

Hg(II) Selective Complexation by Chromoionophoric Calix[4]arene Derivative

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Abstract The present article describes an exploration regarding Hg(II) selective complexation behavior of 5,11,17,23-tetrakis[(N,N-dimethylamino)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (**4**). The binding affinity of **4** toward selected transition metal ions such as Cd(II), Co(II), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II) have been investigated by UV-visible and fluorescence spectroscopic techniques. From the results it has been noticed that **4** confers a pronounced preference for Hg(II) in complexation phenomenon even in the presence of other metal ions. The results of Job's plot analysis reveal 1:1 host-guest complex formation between Hg(II) and **4**. The FT-IR spectroscopy also supports the complexation affinity of **4** for Hg(II).

Keywords Calixarene · Solvatochromic effect · Complexation · Metal ions · Supramolecular chemistry

Introduction

Mercury is one of those elements that accumulate in living tissues, thereby causing many harmful effects on human health [1, 2]. It might be brought into the environment by various processes including human activities; which has influenced and modified the natural cycles. However, over the last two decades, the need has increased for the

determination of extremely low concentrations of mercury in various samples. Thus, the design and development of efficient ligands that may be used to selectively complex these metal ions are turning out to be extremely important. To this end, calixarenes a class of macrocyclic ligands has been extensively studied [3]. They have received considerable attention because of their potential for the synthesis of highly efficient and selective receptors [4, 5].

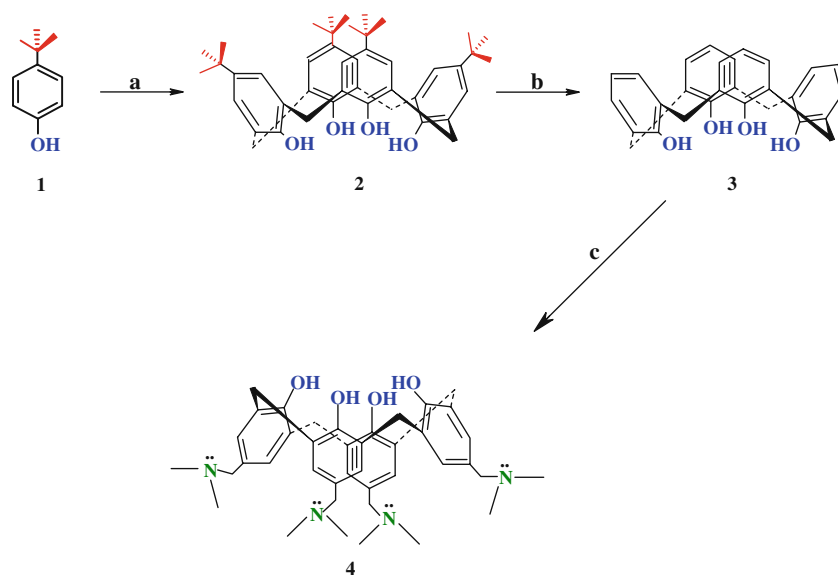
Recently, some selective fluorescent chemosensors for mercury(II) have been reported based on calixarenes [6–9], quinolines [10–14], fluorescein [15–18], rhodamine [19–25], pyrene [26, 27], naphthalimide [28–30] and other structural moieties [31–35]. However, most of them have disadvantage in practical use, such as interference from other metal ions, strict reaction condition or complicated synthetic route. Consequently, it has been shown that the presence of soft donor atoms in ligands results in a considerable increase in stability of their complexes with soft cations such as mercury, while diminishing the stability of their alkali, alkaline earth metal ions and hard transition metal ion complexes [36, 37]. Therefore, development of simple fluorescent chemosensor that can selectively sense Hg(II) is significant.

In view of the above studies and our previous experience [38], herein we report an investigation regarding synthesis, solvatochromic effect and complexation behavior of 5,11,17,23-tetrakis[(N,N-dimethylamino)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (**4**) using UV-visible, fluorescence and FT-IR techniques.

