A highly copper selective chromogenic calix[4]arene derivative

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In this article, copper selective complexation behavior of 5,11,17,23-tetrakis[(*N*,*N*-dicyclohexylamino)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (**4**) has been explored. Besides this, the binding ability of **4** toward different metal ions such as Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} has been investigated by UV-visible and fluorescence spectroscopies. The chromoionophore **4** shows pronounced selectivity for Cu^{2+} even in the presence of other metal ions. The results reveal that Cu^{2+} forms 1 : 1 host–guest complex with **4**. The FT-IR spectroscopic method has also been applied for further confirmation of complex formation between **4** and Cu^{2+} and found to be satisfactory.

Introduction

In the recent years, the development of robust chromoionophoric receptors or optical chemical sensors remains an important venture for the recognition of heavy metals *via* ionic or molecular interactions because of their applications in areas of biological, environmental and chemical systems.[1–8] Among the heavy metals copper is an essential element that is very important for creatures however, its excessive or inadequate uptake causes several health hazards.[9–12] Therefore, it is very important and meaningful to develop better methods to detect copper in the environment and biological systems.

Although various intriguing aspects of complexation of alkali and alkaline earth metal ions were disclosed by studying the absorption behavior of chromophoric groups.[13,14] Nevertheless, there are relatively few reports on the design of sensors for heavy metal ions.[15] Because, unlike alkali and alkaline earth metals, heavy metals do not differ too much in size, and possess similar chemistry. However, they can establish coordinative interactions of very different energies, which can be used for discriminative purposes, especially for fluorescent sensing.

In this regard, calixarenes have received considerable attention because of their potential for the synthesis of highly efficient and selective receptors.[16–18] Several fluorescent chemosensors based on calixarenes have been synthesized and show highly specific recognition, especially towards alkali metal cations. However, the generation of fluorescent sensors for heavy metals is of increasing importance in calixarene chemistry. Consequently, many excellent studies of Cu^{2+} sensing by synthesized colorimetric/fluorescent probes have been reported and investigated for selective complexation of metal ions,[19–26] which reveal that the sensing ability and selectivity depends upon the nature of substituents, size and conformation of calix[4]arene molecule.

In view of the above studies and our previous experience,[3] herein we report an investigation regarding synthesis of metal complexes and solvatochromic effect of 5,11,17,23-tetrakis[(*N*,*N*-dicyclohexylamino)methyl]-25,26,27,28-tetrahydroxycalix[4]-arene (**4**) using UV-visible, fluorescence and FT-IR techniques.

Result and discussions

The *p-tert*-butylcalix[4]arene **2** as well as its derivatives **3** and **4** illustrated in Scheme 1 were prepared by methods described previously.[27–29] The characterization of the compounds for the confirmation of their structure and purity was made by various techniques such as melting point, TLC, IR, and elemental analysis.

Solvatochromic effect

It is a general perception in solvatochromic study that ground state is less polar than the excited state for almost all molecules. Therefore, a polar solvent will tend to stabilize the excited state more than the ground state. If a red shift (bathochromic effect) is observed in the absorption spectrum with an increase in the polarity of solvent, it is termed as "positive solvatochromism" and *vice versa* is true for less polar solvents.[30] Spectral investigations of ligand **4** were evaluated in various solvents (Fig. 1) like acetone (ACO), acetonitrile (ACN), chloroform (CF), dichloromethane (DCM), tetrahydrofuran (THF), methanol (MeOH), dimethylformamide (DMF) and dimethylsulfoxide (DMSO). UV-visible spectroscopic data, *i.e.* λ_{max}, and molar extinction coefficient (ε in L mol^{-1} cm^{-1}) both are given in Table 1.

Compound **4** shows red shifts in its absorption maxima ($\sim$12 nm range) in DMF and DMSO with respect to CF or DCM. These red shifts can be attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions arising from solvent polarity differences. The color of **4** and changes in the absorption spectrum (Fig. 1 and 2) in different solvents suggest its potential as a probe for these solvents.

Other low polarity solvents like CF, DCM and THF show hypsochromic shifts with a new absorption peak (with reference to DMF and DMSO). From these observations, it may be concluded that probably there is no significant change in the stability of the excited state in the aforementioned

