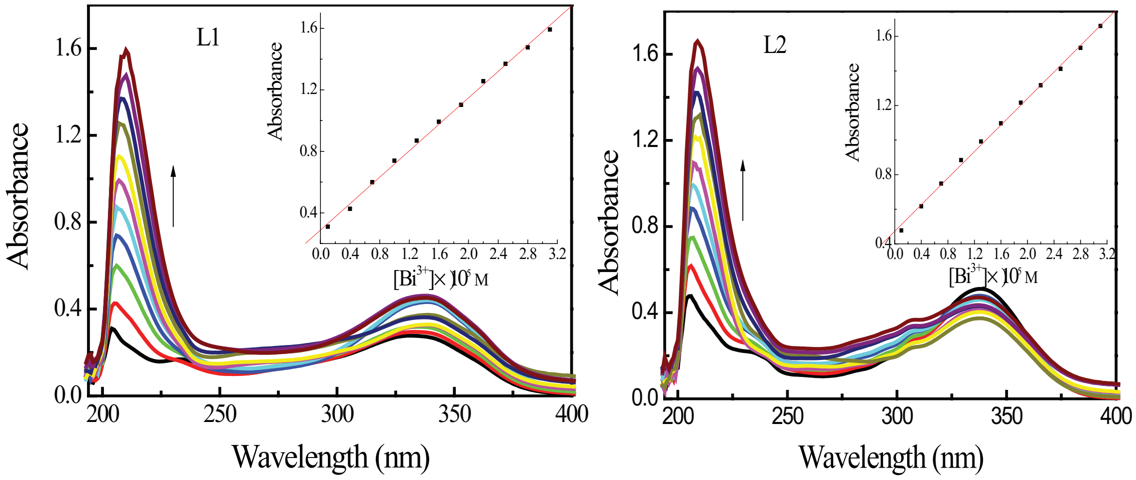

Fig. 7. UV-vis spectra of ligand (1.0 × 10^{-5} M) with gradual addition of of Bi^{3+} ion. Inset: Beer's law plot.

Table 1
Optical parameters for the determination of Bi^{3+} with two ligands

Parameters	Characteristic (L1)	Characteristic (L2)
Beer's law range (μg·mL^{-1})	0.21–6.48	0.21–6.48
Molar absorptivity (L·mol^{-1}·cm^{-1})	3.91 × 10^4	4.43 × 10^4
Limit of detection (μg·mL^{-1})	95.51	55.80
Regression equation[a]	$y = 0.288 + 0.430x$	$y = 0.473 + 0.384x$
Correlation coefficient	0.9988	0.9988
Standard deviation[b]	0.0089	0.0006
Relative Standard deviation (%)[b]	0.23	0.16

[a] y=a+bx where x is the concentration of Bi^{3+} and y is the absorbance
[b] six replicates measurements

limit of detection, regression equation, and correlation coefficient are given in Table 1.

In addition, a comparison is made in Table 2 for some important characteristics like linearity range, detection limit with previously Bi^{3+} sensors reported in the literatures [26–29]. In order to make the comparison more reasonable, we perform the experiments of literatures 27 and 29. Under the same laboratory conditions, we obtained similar results to the literature values. We can get the conclusion from Table 2 that the proposed method is superior to previously reported sensors in some cases, such as low detection limit and wider linear range.

The interference study was performed by using 5.0 × 10^{-5} M of Bi^{3+} ion and variable concentrations of the interfering cations at pH = 3.4. The tolerance limit was defined as the amount of added ions that caused less than 5% relative error in the determination of Bi^{3+}. As is obvious from Table 3, the concentration of the target ions can be selectively determined using the proposed method in the presence of excess amounts of the potential interferences examined.

3.2. DFT calculations

Ligand L2 has structural similarity to ligand L1. However, the sensor based on L2 gives low detection limit. In order to illustrate the difference binding characteristics of the two ligands with Bi^{3+}, the charge distribution and orbital energies of the HOMO and LUMO of ligands were calculated with the quantum-chemical calculation by Gauss view 5.0.8. The calculations were performed using DFT method and the three-dimensional molecular geometry optimizations were performed using the B3LYP and 6-31G basic sets. The results showed that the more negatively charged area is located at oxygen atom and the nitrogen atom of imidazole ring which is on the same side as oxygen atom. The obtained atomic partial charges for oxygen atoms are about –0.43 and –0.45, and those of nitrogen atoms are –0.50, –0.51 for L1 and L2, respectively. The frontier molecular orbitals of two ligands were also calculated (Fig. 9). The calculated total energies and energy gaps for L1 and L2 are –2.93 × 10^4, –2.69 × 10^4 and –5.01, –3.03 eV, respectively. From the results obtained, we can conclude that L2 has higher selectivity towards Bi^{3+}. The results are in good agreement with the results of the association constant from B-H experiments.