The *p*-*tert*-butylcalix[4]arene **2** as well as its derivatives **3** and **4** illustrated in Scheme 1 were prepared by methods describe previously [39–41]. The characterization of the compounds for the confirmation of their structure and

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Scheme 1 Reaction pathway for synthesis of ligand **a** HCHO/NaOH **b** Phenol-AlCl₃/(dry)Toluene **c** Dimethylamine-HCHO Acetic acid: THF



purity was made by various techniques such as, melting point, TLC, IR, and elemental analysis.

Experimental Section

General Experimental Information

Melting points were determined on a Gallenkamp (UK) apparatus in a sealed capillary tube. Thermo Nicolet AVATAR 5700 FTIR spectrometer was used for recording IR spectra using KBr pellets in a wide spectral range, *i.e.* 4000–400 cm⁻¹. Elemental analyses were performed using a CHNS instrument model Flash EA 1112 elemental analyzer. UV-visible spectral studies of ligand **4** (Scheme 1) and its metal complexes were performed on a Perkin Elmer Lambda-35 UV-visible double beam spectrophotometer using standard 1.00 cm quartz cells. Analytical TLC was performed on pre-coated silica gel plates (SiO₂, Merck PF₂₅₄). All the reagents and solvents were of analytical grade and used without further purification.

Synthesis of Ligand 4

The required starting material *p*-tert-butylcalix[4]arene (**2**), calix[4]arene (**3**) and tetra amine derivative (**4**) were prepared by published procedures [39–41].

Synthesis of Metal Complexes with 4

For FT-IR experiments, **4** with a nitrate salt of Hg(II) and KBr were mixed and then ground to powder form in an agate mortar. The resulting mixture was kept in oven at 115 °C for 1 h and then pressed to form pellets [42].

Analytical Procedure

Stoichiometric Ratio of the Hg(II) and 4 in the Complex

Job's method [43] (continual variation method) was used to determine the stoichiometric ratio between **4** and Hg(II) for their complexation in DMF solution. The solutions were prepared by mixing equimolar concentration (4.3×10^{-5} M) of both components in different ratios varying from 1:9 to 9:1. Then the absorbance was measured at 265 nm.

General Procedure for Fluorescence Study

Stock solutions of (1.00 mM) **4** and metal nitrate salts were prepared in DMF. Test solutions were prepared by placing 50 μl of **4** into a cuvette, adding appropriate aliquot (10 eq) of each metal stock, and diluting the solution up to 3.5 mL with DMF. Same equivalents (10 eq) were taken for the interference study of co-existing ions into a solution containing **4**-Hg(II) complex. For all measurements, excitation was 310 nm; excitation and emission slits widths were both 5 nm each.

Results and Discussion

Usually, a red shifting (positive solvatochromism) [44] is observed with increase in polarity of solvent because a polar solvent tends to stabilize the excited state for almost all molecules and vice-versa is true for negative solvatochromism. Moreover, it has been found that solvent plays an important role in complexation phenomena involving ionic or neutral species and macrocyclic ligands in general and calixarenes in particular [45, 46].

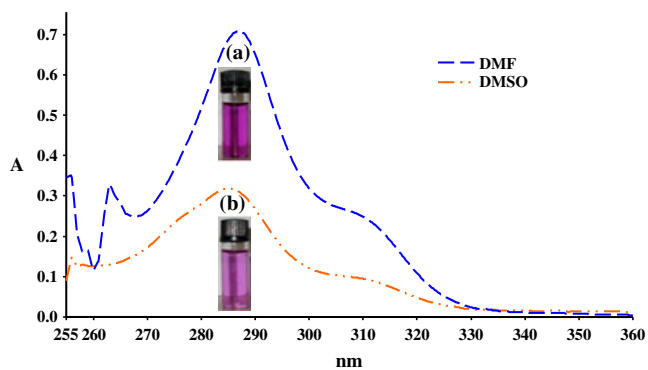


Fig. 1 UV-visible spectral behavior and inset naked eye color changes of compound **4** in **a** DMF **b** DMSO (4.3×10^{-5} M)

In order to determine solvatochromic property of ligand **4**, different solutions of ligand **4** have been prepared with a fixed concentration of 4.3×10^{-5} M in various solvents (Fig. 1) such as acetone (ACO), acetonitrile (ACN), chloroform (CF), dichloromethane (DCM), tetrahydrofuran (THF), methanol (MeOH), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) to evaluate the spectral changes in these solvents.