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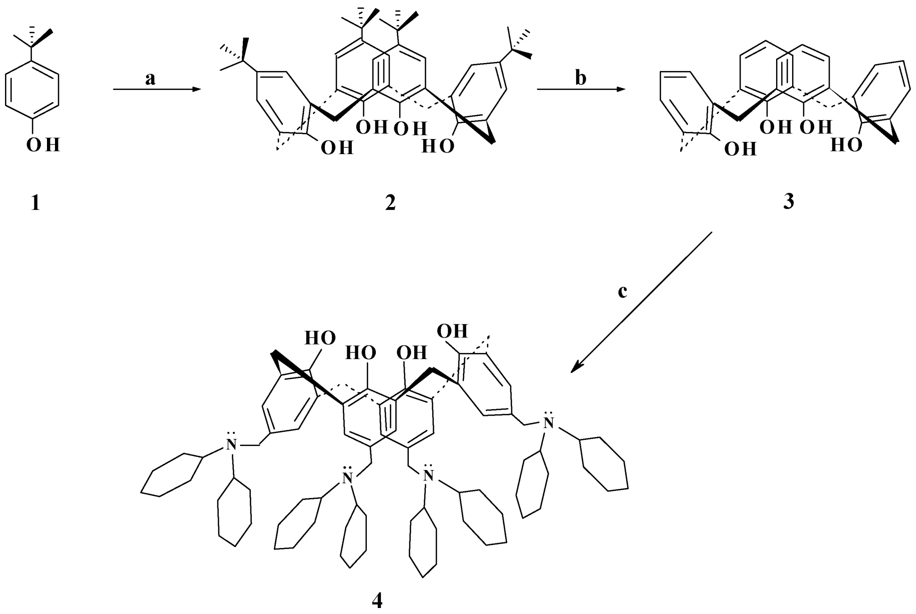

Scheme 1 Reaction pathway for the synthesis of ligand: (a) HCHO/NaOH, (b) phenol – $AlCl_3$/(dry) toluene, (c) dicyclohexylamine–HCHO/acetic acid : THF.

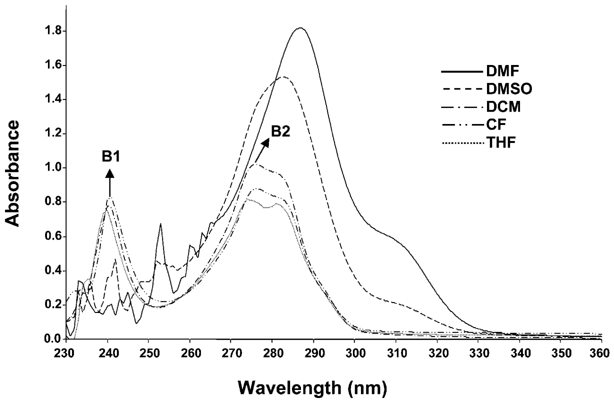

Fig. 1 UV-visible spectral data of ligand **4** in different solvents (4.3×10^{-5} M).

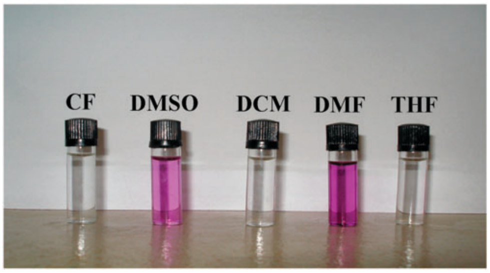

Fig. 2 Naked eye color changes of **4** in DMF and DMSO (4.3×10^{-5} M).

solvents. Moreover, **4** is devoid of groups such as carboxylic or ester groups and possesses moderately intermediate nature bearing nitrogen atom, and it interacts with less polar solvents. That's why it gives blue shifting (*i.e.* negative solvatochromism) in less polar solvents like CF, DCM, and THF with well defined absorption bands B1 and B2 in the regions of 240 and 270–280 nm through $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively.

Table 1 UV-visible spectroscopic data (λ/nm and ε/L mol^{-1} cm^{-1}) of **4** in selected solvent system and the effect of acid and base on it

	Absorption coefficient (L^{-1} mol^{-1} cm^{-1}) at specific λ	
Medium	B1 (ε)	B2 (ε)
DCM	18 605 (240 nm)	23 256 (275 nm), 20 930s (281 nm)
DCM + piperidine	23 256 (246 nm)	23 256 (275 nm), 24 884s (287 nm)
DCM + acetic acid	11 628 (240 nm)	20 930 (275 nm), 18 605s (281 nm)
CF	19 302 (240 nm)	20 930 (276 nm), 19 070s (282 nm)
CF + piperidine	16 279 (243 nm)	23 256 (276 nm), 20 930s (282 nm)
CF + acetic acid	18 605 (240 nm)	18 605 (276 nm), 18 605s (282 nm)
THF	17 442 (240 nm)	18 605 (275 nm), 18 605s (281 nm)
THF + piperidine	53 488 (246 nm)	13 953 (283 nm), 9302s (287 nm)
THF + acetic acid	22 093 (240 nm)	16 279 (275 nm), 16279s (281 nm)
DMF	—	42 325 (287 nm), 13 953s (309 nm)
DMF + piperidine	—	32 558 (287 nm), 11 628s (309 nm)
DMF + acetic acid	—	27 674 (287 nm), 9302s (309 nm)
DMSO	—	35 581 (283 nm), 4651s (310 nm)
DMSO + piperidine	—	34 651 (283 nm), 11 628s (310 nm)
DMSO + acetic acid	—	30 232 (287 nm), 4651s (310 nm)

Many attempts have been made to observe the solvatochromic behavior of **4** in MEOH, THF, ACO and ACN even at low concentration; but due to aggregation and too much noise in the spectra, all of them have been discarded. Thus, DCM was preferred for absorption as well as fluorescence studies since it gives maximum number of absorption bands within standard absorption limits and shows no aggregation as compared with DMF or DMSO.

