

# Analytical Evaluation of Cu<sup>2+</sup> Selective Behavior of calix[4]arene Derivative

Mansoor Ahmed Qazi · Imdadullah Qureshi · Shahabuddin Memon

Received: 22 November 2010 / Accepted: 13 February 2011 / Published online: 4 March 2011  
© Springer Science+Business Media, LLC 2011

**Abstract** The present article describes the solvatochromic effect including solvent system selection, time study and a detailed complexation study along with exploration of extraction properties of 5,11,17,23-tetrakis[(diethylamino)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (**4**) that bears nitrogen atom as a donor group available for chelating metal ions. Complexation properties of **4** toward selected transition metal ions have been investigated by UV-visible and fluorescence spectroscopies. The efficiency of **4** toward selected transition metal ions was found in order Cu<sup>2+</sup> > Ni<sup>2+</sup> > Hg<sup>2+</sup> > Zn<sup>2+</sup> > Co<sup>2+</sup> > Cd<sup>2+</sup> > Pb<sup>2+</sup>. It has been noticed that **4** is not only proved to be an efficient Cu<sup>2+</sup> selective chromoionophore but also possesses an effective extraction property for transferring Cu<sup>2+</sup> ions from an aqueous to dichloromethane layer. The FT-IR spectroscopic method has also been applied for further confirmation of the complexation phenomenon of **4** with Cu<sup>2+</sup> ion and found adequate.

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

## Introduction

Detection of cations, anions and molecular species *via* artificial receptors are one of the exigent areas of current

research pertinent to the receptor design and development due to its wide application in chemical, biological and environmental assays. In the recent years, there is an emergent need of developing receptors/chemosensing materials for soft transition-metal ions. Copper is one of the soft heavy metals which can easily access both +1 and +2 oxidation states and therefore act as charge carrier [1–3]. It is the third most abundant essential heavy metal ion (after Fe<sup>2+</sup> and Zn<sup>2+</sup>) present in human body and plays an important role in fundamental physiological processes in organisms ranging from bacteria to mammals [4–6]. However, copper can be toxic if the level exceeds cellular needs. It is also capable of displacing other metals, which act as co-factors in enzyme-catalyzed reactions [7, 8].

Many interesting aspects of complexation of alkali, alkaline earth metal and transition metal ions were disclosed by studying the absorption behavior of chromophoric groups [9–11]. Among them, complexation of ligand with copper through extraction has become an important process and is used in several hydrometallurgical plants to recover copper [12]. In addition, being a heavy metal, efficient removal and recovery of copper from industrial waste streams prior to discharge is a major challenge in order to prevent metal accumulation in biological sludge [13, 14].

In this regard calixarenes based derivatives are an important class of macrocyclic compounds and also an ideal platform for the detection and development of complexing agents as well as remedial milestones for heavy and transition metal ions [15, 16]. Such compounds may find application in modern methods of separation: membrane transport, chromatography, and extraction. Their selectivity depends on the kind of substituent added, size and in particular, on the conformation of calix[4]arene molecule. Calix[4]arene derivatives bearing nitrophenol, nitrophenyl, indoaniline, indophenol and azophenol have

M. A. Qazi (✉) · I. Qureshi · S. Memon (✉)  
National Center of Excellence in Analytical Chemistry,  
University of Sindh,  
Jamshoro 76080, Pakistan  
e-mail: great\_mansoor91@yahoo.com

S. Memon  
e-mail: shahabuddinmemon@yahoo.com

been reported and observed high selectivity in terms of recognition for cations and neutral molecules [17–26]. Moreover, calixarenes incorporated with azo groups (so called azocalixarenes) belong to a class of organic colorants that also behave as excellent host molecules for selective complexation of metal ions [27, 28].

Herein, we report a study regarding solvatochromic effect, synthesis of complexes, their characterization and the extraction properties of 5,11,17,23-tetrakis[(diethyl amino)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (**4**) and explored its complexation efficiency toward the selected metal ions using UV-visible as well as FT-IR spectroscopy.

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 [29–31]. The characterization of the compounds was made by various techniques such as, melting point, TLC, IR, and elemental analysis, which confirm the structure and purity of the compounds.

## Experimental

### General Section

Melting points were determined on a Gallenkamp (UK) apparatus in a sealed capillary tube and are uncorrected. Thermo Nicolet AVATAR 5700 FTIR spectrometer was used for recording IR spectra using KBr pellets in a wide spectral range, i.e. 4,000–400  $\text{cm}^{-1}$ . 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 and DMF as a solvent. Analytical TLC was performed on pre-coated silica gel plates ( $\text{SiO}_2$ , Merck PF<sub>254</sub>). All

the reagents and solvents were commercial and used without further purification.

### Synthesis of **4**

The required starting material *p*-*tert*-butylcalix[4]arene (**2**), debutylated product (**3**), diamine derivative (**4**) were prepared by published procedures [29–31].