In DCM, CF and THF, the UV-visible spectra of **4** show aggregation and too much noise even at low concentration, whereas in ACO and ACN, **4** has partial solubility therefore, all of them have been discarded. The color of ligand **4** and changes in the absorption spectrum (Fig. 1) in DMF and DMSO suggest its potential as a probe for these solvents. Ligand **4** shows its absorption maxima at 285 nm accompanied by its shoulder at 310 nm in DMF/DMSO may be attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

The naked eye color changes of **4** in DMF gives clear evidence for hydrogen bonded interactions (i.e. $N \cdots H$) between DMF and ligand **4**. Thus, DMF was preferred for absorption as well as fluorescence studies since it gives

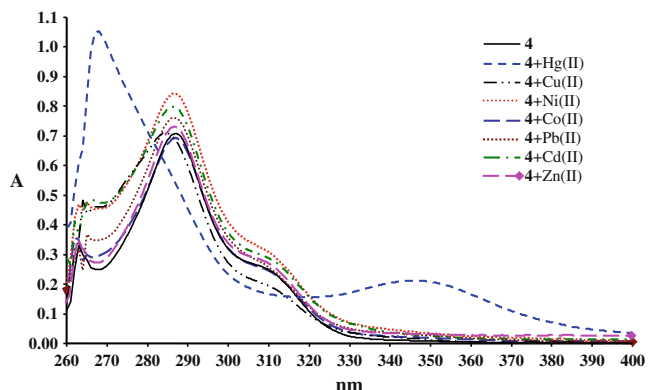


Fig. 2 Comparative UV-visible spectra of **4** (4.3×10^{-5} M) before and after titration with selected transition metals (10 eq)

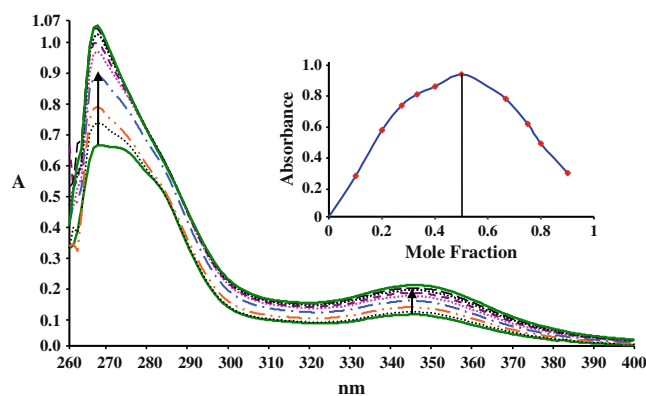


Fig. 3 UV-visible titration spectra of **4** (4.3×10^{-5} M) upon addition of various equivalents of Hg(II); (inset) Job's plot of **4** and Hg(II)

absorption band of maximum intensity within standard absorption limits and shows no any aggregation as compared with DMSO or other solvents.

Complexation Behavior of **4**

Macrocyclic based Mannich bases (i.e. calixarene) have been proved to be ideal candidates for the formation of stable complexes with soft/borderline metal cations such as Cu(II), Hg(II) and Pb(II) etc [47]. Therefore, in this work, we have selected calix[4]arene derived Mannich base for its complexation study owing to ease of its synthesis and possessing borderline nitrogen donor atom with macrocyclic effect.

Thus, different titration experiments were carried out in order to determine whether ligand **4** can form complexes with the selected metals and consequently different parameters were checked to evaluate its selectivity.