Effect of acid and base in different solvent systems

A change in the nature of medium in which the compound is dissolved may cause significant effect on its spectral behavior, because interactions between solute and solvent are disturbed and thus, the shapes of bands and their positions are changed. In pursuit of acid and base influence on the equilibrium state of **4**, acetic acid and piperidine were added in its various solvent systems. UV-visible spectra showed that except in THF, no significant change in the spectra was observed when a small amount of piperidine was added to the solutions of **4** in CF, DCM, DMSO and DMF separately. Addition of piperidine in THF caused a dramatic effect (Fig. 3a–e) where appreciable enhancement along with red shifting was observed in both bands (B1 and B2) at 240 and 275 nm (along with shoulder at 281 nm), which shifted to 246 and 283 nm, respectively. Absorption peaks at the longest wavelength indicate that the compound may exist in a dissociated form in DMF and DMSO due to deprotonation of phenolic hydrogens. However, the addition of acid (*i.e.* acetic acid) did not cause a significant effect. The changes in the molar

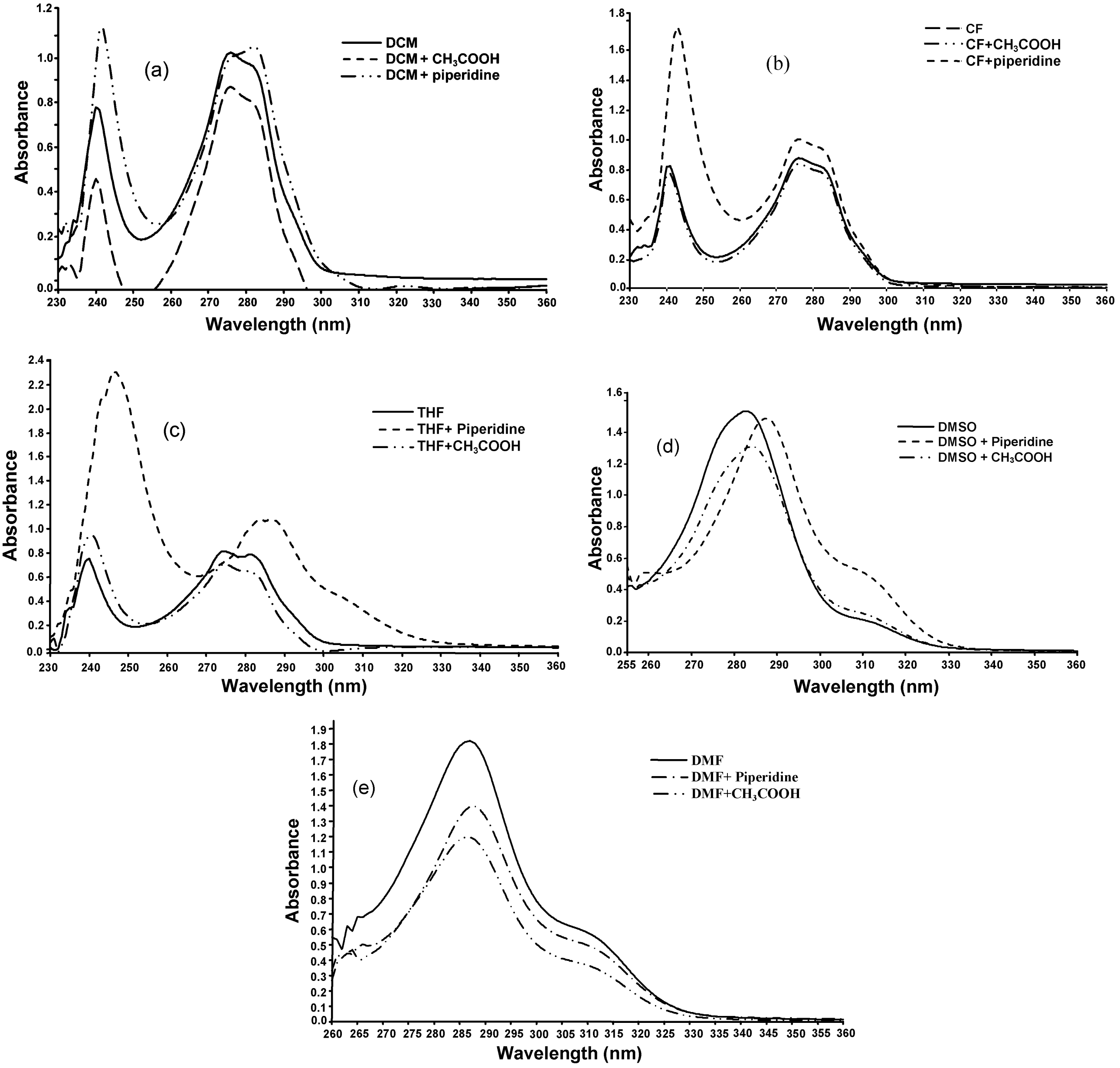

Fig. 3 UV-visible spectral data of **4** (4.3×10^{-5} M) before and after the addition of piperidine and acetic acid in (a) DCM, (b) CF, (c) THF, (d) DMSO, (e) DMF.

extinction co-efficient values of respective absorption bands in different solvents are given in Table 1.

Stability of 4 in selected solvent

After solvent selection, stability determination of compound in a particular solvent is an important parameter, which tells whether the compound used in complexation studies in that solvent is stable or not even after a long time. Therefore, the UV-visible absorption spectra of **4** in DCM were immediately obtained after continuous UV irradiation with the passage of 0, 20, 40, 60, 80, 100, 120 and 140 minutes.[31] The results confirm the stability of **4** in DCM as there was no change appearing in the spectra with the passage of time (Fig. 4).

Complexation studies