### Synthesis of $\text{Cu}^{2+}$ Complex with **4**

For FT-IR experiments, **4** with a nitrate salt of  $\text{Cu}^{2+}$  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 [32].

### Analytical Procedure

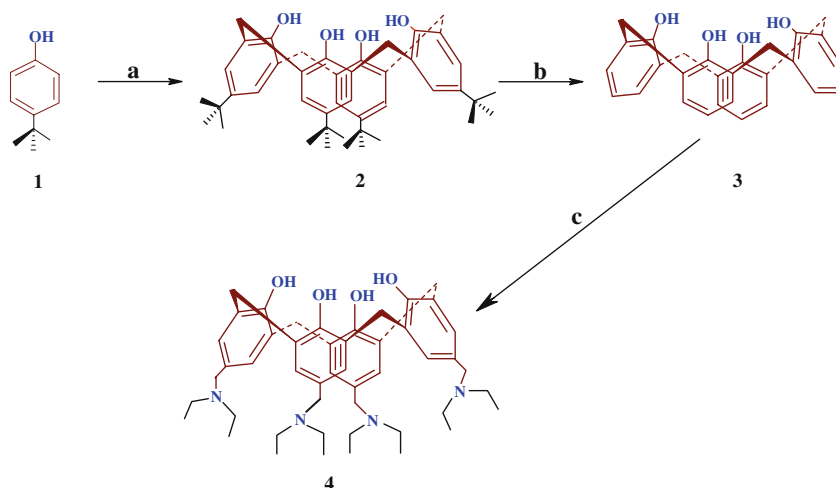
#### Stoichiometric Ratio of the Metal and Ligand in the Complex

Job's method [33] (continual variation method) was used to determine the stoichiometric ratio between the **4** and the  $\text{Cu}^{2+}$  ion for their complexation in DMF; the solutions were prepared by mixing of equimolar concentration ( $2.5 \times 10^{-5}$  M) solutions of both components in different ratios varying from 1:9 to 9:1. Then the absorbance was measured at 291.48 nm.

#### General Procedure for Fluorescence Study

Stock solutions of ( $2.5 \times 10^{-5}$  M) of those metal nitrate salts as well as **4** were prepared using DMF. Test solutions were prepared by placing 50  $\mu\text{l}$  of **4** into a cuvette, adding appropriate aliquot (50 eq) of each metal stock, and diluting the solution to 3.5 ml with DMF. Same equivalents (50 eq) were taken for the interference study of co-existing ions into a solution containing **4**- $\text{Cu}^{2+}$  complex.

**Scheme 1** Synthetic pathway for the preparation of **4** (a) HCHO (37%)-NaOH/Diphenyl ether (b) Phenol- $\text{AlCl}_3$ /Toluene (dry) (c) Diethylamine-HCHO/Acetic acid: THF



## Solvent Extraction

Picrate extraction experiments were performed following Pedersen's procedure [34]. 20 mL mixture of a aqueous picrate solution ( $2.5 \times 10^{-5}$  M) and calixarene in  $\text{CH}_2\text{Cl}_2$  ( $1 \times 10^{-3}$  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  $25^\circ\text{C}$  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 [35]. Blank experiments showed that no picrate extraction occurred in the absence of calixarene.

$$(E\%) = A_o - A/A_o \times 100$$

where  $A_o$  and  $A$  are the initial and final Absorbances of metal picrate before and after extraction respectively.

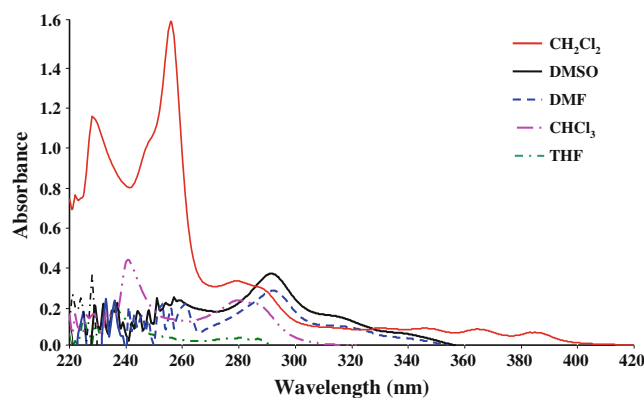
The transition metal picrates were prepared by stepwise addition of a  $1 \times 10^{-2}$  M of metal nitrate solution to a  $2.5 \times 10^{-5}$  M aqueous picric acid solution and shaken at  $25^\circ\text{C}$  for 1 h.