3.3. Application of the method

The feasibility of the proposed method was explored by using it for the determination of trace amounts of Bi^{3+} in water samples and in bismuth potassium citrate particles. Water samples were collected without adding any preservative in polyethylene bottles and analyzed within 6 h. Water samples were filtered through filter paper before use. The weighted stomach medicine samples 110 mg were dissolved in 15 mL of nitric acid (1+1). Then the solutions were transferred to a 100 mL volumetric flask and diluted with nitric acid (1+1). Then 1.0 mL of the resulting solution was transferred to a 100 mL volumetric flask, 5 mL of HNO_3

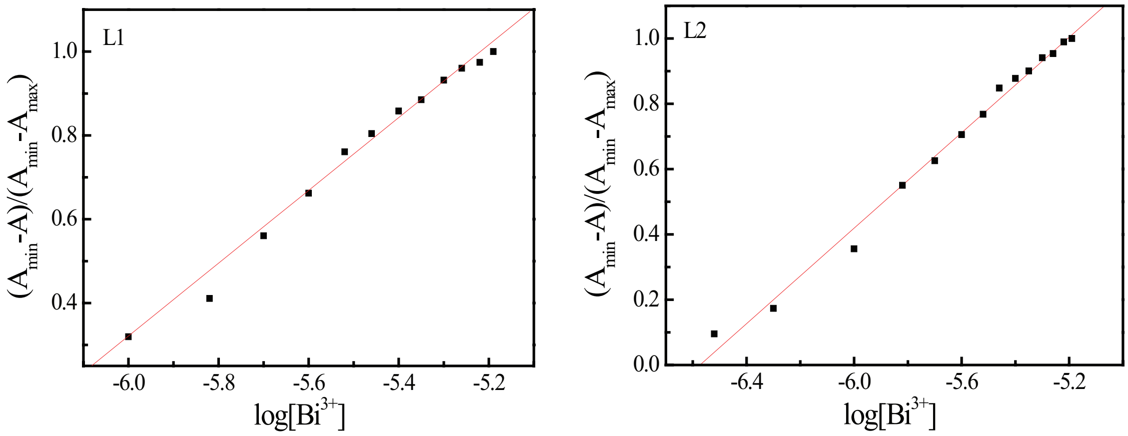

Fig. 8. Normalized response of UV-vis absorbance calibration value as a function of Bi^{3+} concentration in CH_3OH solutions.

Table 2
Comparison of the proposed method with other reported methods for determination of bismuth (III)

Reagent	pH	LOD (ng·mL^{-1})	Linear range (μg·mL^{-1})	Ref.
(2,6-Dichloroarsenazo)	0.6 M $HClO_4$	–	0.00–1.00	[26]
o-Phenanthroline and eosin	5.0	–	0.40–2.00	[27]
	5.0	38.7	0.39–2.09	Our work
dithizone	5.0	50	0.50–2.51	[28]
5-(2-bromophenylazo)-6-hydroxy pyrimidine-2,4-dione	2.5	99.5	0.25–7.25	[29]
	2.5	100.3	0.27–7.31	Our work
L1	3.4	95.51	0.21–6.48	Present work
L2	3.4	55.80	0.21–6.48	Present work

Table 3
Effect of diverse species on the spectrophotometric determination of Bi^{3+} (5.0×10^{-5} mol × L^{-1}), where A_0 is the absorbance before foreign metal ions addition

Foreign ions	L1		L2	
	Tolerance limit (mol × L^{-1})	Relative error (%) $\lvert\Delta A\rvert/A_0 \times 100$	Tolerance limit (mol × L^{-1})	Relative error (%) $\lvert\Delta A\rvert/A_0 \times 100$
Na^+	1.0×10^{-3}	1.76	1.0×10^{-3}	1.38
K^+	1.0×10^{-4}	1.20	1.0×10^{-3}	3.42
Mn^{2+}	5.0×10^{-4}	2.95	1.0×10^{-3}	4.38
Ni^{2+}	1.0×10^{-3}	4.97	1.0×10^{-3}	0.87
Co^{2+}	5.0×10^{-4}	3.71	1.0×10^{-3}	2.30
Ca^{2+}	5.0×10^{-4}	3.82	1.0×10^{-3}	4.72
Cd^{2+}	5.0×10^{-4}	1.19	1.0×10^{-3}	4.30
Ag^+	1.0×10^{-5}	2.38	5.0×10^{-4}	1.45
Cu^{2+}	1.0×10^{-5}	0.61	5.0×10^{-4}	4.74
Mg^{2+}	1.0×10^{-4}	3.29	1.0×10^{-4}	3.08
Hg^{2+}	1.0×10^{-4}	0.33	1.0×10^{-3}	4.62
Zn^{2+}	1.0×10^{-4}	1.15	1.0×10^{-4}	2.10
Pb^{2+}	1.0×10^{-4}	4.12	1.0×10^{-4}	4.37
Fe^{3+}	1.0×10^{-4}	1.43	1.0×10^{-4}	4.86
Cr^{3+}	5.0×10^{-4}	2.38	5.0×10^{-4}	4.67
Al^{3+}	1.0×10^{-4}	2.93	1.0×10^{-4}	3.99