In this work, we have chosen a calix[4]arene derived Mannich base for synthesis and complexation study because of ease of its synthesis, possessing a borderline nitrogen donor atom with macrocyclic effect that may prove to be a promising candidate for the formation of stable complexes with soft/borderline metal cations such as Cu^{2+}, Hg^{2+} and Pb^{2+} *etc.*[32]

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

Liquid–liquid extraction study

Liquid–liquid extraction experiments were performed to evaluate the extraction ability of ligand **4** in transferring heavy metals, such as Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}, from aqueous into organic phase, *i.e.* DCM. From the data given in Fig. 5 (Table 2), it has been observed that **4** shows greater affinity toward Cu^{2+} among the metal cations used in the experiments as compared to the parent compound **2**. The extraction ability of **4** toward the metal cations is in the order $Cu^{2+} > Zn^{2+} > Hg^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+} > Pb^{2+}$. The increased extraction of Cu^{2+} with **4** may be due to the presence of borderline nature of both Cu^{2+} and the binding sites (*i.e.* nitrogen containing functionalities). Moreover, the enhanced extraction may reflect the arrangement of binding sites according to the geometry of Cu^{2+}, *i.e.* square planar; as well as the compatibility between the cavity size and ionic radii of **4**. This is in accordance with our previous work.[33,34] This characteristic enhances the utility of **4** in various fields such as food/environmental chemistry, membrane technology, ion selective electrodes technology and phase-transfer reactions.

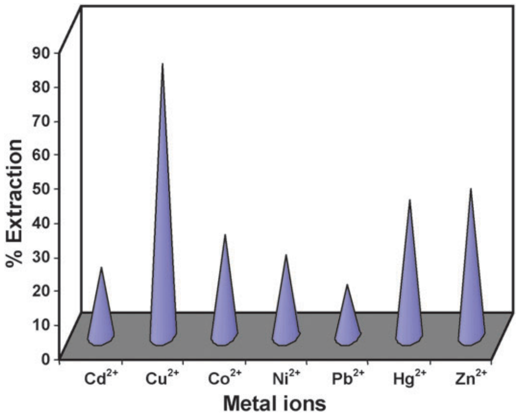

Fig. 5 %Extraction of the selected metal picrates. Aqueous phase, [metal picrate] = 2.5 × 10^{-5} M; organic phase, dichloromethane, [**4**] = 1 × 10^{-3} M at 25 °C for 1 h.

Table 2 Comparative %extraction efficiency of **2** and **4** with selected metal picrates

	Extracted metal picrates (%)						
Ligand	Cd^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}	Hg^{2+}	Zn^{2+}
2[a]	9.4	9.9	7.9	6.3	<1	15.5	—
4	20	80	30	24	15	40	43

[a] Ref. 35.