## Result and Discussion

### Solvatochromic Effect

It is experimentally verified that the ground state is less polar than the excited state for almost all molecules. A polar solvent will tend to stabilize the excited state more than the ground state. It has been noticed that with increase in the polarity of the solvent, a red shift (bathochromic effect) is commonly observed in the absorption spectrum, which is termed as "positive solvatochromism" and vice versa is true for less polar solvents [36]. Moreover, various studies indicate that the solvent has an important effect on the complexation processes involving ionic or neutral species and macrocyclic ligands in general and calixarenes in particular [37, 38]. In this work different solvents were taken to observe solvatochromic effect based on prominent absorption spectroscopic results. Thus, UV-visible spectroscopic studies of compound **4** were investigated in different solvents such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$ , DMSO, DMF and THF at a concentration of  $2.5 \times 10^{-5}$  M; the recorded results are shown in Fig. 1.

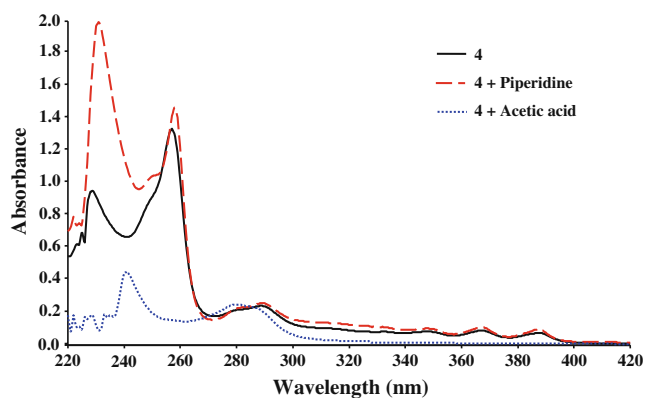
The difference between the polarities of organic solvents used was likely responsible for the changes of the band shape and their shifting to longer wavelength indicating that compound **4** is significantly sensitive to solvents environment. In Fig. 3, it was observed that the absorption spectra of the **4** in different solvents are different with respect to the absorption spectra in  $\text{CH}_2\text{Cl}_2$ . In DMF and DMSO, the



**Fig. 1** UV-visible spectral data of compound **4** in different solvents ( $2.5 \times 10^{-5}$  M)

$\lambda_{\text{max}}$  of **4** shifted considerably to longer wavelengths, i.e. 291 nm with respect to  $\text{CH}_2\text{Cl}_2$  where  $\lambda_{\text{max}}$  was found at 255 nm with appreciable absorbance. Other low polarity solvents like  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  shows hypsochromic shifts with three extra absorption peaks (except  $\text{CHCl}_3$ ) supports the equilibrium of **4** may exist in between associated and un-dissociated form. It indicates that **4** may exist in partly dissociated in  $\text{CH}_2\text{Cl}_2$ . Actually, presence of the non-bonding electron pairs of the nitrogen atoms of amino groups enable the compound **4** for strong  $n \rightarrow \pi^*$  transitions. Therefore, in polar aprotic solvent (DMF) the lone pair of electrons is engaged in hydrogen bonding and the promotion of these electrons to a  $\pi^*$  orbital requires energy to weaken or break the hydrogen bond in addition to the normal transition energy. This results in absorption at shorter wavelength or rather a blue shift in order of decreasing polarity of solvents [39]. Many attempts have been made to observe the solvatochromic behavior of **4** in THF and Acetonitrile even at lower concentration but due to aggregation and too much noise in the spectra both of them have been discarded. Moreover, a dramatic increase in the absorption intensity of bands 228 and 255 nm in  $\text{CH}_2\text{Cl}_2$  in comparison to other solvents is also favors  $\text{CH}_2\text{Cl}_2$  being used as a solvent of preferable choice for **4**.

In quest of acid and base influence on the equilibrium state of **4**, different bases were added in its various solvent systems. UV-visible spectra showed that there was no significant change in the spectra when small amount of Piperidine/Triethylamine (TEA) was added to the solution of **4** in DMSO, DMF,  $\text{CHCl}_3$  and/or  $\text{CH}_2\text{Cl}_2$ . A prominent response was found in  $\text{CH}_2\text{Cl}_2$  (Fig. 2) where appreciable enhancement with small bathochromic shifting was observed. However, the addition of acid (i.e. acetic acid) causes dramatic effect where noticeable shifting of band from 229 to 240 nm respectively, has been taken place which infers the non availability of lone pair of electrons due to protonation at nitrogen atoms.