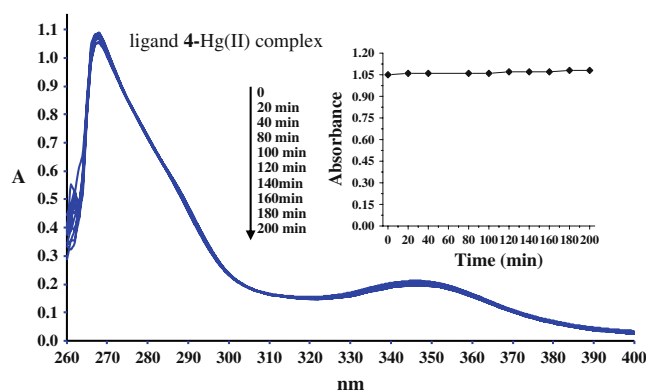


Fig. 4 Time-dependent UV-visible spectrum of **4**-Hg(II) complex (4.3×10^{-5} M) in DMF upon continuous irradiation of UV light; (inset) graph showed stability of **4**-Hg(II) complex with respect to time

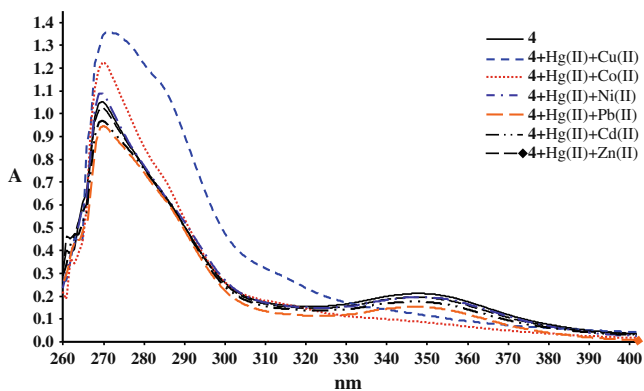


Fig. 5 Interference study of Hg(II)-complex of **4** with selected transition metals (10 eq) in DMF

UV-Visible Study

Preliminary measurements were made to check out the complexation behavior of **4** in DMF solution (4.3×10^{-5} M) for selected metal ions such as Cd(II), Co(II), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II). The UV-visible spectra of **4** (free) show a strong band at 285 nm which is attributed to $\pi \rightarrow \pi^*$ and its shoulder at 310 nm due to $n \rightarrow \pi^*$ transition (Fig. 2). Generally, an enhancement in the intensity of the band, appearance of new bands and/or shifting of bands to shorter or longer wavelengths than that of the free ligand after complexation is an informative sign of the complex formation. However, in this case, addition of each metal cation (10 equiv) in **4** causes little enhancement in the absorption intensity of the previous bands as shown in Fig. 2, whereas addition of Hg(II) ion causes significant hypsochromic shifting of band to 265 nm (~ 20 nm) along with appearance of new band at 345 nm. This shifting and appearance of new band could be assigned to metal-ligand charge transfer (MLCT) absorp-

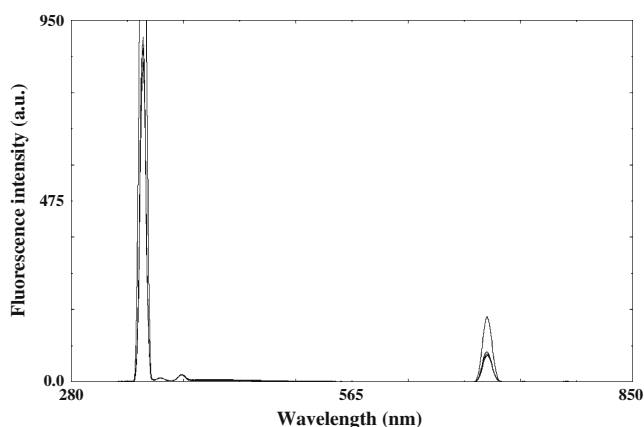


Fig. 6 Fluorescence spectra of selected (free) transition metal ions (4.3×10^{-5} M) in DMF solution