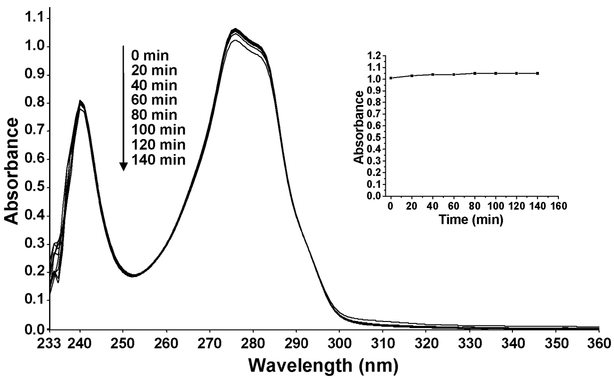

Fig. 4 Time dependent UV-visible absorption spectra of **4** in DCM (4.3 × 10^{-5} M) upon irradiation of UV light.

UV-visible study

The solvatochromic behavior of **4** suggested DCM as a solvent of preferable choice however, attempts have been made to use DCM with a series of different solvents such as methanol, ethanol and isopropanol. Since most of the metal nitrate salts were insoluble in DCM therefore, DCM–MeOH as a binary solvent system was found to be appropriate and selected for complexation studies.

Preliminary measurements were made to checkout the complexation behavior of **4** in DCM–MeOH solution (4.3 × 10^{-5} M) for selected metal ions such as Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}. The UV-visible spectra of free ligand **4** show a strong band at 230–240 nm which is attributed to $\pi \rightarrow \pi^*$ and another band at 270–290 nm due to $n \rightarrow \pi^*$ transition (Fig. 6). Generally, the bands of complexes are shifted to shorter or longer wavelengths than that of the free ligand, but the high intensity of the bands after complexation is also an indication of the complex formation. However, the addition of each metal cation (5 equiv.) in ligand **4** causes enhancement in the intensity of the previous bands as shown in Fig. 6. The electronic spectra of the complexes observed at 230–240 and 270–290 nm could be assigned to nitrogen–metal charge transfer absorption.[36] Upon complexation with metal ions, **4** showed high specificity toward Cu^{2+} because considerable enhancement in the absorptions of bands has been observed as

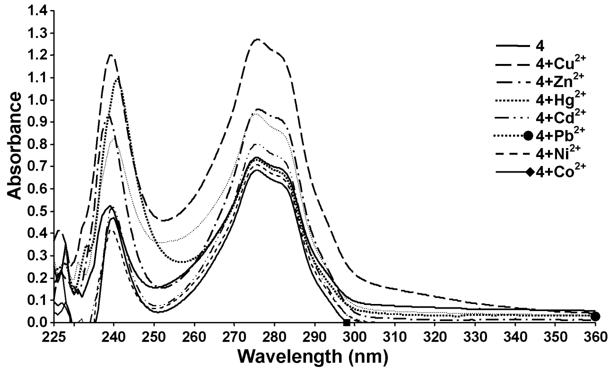

Fig. 6 UV-visible response of **4** (4.3×10^{-5} M) before and after titration with selected metal ions (5 eq.).

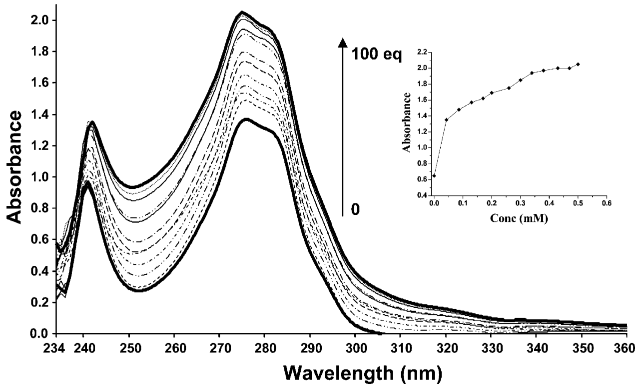

Fig. 7 UV-visible titration spectra of **4** (4.3×10^{-5} M) upon addition of various equivalents of Cu^{2+}.

compared with free ligand **4** or other ions including Hg^{2+} and Zn^{2+}. The results imply that **4** is highly selective for Cu^{2+}.

In an attempt to have further insight into the chromogenic behavior of **4**, the absorption profile as a function of metal ion concentration was obtained followed by increase in the intensity of absorbance with respect to increased Cu^{2+} ion concentration (Fig. 7).

For the determination of stoichiometric ratio between the ligand and metal ion, the Job's plot experiment was conducted by varying the concentration of both ligand **4** and Cu^{2+}. Fig. 13 shows typical Job's plots of ligand–metal complexation. For **4**–Cu^{2+} complex, measured at 275 nm, the maximum value of the mole fractions was found as 0.5, which refers to ligand–metal ratio of 1 : 1 in the complex as shown in Fig. 8.

Response time and the stability of complex in DCM–MeOH

Response time measurement of chromoionophores/chemosensors based on macrocyclic compounds is an intense area of study. However, it has been aimed to investigate the response time and stability of **4**–Cu^{2+} complex. The results reveal that **4** responds very fast and when titrated with $Cu(NO_3)_2{\cdot}3H_2O$, a significant enhancement in absorption of a band in the region of 270–280 nm occurs very rapidly within 1 min and remains stable up to a long time (Fig. 9), *i.e.* remains the same even after three days.