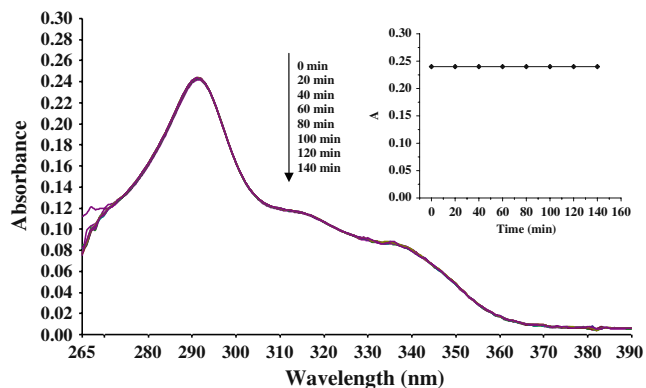


**Fig. 2** UV-visible spectral data of **4** before and after the addition of Piperidine and acetic acid in  $\text{CH}_2\text{Cl}_2$  ( $2.5 \times 10^{-5}$  M)

As Solvatochromic study of **4** suggested  $\text{CH}_2\text{Cl}_2$  as a solvent of preferable choice however, for complexation study, it is not suitable because majority of nitrate salts of transition metals are not soluble in this solvent. Many attempts have been made to use  $\text{CH}_2\text{Cl}_2$  with a series of different solvents but failed may be due to a lot of aggregation and noise. Since DMF is also a best solvent for complexation study and approximately all of the nitrates salts of transition metals are soluble in this solvent thus, all of complexation studies were performed in this solvent. In order to check the stability of **4** in DMF with respect to time, UV-visible absorption spectra of **4** in DMF were immediately obtained after UV light irradiation in 0, 20, 40, 60, 80, 100, 120 and 140 min respectively [40]. The results show that there was no spectral change appearing in the spectra with the passage of time and hence, it has been concluded that our compound is stable in DMF (Fig. 3).

### Complexation Studies

Mannich bases are primary, secondary or tertiary amines, depending on the nature of the starting amine. The carbon



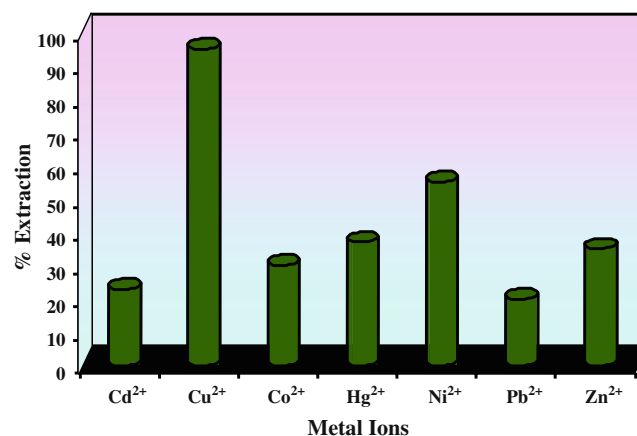
**Fig. 3** Time-dependent UV-visible absorption spectra of **4** ( $2.5 \times 10^{-5}$  M) in DMF upon irradiation of UV light; (inset) graph shows stability of **4** with respect to time

atoms contain an  $\alpha$ -hydrogen atom activated by a carbonyl or a hydroxyl group so that except for the amine, the Mannich base contains another potential donor atom close to a chelate ring with a metal ion. The preorganizing ability is increased if the Mannich base is obtained from a diamine [41]. Mannich bases having soft coordination centres have proved to possess potential ability of forming stable complexes with soft metal cations. Such as  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ag}^{2+}$  etc. In order to determine whether **4**, which possess soft donor atoms, can form a complex with these transition metals, different techniques were used to evaluate its selectivity.

### Liquid-liquid Extraction Studies

It has been found that calix[4]arene derivatives functionalized at lower rim are very effective extractants for metal cations [42–45]. As far as this work is concerned, it is focused on identifying the strategic requirements for the two-phase extraction, and the binding abilities of **4** toward selected transition metal ions such as  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$ . Solvent extraction procedure has been used to evaluate the % extraction efficiency of **4** toward metal picrates (Fig. 4), and the results are summarized in Table 1.

The data have been obtained by using dichloromethane solution of the **4** to phase transfer metal picrates from aqueous solution. The equilibrium concentration of the metal picrate in the aqueous phase was then determined spectrophotometrically. Extraction data given in Fig. 1 reveals that compound **4** is selective to  $\text{Cu}^{2+}$  whereas little % extraction efficiency was found toward  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ , which infers as intermediate nature of four available nitrogen atoms toward soft metal ions. The results obtained through an experiments per-



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

**Table 1** Comparative (%) Extraction results of selected transition metals by **1** and **4**

Ligand	Extracted Metal Picrates (%)						
	Cd <sup>2+</sup>	Cu <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Pb <sup>2+</sup>	Hg <sup>2+</sup>	Zn <sup>2+</sup>
<b>1</b> <sup>a</sup>	9.4	9.9	7.9	6.3	<1	15.5	—
<b>4</b>	23	95	30	55	20	37	35