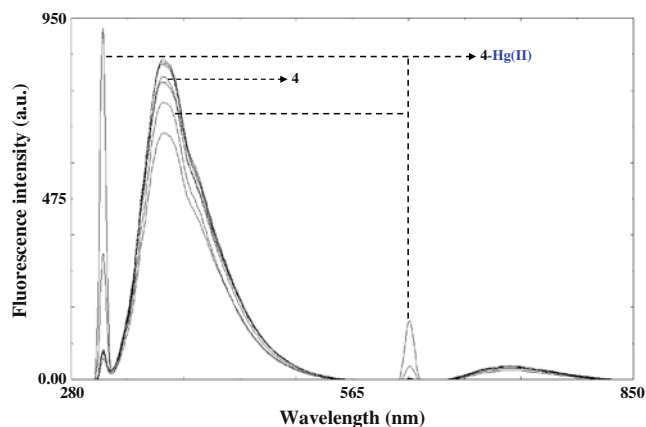


Fig. 7 Fluorescence spectra of **4** (4.3×10^{-5} M) in DMF solution before and after adding nitrate salt of transition metals (10 eq)

tions between Hg(II) and the nitrogen atoms of amine functions on macrocycle [48]. However, other metal ions even borderline metal ions like Co(II), Cu(II), Ni(II) and Zn(II) does not take significant part in complexation process with **4**. This shows that alone soft/hard nature of ligand or metal ion is not only the important factor for selectiveness but also other factors like thermodynamic stability, ionic radii, cavity size as well as geometry of ligand and metal ion confers the selectivity of ligand toward a specific metal ion.

In an attempt to investigate the quantitative analytical behavior of ligand **4** (4.3×10^{-5} M) for Hg(II) complexation. The absorption profile as a function of metal ion concentration was obtained followed by increase in the intensity of absorbance with respect to increased Hg(II) concentration (Fig. 3). After 10 equiv, the intensity did not significantly change, which implies that **4** could quantitatively intimate the concentration of Hg(II) up to 4.3×10^{-4} M.

The method of continuous variation was applied by varying the concentration of both ligand **4** and Hg(II) to

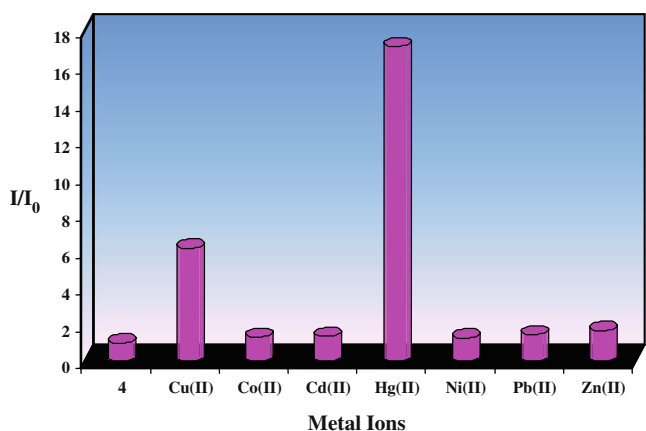


Fig. 8 Ratiometric behavior (I/I_0) of **4** in the presence of selected transition metals in DMF solution