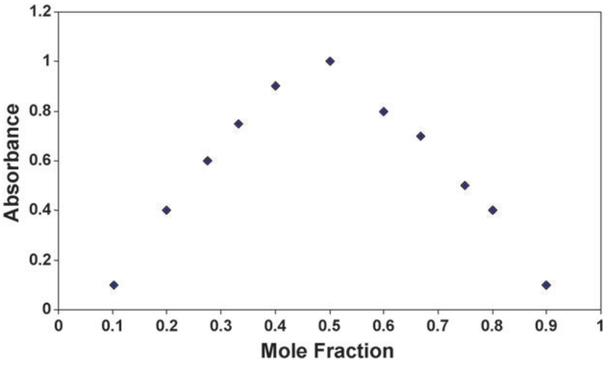

Fig. 8 Job's plot of **4** and Cu^{2+}. The concentration of **4** and Cu^{2+} was kept fixed, *i.e.* 4.3×10^{-5} M. The absorbance was measured at 275 nm.

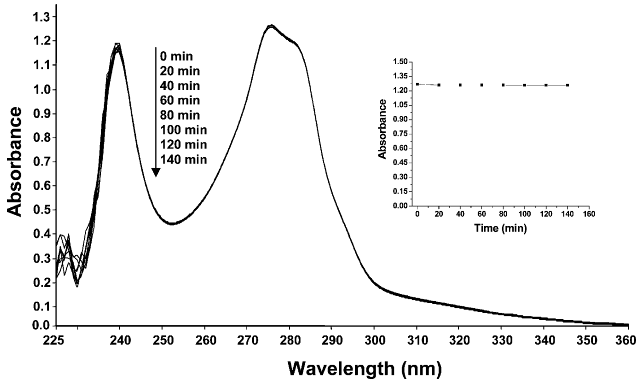

Fig. 9 Time-dependent UV-visible absorption spectra of **4**–Cu^{2+} complex (4.3×10^{-5} M) in DCM–MeOH upon irradiation of UV light; (inset) graph showed stability of **4** with respect to time.

Interference study of competing ions

Selectivity of **4** toward Cu^{2+} in the presence of co-existing ions was determined by the competition experiments carried out in the presence of Cu^{2+} (5 eq.) mixed with Cd^{2+}, Co^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} (5 eq. each) separately as shown in Fig. 10. It was observed that metal ions such as Cd^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+} do not interfere with the absorption enhanced

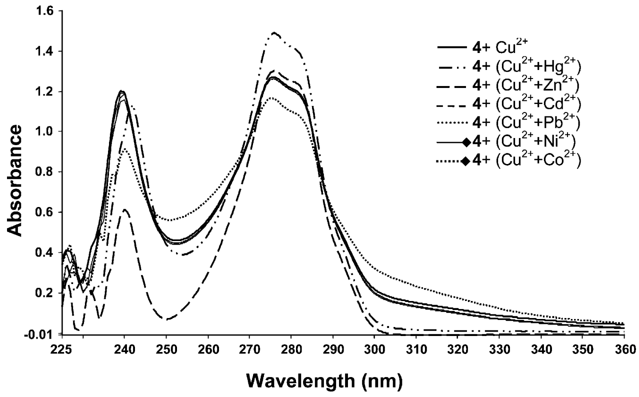

Fig. 10 Interference study of Cu^{2+}-complex of **4** with selected metal ions (5 eq.) in DCM–MeOH.

spectra of **4**–Cu^{2+} complex except Hg^{2+} and Zn^{2+}, which show a little interference.

Fluorescence study

The fluorescence response of **4** toward various cations is illustrated in Fig. 11–13. In cationic fluorescence sensing, upon addition of 5 eq. of each cation, despite the border line nature of Co^{2+}, Zn^{2+} and Ni^{2+}, a little response has been observed with **4** as compared to Cu^{2+}, which causes a dramatic quenching in fluorescence intensity, *i.e.* considerable reduction in the emission intensity from 886 to 458 a.u. at 308 nm.

Such a significant difference in fluorescence intensity between Cu^{2+} and other metal ions indicates that not only the binding sites of **4** are more suitable for Cu^{2+} than for other metal ions but there are other factors that are also responsible for the selective complexation as discussed earlier. This may be attributed to stronger complex formation with the metal ion in preference over others, following Irving–Williams order of stability.[37] Moreover, paramagnetic character and borderline nature of both ligand and metal ion may also impart the selectivity of **4** toward Cu^{2+} ions.