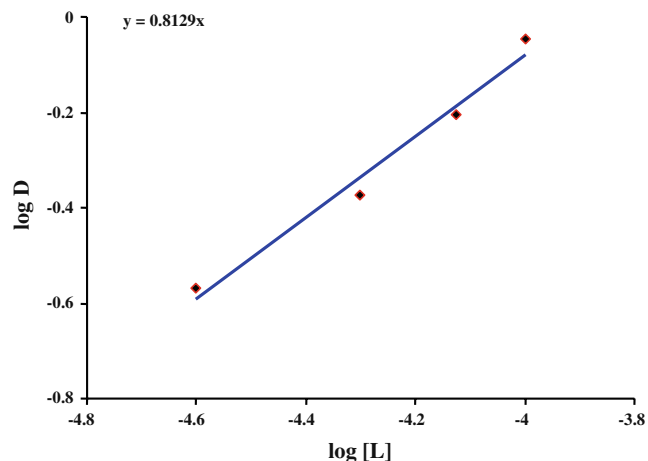
<sup>a</sup>Reference [48]

formed with the *p-tert*-butylcalix [4]arene **1** itself also verifies the significance of amine groups along with calixarene frame work. The effectiveness in transferring the Cu<sup>2+</sup> ions indicate that it is captured by the functional groups rather than by phenolic oxygens, this phenomenon belongs to Pearson’s classification and is consistent with soft hard acid base principle [46, 47].

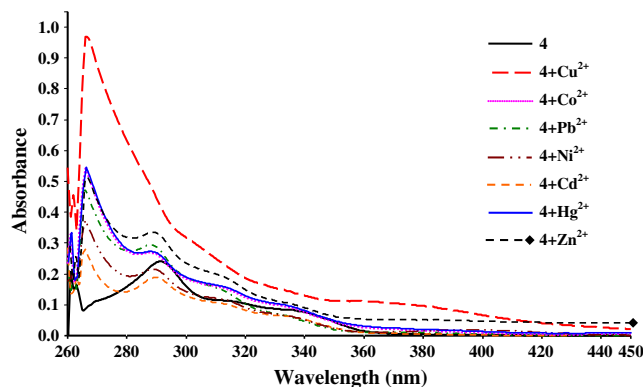
All these aforementioned discussion reveals that in the complexation phenomenon, beside the size of aromatic ring, other factors such as appropriate cationic size, presence of four donor nitrogen atoms in the binding sites of the ionophore in a periphery, their, effectiveness aggregation, and their collective/cooperative behavior also play an important role in complexation.

Log-Log Plot Analysis

In order to characterize the extraction ability, the dependence of the distribution coefficient D of the cation between the two phases upon the calixarene concentration was examined. If the general extraction equilibrium is assumed to be Eq. 1 with M<sup>n+</sup> metal ion, L neutral ligand and the over lined species referring to species in the organic phase, the overall extraction equilibrium constant is given by Eq. 2. If we introduce the distribution coefficient D, as



**Fig. 5** Log D versus log [L] for the extraction of Cu picrate (♦) by compound **4** from an aqueous phase to organic phase, i.e. dichloromethane at 25°C



**Fig. 6** UV-visible response of **4** ( $2.5 \times 10^{-5}$  M) before and after titration with different transition metals (50 eq)

given in Eq. 3, and taking log of both sides, we obtain Eq. 4.

$$M_{aq}^{n+} + nPic^{-}_{aq} + x[L]_{(org)} \rightleftharpoons [M(pic)_n(L)_x]_{org} \quad (1)$$

Extraction equilibrium constant is expressed as Eq. (2)

$$K_{ex} = \frac{[M(pic)_n(L)_x]}{[M^{n+}][Pic^-]^n[L]^x} \quad (2)$$

and the distribution ratio D would be defined by the Eq. (3).

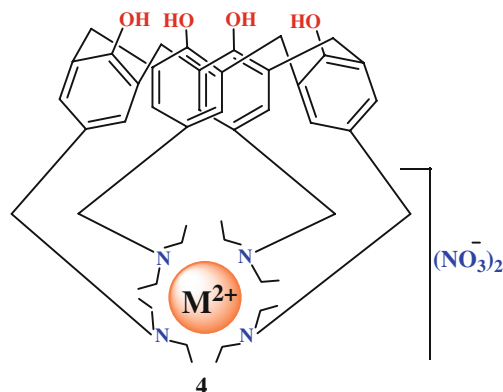
$$D = \frac{[M(pic)_n(L)_x]}{[M^{n+}]} \quad (3)$$

One obtains Eq. (IV), by introducing it into equation (II) and taking log of both sides

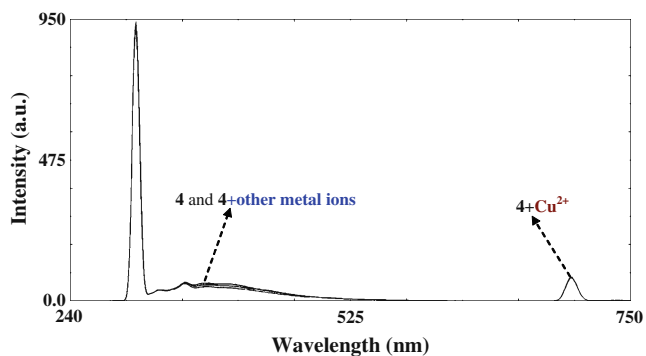
$$\text{Log } D = \text{Log } (K_{ex}(Pic^-)^n) + x \text{Log}[L] \quad (4)$$

With these assumptions a plot of the log D vs. log [L] should be linear and its slope should be equal to the number of ligand molecules per cation in the extraction species.