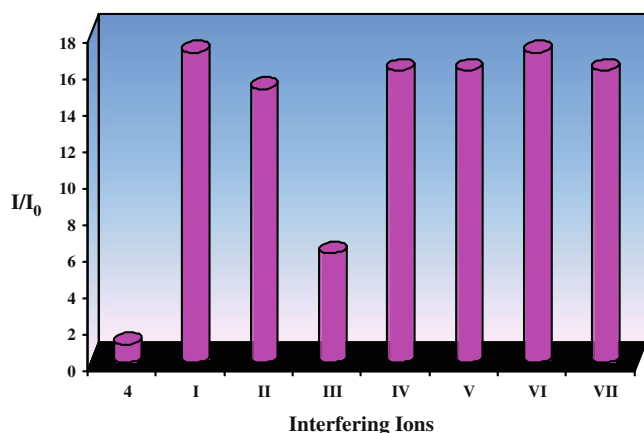


Fig. 9 Ratiometric behavior (I/I_0) of **4** in the presence of Hg(II) and other co-existing ions in DMF solution. I=**4**+Hg(II), II=**4**+Hg(II)+Cd(II), III=**4**+Hg(II)+Cu(II), IV=**4**+Hg(II)+Pb(II), V=**4**+Hg(II)+Ni(II), VI=**4**+Hg(II)+Co(II), VII=**4**+Hg(II)+Zn(II)

determine the stoichiometry of **4**-Hg(II) complex. Fig. 3 (inset graph) shows typical Job's plots of **4**-Hg(II) complexation at 265 nm, the maximum point of the mole fractions was found as 0.5, which refers to ligand-metal ratio of 1:1 in the complex.

Response time measurement of chromoionophore based on macrocyclic compounds is an intense area of study. Therefore, it has been aimed to investigate the response time and stability of **4**-Hg(II) complex. The results reveal that **4** responds very fast and when titrated with Hg(NO₃)₂, a significant hypsochromic shifting accompanied by enhancement in absorption of a band at 265 nm and appearance of new band at 345 nm occurs very rapidly within 1 min. and remains stable up to a long time (Fig. 4), i.e. remains same even after three to 4 days.

Selectivity of ligand **4** toward Hg(II) ion in the presence of interfering ions was examined by the competitive experiments carried out in the presence of Hg(II) by mixing Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) (in 1:1 ratio) separately as shown in Fig. 5. It was observed that except Cu(II), other metal ions do not interfere on the absorption spectra of **4**-Hg(II) complex.

Fluorescence Study

Fluorescence spectral properties of free metal ions as well as cationic fluorescence sensing ability of ligand **4** toward these cations was investigated and illustrated in Figs. 6 and 7. Upon addition of 10 eq. of each cation, despite the border line nature of Cu(II), Co(II), Ni(II) and Zn(II), all metal ions give more or less same response as **4**. However, addition of Hg(II) causes remarkable enhancement in the emission intensity of band from 51 to 873 a.u at 373 nm followed by appearance of new band at 623 nm. Such a considerable difference between Hg(II) and other metal ions

in terms of appearance of new band as well as enhancement in emission intensity indicates that not only the binding sites of ligand **4** are more compatible to Hg(II) than other metal ions but there are other factors that are also responsible for the selective complexation as discussed earlier.

The ratiometric behavior of **4** in the presence of selected transition metal ions also supports the pronounced Hg(II) selectivity of **4** (Fig. 8); where upon interaction of **4**, the ratio (I/I_0) for the **4**-Hg(II) system increased 17-fold compared with free ligand (**4**) and 3-fold with Cu(II).

To gain more insight into the practical applicability of **4** in Hg(II) signaling, competitive experiments on the signaling of Hg(II) ions by ligand **4** in the presence of various co-existing ions were carried out as illustrated in Fig. 9. Fluorescence spectroscopic study of interfering ions also supports the results obtained in the UV-visible spectra; showing no any shifting (bathochromic or hypsochromic shift), quenching or enhancement in the fluorescence intensity of **4**-Hg(II) complex after the addition of metals and gave approximately similar results except Cu(II). Moreover, fluorescence changes (I/I_0) of the **4**-Hg(II) were not significantly affected by presence of 10 equiv of other metal ions except Cu(II).

Regarding another complexation possibility between the phenolic OH functionalities of host and the metal ions, it may be presumed that the metal may be able to interact with the phenolic moieties at lower rim of calix[4]arene [49, 50], but due to intramolecular hydrogen bonding of lower rim, metal ion may not be accommodated within this region of lower cavity of calix[4]arene. Nonetheless, all the UV-visible and fluorescence spectra suggest that **4** may be used as a potential Hg(II) selective chromoionophore. Thus, according to the Job's plot analysis as discussed above, it has been revealed that Hg(II) forms 1:1 metal ligand complex with **4**. Therefore, the proposed mechanism for metal-ligand interaction is shown in Fig. 10 [51–55].