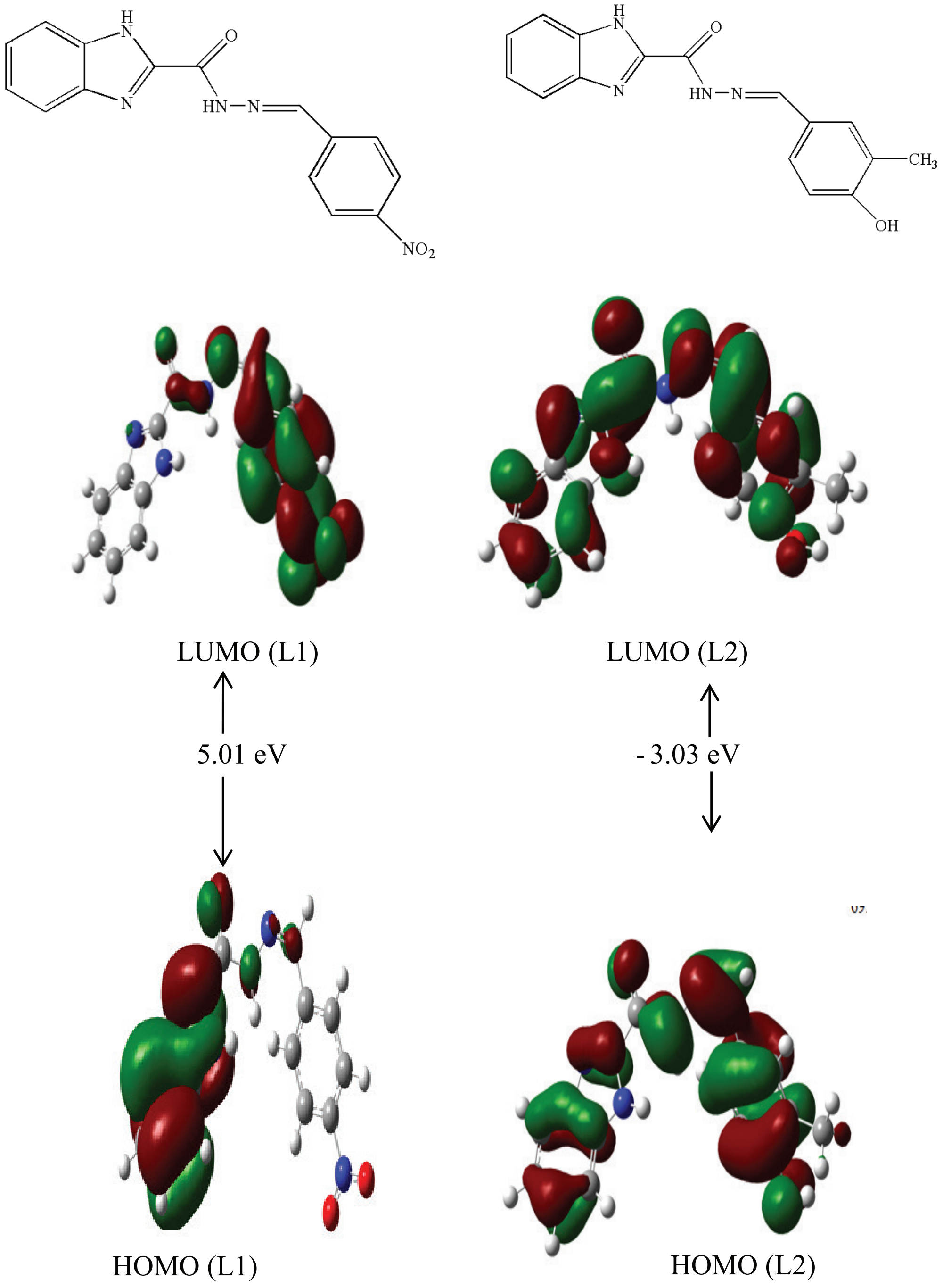

Fig. 9. Computational analysis of HOMO and LUMO levels of L1 and L2.