Figure 5 shows plot of Log D versus Log [L] for the extraction of Cu<sup>2+</sup> by ionophore **4**. A linear relationship between Log D and -Log [L] with the slope of lines of Cu<sup>2+</sup>



**Fig. 7** Plausible interaction between compound **4** and metal ion

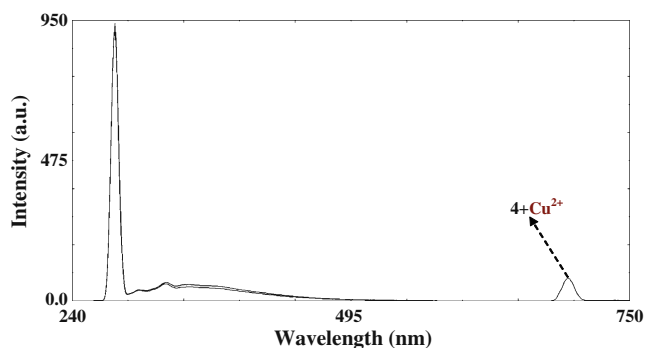


**Fig. 8** Fluorescence spectra of **4** ( $2.5 \times 10^{-5}$  M) in DMF solution before and after addition of nitrate salt of different transition metal (50 eq)

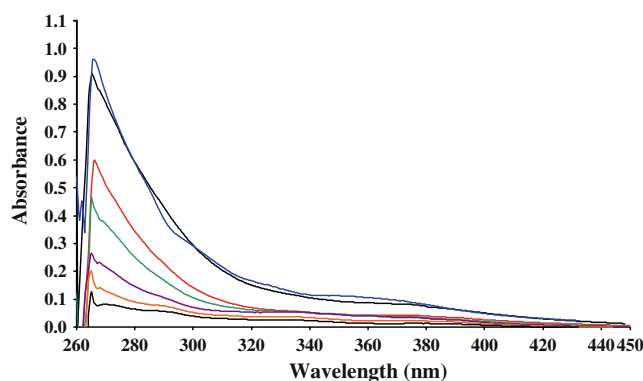
roughly equal to 0.81 respectively, suggesting that **4** forms 1:1 complex with  $\text{Cu}^{2+}$ .

#### UV-visible and Fluorescence Study

The binding ability of compound **4** for cations was investigated using the UV-visible absorption method. Preliminary measurements of **4** in DMF solution  $2.5 \times 10^{-5}$  M concentration for selected transition metals,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  were examined to check its selective complexation. The UV-visible spectra of **4** after the addition of each metallic cation (50 equiv) are shown in Fig. 6. Among the tested transition metals ions, the  $\text{Cu}^{2+}$  ion showed the most pronounced response with disappearance of band near 290 nm as well as inducing absorbance intensity at 265 nm. The result implies that **4** is highly selective for  $\text{Cu}^{2+}$ . Although the other transition metal ions do complex well, but that is not as strong as copper ions. They only lead to a slightly increase of the band at 265 nm. Concerning another complexation possibility between the OH group of host and the metal ions, metal cation is able to interact with the phenolic moieties at lower rim of calix[4]arene [49, 50] however, due to intramolecular hydrogen bonding of lower rim, metal ions may not be accommodat-



**Fig. 9** Fluorescence spectra of **4** ( $2.5 \times 10^{-5}$  M) in DMF solution before and after addition of nitrate salt of  $\text{Cu}^{2+}$  (50 eq)



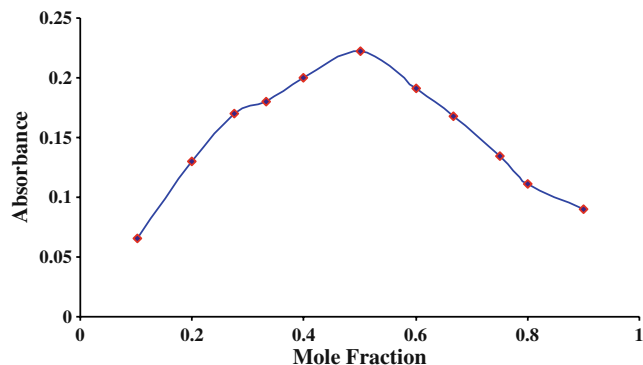
**Fig. 10** UV-visible titration spectra of **4** ( $2.5 \times 10^{-5}$  M) upon addition of various equivalents of  $\text{Cu}^{2+}$  (1–50 eq)

ed within this region of lower cavity of calix[4]arene. Thus, proposed mechanism for metal-ligand interaction is given below (Fig. 7).