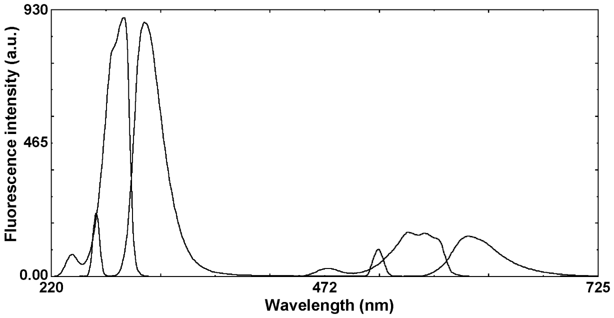

Fig. 11 Excitation and emission spectra of **4** (4.3×10^{-5} M).

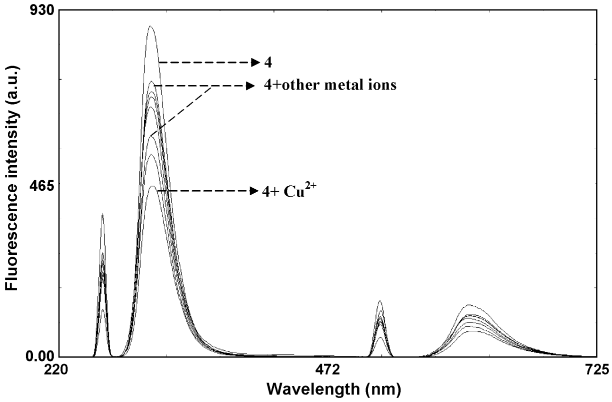

Fig. 12 Fluorescence spectra of **4** (4.3×10^{-5} M) in DCM–MeOH solution before and after adding nitrate salt of selected metal ions (5 eq.).

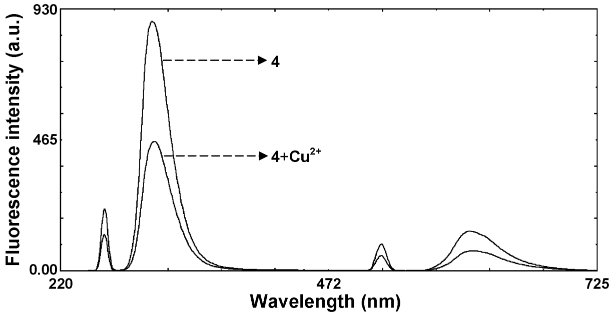

Fig. 13 Fluorescence spectra of **4** (4.3×10^{-5} M) in DCM–MeOH solution before and after adding nitrate salt of Cu^{2+} (5 eq.).

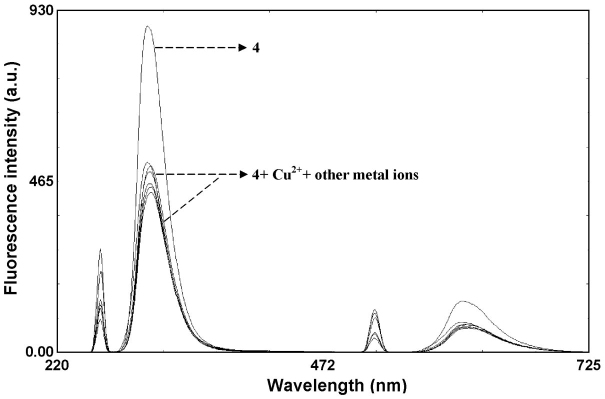

Fig. 14 Interference study of Cu^{2+}-complex of **4** with selected metal ions (5 eq.) in DCM–MeOH using fluorescence spectroscopy.

Fluorescence spectroscopic study of interfering ions also supports the results obtained in the UV-visible spectra as there was no shifting (bathochromic or hypsochromic shift), quenching or enhancement in the fluorescence spectra of **4**–Cu^{2+} complex after the addition of metals and gave approximately similar results (Fig. 14).

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[38,39] 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 Cu^{2+} selective chromoionophore. Thus, according to the Jobs' plot analysis as discussed above, it has been revealed that Cu^{2+} forms 1 : 1 metal–ligand complex with **4**. The proposed mechanism for metal–ligand interaction is shown in Fig. 15.

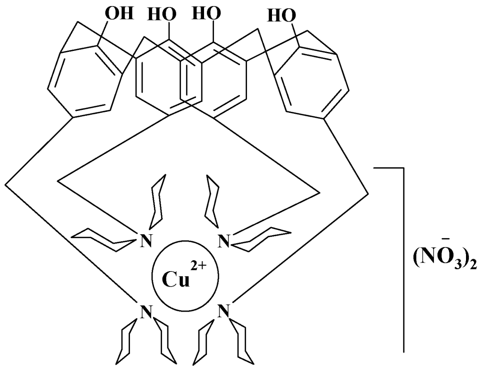

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Fig. 15 Proposed interaction between compound **4** and Cu^{2+}.