(1 + 1) was added and the solution was diluted with water again. 0.1 mL stock solution of ligand was mixed with 0.2 mL sample solution in a volumetric flask and then the solution was spiked with different known concentrations of Bi^{3+}. The solution was analyzed via a UV-vis spectrometer. The measured absorbance values were calculated for the Bi^{3+} concentrations using the standard addition method.

To ensure that the method is valid and has reasonable accuracy and precision, recoveries of the Bi^{3+} in water samples and stomach medicine were determined. The results shown in Tables 4 and 5 indicate good recoveries in the range of 94–105%. The relative standard deviations (R.S.D) were found to be <5%. The calculated t-values listed in Tables 4 and 5 were less than the critical (tabulated) value 2.78. Thus, there is no significant difference between averages and variances of results for 95% level of significance. These results indicate the capability of the method in the determination of Bi^{3+} in the real samples.

Table 4
Application of recommended method for determination of Bi^{3+} in water samples (n = 5)

Sample	L1				L2			
	Added ($mg\cdot L^{-1}$)	Found ($mg\cdot L^{-1}$)	Recovery (%)	t-test	Added ($mg\cdot L^{-1}$)	Found ($mg\cdot L^{-1}$)	Recovery (%)	t-test
Tap water	1.0450	0.9893	94.67	0.27	1.0450	0.9982	95.52	1.77
	2.0900	2.1473	102.74	2.78	2.0900	1.9829	94.88	2.54
	3.1350	3.0426	97.05	0.99	3.1350	2.9517	94.15	2.24
	4.1800	4.0690	97.35	2.69	4.1800	4.2348	101.31	1.54
	5.2250	5.2944	101.33	1.48	5.2250	5.2785	101.02	1.57
Pond water	1.0450	1.0937	104.66	0.29	1.0450	1.0335	98.30	0.99
	2.0900	2.0175	96.53	1.46	2.0900	2.1218	101.52	0.57
	3.1350	3.2253	102.88	2.67	3.1350	3.0629	97.70	2.37
	4.1800	4.2203	100.97	0.90	4.1800	4.1836	100.09	1.60
	5.2250	5.2137	99.78	2.04	5.2250	5.2279	100.06	1.65
Lake water	1.0450	0.9907	94.80	2.03	1.0450	1.0826	103.60	0.02
	2.0900	2.0775	99.40	1.73	2.0900	2.1318	102.00	0.89
	3.1350	3.1768	101.33	1.61	3.1350	3.0932	98.67	0.89
	4.1800	4.1890	105.00	2.13	4.1800	4.1591	99.50	2.39
	5.2250	5.2041	99.60	0.78	5.2250	5.1787	97.20	1.95

Table 5
Application of recommended method for determination of Bi^{3+} in bismuth potassium citrate particles (n = 5)

L1					L2				
Measured value ($mg\cdot g^{-1}$)	Added ($mg\cdot g^{-1}$)	Found ($mg\cdot g^{-1}$)	Recovery (%)	t-test	Measured value ($mg\cdot g^{-1}$)	Added ($mg\cdot g^{-1}$)	Found ($mg\cdot g^{-1}$)	Recovery (%)	t-test
107.72	0	106.75	–	1.82	103.63	0	103.51	–	0.28
	10	117.83	101.10	0.21		10	114.12	104.90	1.87
	20	128.59	104.35	1.63		20	122.97	96.70	1.56

4. Conclusions

The recognition of two benzyl-functionalized benzimidazolylidene ligands (L1 and L2) towards transition metal ions was studied by UV-vis spectrophotometry. According to the red shift of characteristic peak and enhancement of absorbance at 205 nm when ligands coordinated with transition metal ions, Bi^{3+} ion can be qualitatively distinguished and accurately quantified. Stoichiometric ratio was 1:1. Beer's law was found to obey for Bi^{3+}-L1 and Bi^{3+}-L2 in the concentration range of 0.21–6.48 $\mu g\cdot mL^{-1}$. The detection limits of L1 and L2 towards Bi^{3+} were 95.51 and 55.80 $\mu g\cdot mL^{-1}$. The obtained results showed that the proposed method is efficient for recognizing Bi^{3+} ion with possible analytical applications. The DFT calculation results were in good agreement with the results of UV-vis experiments which showed the higher selectivity of L2 towards Bi^{3+} ion.

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