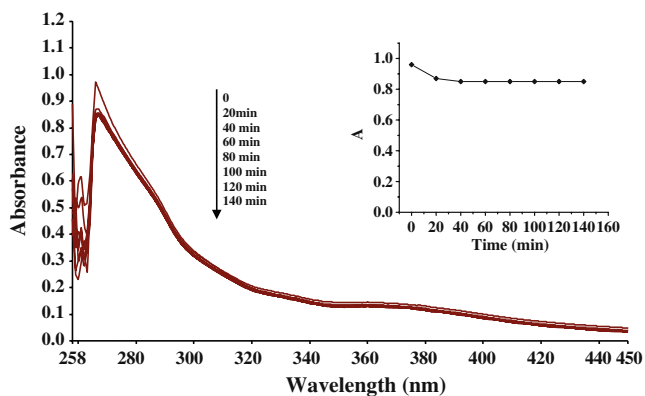
Fluorescence spectra also support the stronger complexation of  $\text{Cu}^{2+}$  with **4** in DMF (Figs. 8 and 9) since; there is comparatively slight emission at 695 nm after complexation. This low fluorescence nature of band gives clear evidence for complex formation between **4** and  $\text{Cu}^{2+}$  ion as compared to other transition metals which give more or less same response as free ligand **4**.

In order to have further insight into the chromogenic behavior of **4**, the absorption as a function of metal ion concentration was obtained followed by increase in the intensity of absorbance with respect to  $\text{Cu}^{2+}$  ion concentration increased (Fig. 10).

For the stoichiometric ratio between ligand and metal ion, the Job's plot experiment was conducted by varying the concentration of both host and metal ion. Figure 11 shows typical jobs plots of ligand- metal complexation. For **4**- $\text{Cu}^{2+}$  complex, it was conducted at 291.48 nm and the maximum point at the mole fraction was about 0.5 which refers to ligand-metal complex ratio of 1:1 as shown in Fig. 11.



**Fig. 11** Job plot of a 1:1 complex of **4** and  $\text{Cu}^{2+}$  ion where the absorbance at 291.48 nm was plotted against the mole fraction of **4** at invariant total concentration of ( $2.5 \times 10^{-5}$  M)

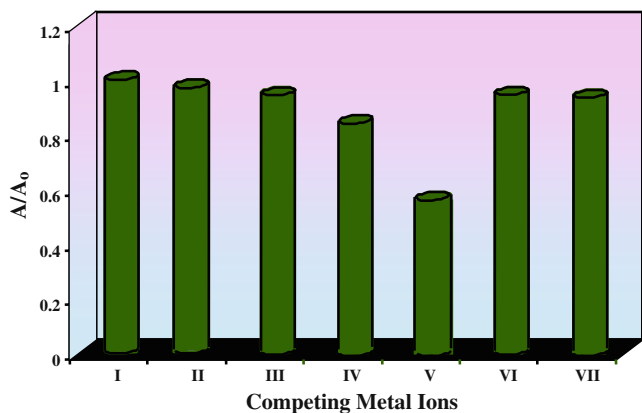


**Fig. 12** Time-dependent UV-visible absorption spectra of 4-Cu<sup>2+</sup> complex in DMF upon irradiation of UV light; (inset) graph showed stability of 4 in DMF with respect to time

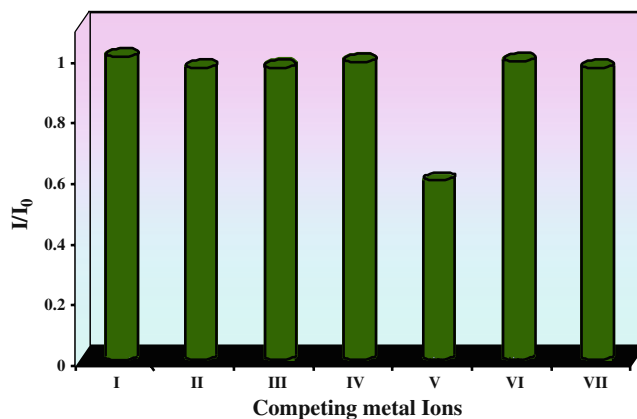
The 1:1 host–guest interaction was analyzed according to Benesi–Hildebrand equations for spectroscopic UV-visible titration (Eq. (1)) [51]. A<sub>0</sub> and A are the absorbance of 4 in the absence and presence of the cation analytes, respectively; ε<sub>0</sub> and ε are the corresponding molar absorption coefficients of 4 in the absence and presence of the anion analytes, respectively. [substrate] is the concentration of the titrants and K<sub>B</sub> represents the binding constant of host–guest complexation. The binding constants log K<sub>ass</sub> of 4 for Cu<sup>2+</sup> was calculated to be 5.2 (R<sup>2</sup>=0.98). While in case of Cd<sup>2+</sup>, Co<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>, the spectral changes were too small therefore, the binding constants for these metal ions could not be calculated.