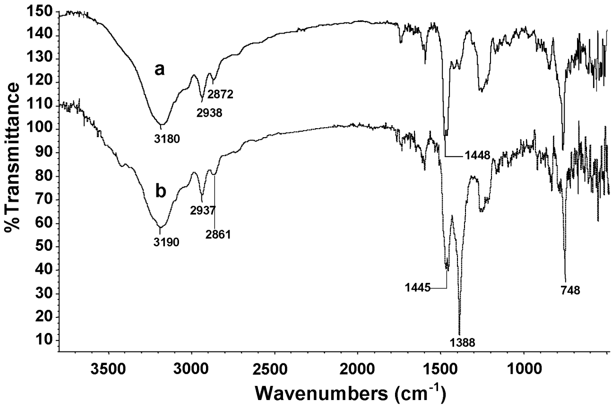

Fig. 16 Comparative FT-IR spectra for (a) compound **4**, and (b) Cu^{2+}-complex of **4**.

FT-IR study

FT-IR spectroscopic technique also provides strong evidence of complexation of **4** with Cu^{2+}. FT-IR spectrum showed characteristic bands of this ligand (KBr/cm^{-1}) at 3180 [ν(O···H) intermolecular hydrogen bond], 2938 $\nu(CH_2)$, 2872 $\delta(CH_2)$, 1379 ν(C–N). Coordination of the Cu^{2+} ion was readily evidenced in the FT-IR spectrum of the complexes. Fig. 16 clearly gives the stronger evidence for complexation as shifting in various frequencies of specific functional groups occurred as a result of introduction of Cu^{2+} into receptor cavity. For example, marked changes appeared in the region of 1370–1450 cm^{-1}, where considerable decrease in the intensity of band at 1448 cm^{-1} and appearance of a new sharp band at 1388 cm^{-1} for ν((C–N)–Cu^{2+}) complexation indicates the involvement of N donor atom of secondary amine in the binding process with Cu^{2+}. This clearly indicates the formation of **4**–Cu^{2+} complex. Other prominent bands at 3180 and 2872 are also shifted to 3190 and 2861 cm^{-1}, respectively, which give informative sign for changes in the geometry of **4** after complexation.

Conclusions

In the present work, the chromogenic potential of **4** was found with high specificity toward Cu^{2+} among a series of selected metal ions that attributed to the changes in intensities of the spectral lines observed in UV-visible and fluorescence spectra of Cu^{2+}–**4** complex. It is also confirmed by 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 Cu^{2+}. 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 Cu^{2+}.

Experimental section

General experimental information

Melting points were determined on a Gallenkamp (UK) apparatus in a sealed capillary tube and are uncorrected. Thermo Nicollet 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 **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 (SiO_2, Merck PF_{254}). All the reagents and solvents were of analytical grade and used without further purification.

Synthesis of 4

The required starting materials *p*-*tert*-butylcalix[4]arene (**2**), calix[4]arene (**3**) and tetraamine derivative (**4**) were prepared by published procedures.[31–33]

Synthesis of metal complexes with 4

For FT-IR experiments, **4** with a nitrate salt of Cu^{2+} and KBr were mixed and then ground to powder form in an agate mortar. The resulting mixture was kept in an oven at 115 °C for 1 h and then pressed to form pellets.[40]

Analytical procedure

Solvent extraction. Picrate extraction experiments were performed following Pedersen's procedure.[41] A 20 mL mixture of aqueous picrate solution (2.5×10^{-5} M) and **4** in CH_2Cl_2 (1×10^{-3} M) in 1 : 1 ratio were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min then magnetically stirred in a thermostated water-bath at 25 °C for 1 h, and finally left standing for an additional 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined through UV-visible spectrophotometry as previously described.[42]

The transition metal picrates were prepared by stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 2.5×10^{-5} M aqueous picric acid solution and shaken at 25 °C for 1 h.

Stoichiometric ratio of the metal and ligand in the complex. Job's method[43] (continual variation method) was used to determine the stoichiometric ratio between **4** and Cu^{2+} for their complexation in a binary solvent *i.e.*, DCM–MeOH. 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 275 nm.

General procedure for fluorescence study. Stock solutions of (1.00 mM) **4** and metal nitrate salts were prepared in DCM and MeOH, respectively. Test solutions were prepared by placing 50 μL of **4** into a cuvette, adding appropriate aliquot (5 eq.) of each metal stock, and diluting the solution up to 3.5 mL with DCM. Same equivalents (5 eq.) were taken for the interference study of co-existing ions in a solution containing **4**–Cu^{2+}complex. For all measurements, excitation was 260 nm; excitation and emission slit widths were both 5 nm each.

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