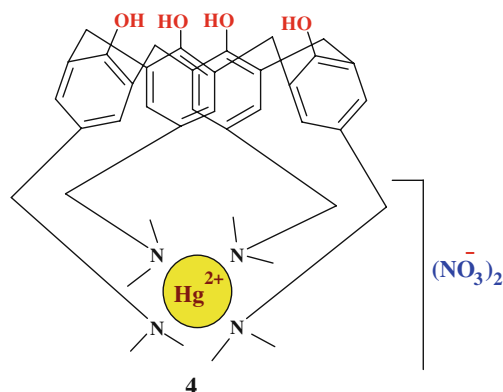
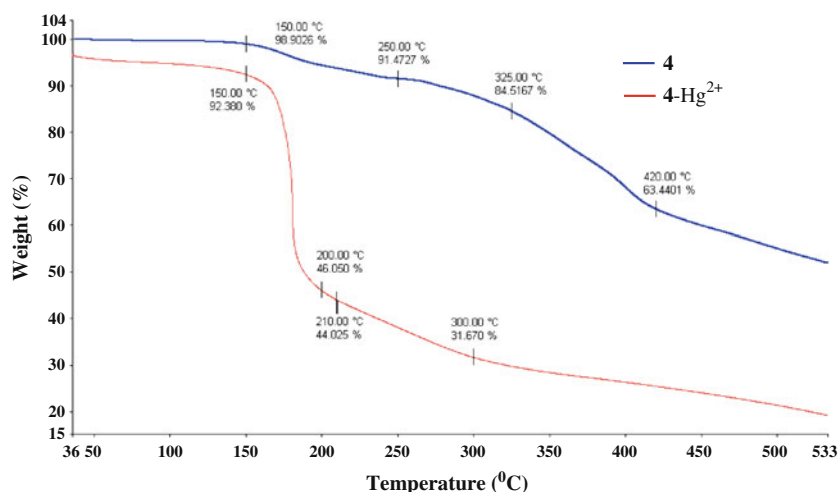


Fig. 10 Proposed interaction between compound **4** and Hg(II).

Fig. 11 The TG curves of compound **4** and its complex with Hg(II) in N₂ atmosphere



Thermal Analysis

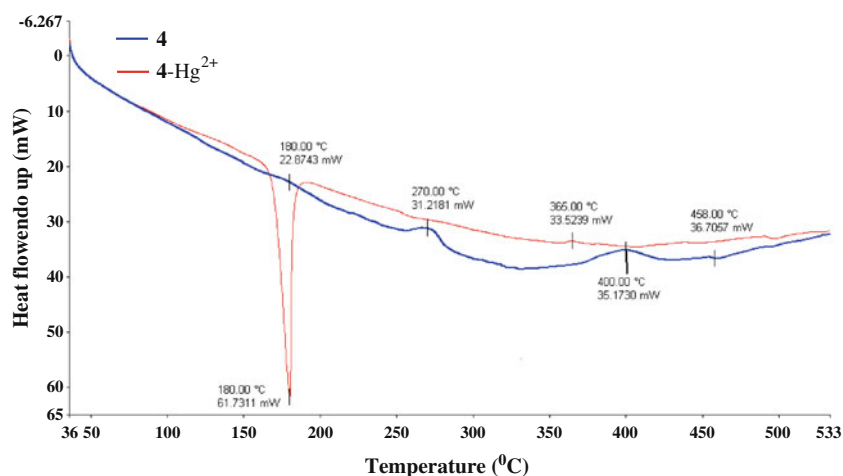
The thermo gravimetric curves enable us to establish information on thermal stability, amount confirmation and purity of the compounds. Thus, thermal stability of the ligand **4** and its Hg(II) complex was evaluated by thermal analysis (TG/DTA). It was found that **4** undergo a two-step thermal degradation (Figs. 11 and 12). The first step (150–250 °C) could be attributed to the loss of the relative amino groups of **4**, while the second (325–420 °C) is due to the cleavage of the calixarene backbone. As seen from TG curve of Hg(II)-**4** complex, it shows less stability than its parent molecule as it shows 46% (1.258 mg) mass loss in the first step (150–200 °C) whereas it was reduced to 31% (0.34 mg) by wt at 300 °C in the second step. The DTA result of the **4** showed the weight loss endothermic weight loss endothermic peaks whereas **4**-Hg(II) complex showed surprisingly sharp weight loss exothermic peak temperature of 180 °C, while others at 270, 400 and 458 °C in the

parent molecule becomes absent. The results indicated a remarkable interaction between the amino groups of **4** and the Hg(II). In general, the processing temperature limit of Hg(II) complex of **4** is up to 150 °C.

FT-IR Study

Binding mode of ligand **4** with Hg(II) was further confirmed through FT-IR spectroscopic analysis since it provides strong evidence of complexation between ligand and metal ion. FT-IR spectrum showed characteristic bands of this ligand (KBr/cm⁻¹) at 3180 [ν (O...H) intermolecular hydrogen bond], 2935 ν (CH₂), 2872 δ (CH₂), 1377 ν (C-N). Coordination of the Hg(II) ion can be readily verified in the FT-IR spectrum of the complexes. Figure 13 clearly gives the stronger indication for complexation as shifting in various frequencies of specific functional groups occurred as a result of introduction of Hg(II) into ionophoric cavity. For example, marked changes appeared

Fig. 12 The DTA curves of compound **4** and its complex with Hg(II) in N₂ atmosphere



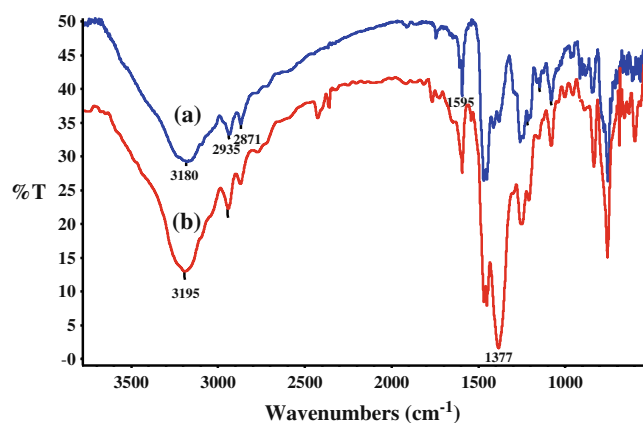


Fig. 13 Comparative FT-IR spectral analysis a Compound **4** (—) b 4-Hg(II) complex (—)

in the region of 1370–1450 cm^{-1} , where considerable decrease in the intensity of band at 1445 cm^{-1} and appearance of a new sharp band at 1377 cm^{-1} for $\nu(\text{C}-\text{N})-\text{Hg}(\text{II})$ complexation indicates the involvement of N donor atoms of amino groups in the complexation process with Hg(II). Other prominent bands at 3180 and 2871 are also shifted to 3195 and 2861 cm^{-1} respectively; which give informative sign for changes in the geometry of **4** after complexation.

Conclusions

In conclusion, the chemosensing/chromoionophoric potential of ligand **4** was found with high selectivity toward Hg(II) among a series of selected metal ions that attributed to the changes in the intensities of spectral lines observed in UV-visible and fluorescence spectra of 4-Hg(II) complex. It is also confirmed by TG/DTA and FTIR spectral analysis. Moreover, the design of **4** that comprises four donor nitrogen atoms as binding sites seems to be an ideal geometry in terms of size, arrangement and accommodation of Hg(II). It infers the importance of pre-organization in designing the ligand. From the results, it may be concluded that the study may be treated as a test for the detection of Hg(II). The study will find its applicability in various fields of analytical and environmental chemistry.

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