$$A_0/A - A_0 = (\epsilon_0/\epsilon_0 - \epsilon)(1/K_B[\text{cation}] + 1)$$

As known, whether chromoionophores or chemosensor, always have a problem of long response time. Consequently, the 4 response very fast and when titrated with Cu



**Fig. 13** UV-visible ratiometric behavior (A/A<sub>0</sub>) of 4 in the presence of Cu(II) and other co-existing ions in DMF solution. I = 4 + Cu<sup>2+</sup>, II = 4 + Cu<sup>2+</sup> + Cd<sup>2+</sup>, III = 4 + Cu<sup>2+</sup> + Co<sup>2+</sup>, IV = 4 + Cu<sup>2+</sup> + Hg<sup>2+</sup>, V = 4 + Cu<sup>2+</sup> + Ni<sup>2+</sup>, VI = 4 + Cu<sup>2+</sup> + Pb<sup>2+</sup>, VII = 4 + Cu<sup>2+</sup> + Zn<sup>2+</sup>

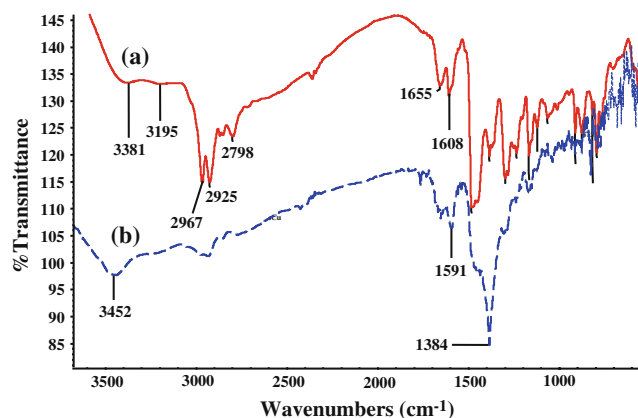


**Fig. 14** Fluorimetric ratiometric behavior (I/I<sub>0</sub>) of 4 in the presence of Cu<sup>2+</sup> and other co-existing ions in DMF solution. I = 4 + Cu<sup>2+</sup>, II = 4 + Cu<sup>2+</sup> + Cd<sup>2+</sup>, III = 4 + Cu<sup>2+</sup> + Co<sup>2+</sup>, IV = 4 + Cu<sup>2+</sup> + Hg<sup>2+</sup>, V = 4 + Cu<sup>2+</sup> + Ni<sup>2+</sup>, VI = 4 + Cu<sup>2+</sup> + Pb<sup>2+</sup>, VII = 4 + Cu<sup>2+</sup> + Zn<sup>2+</sup>

(NO<sub>3</sub>)·3H<sub>2</sub>O, a sharp band appears with appreciable absorption at near 265 nm very rapidly within 1 min. and remains stable to a long time (Fig. 12), i.e. remains same even after 2 days.

To test the practical ability of 4 as Cu<sup>2+</sup> selective chromoionophore, competitive experiments were carried out in the presence of Cu<sup>2+</sup> (50 eq) mixed with Cd<sup>2+</sup>, Co<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> at 50 equivalents as shown in Fig. 13, no significant variation in the UV-visible ratiometric behavior (A/A<sub>0</sub>) of 4+Cu<sup>2+</sup> after addition of interfering ions except Ni<sup>2+</sup> which interfere with the detection of Cu<sup>2+</sup> ions, i. e. the ratio (A/A<sub>0</sub>) for the 4-Cu<sup>2+</sup> system decreased significantly from 1 to 0.56 (Fig. 13).

Similar trend was found in the fluorescence spectroscopic results where the ratiometric behavior (I/I<sub>0</sub>) of 4-Cu<sup>2+</sup> complex in the presence of selected transition metal ions except Ni<sup>2+</sup> was not significantly disturbed which also supports the pronounced Cu<sup>2+</sup> selectivity of 4



**Fig. 15** Comparative FT-IR spectra for (a) 4 (—) (b) Cu<sup>2+</sup> complex of 4 (---)

(Fig. 14); where upon addition of  $\text{Ni}^{2+}$  ions caused the ratio ( $I/I_0$ ) for the 4- $\text{Cu}^{2+}$  system decreased significantly.

All these UV-visible and fluorescence spectra suggest the four nitrogen atoms of amino group play an important very important role in achieving high selectivity for  $\text{Cu}^{2+}$ . Moreover,  $\text{Cu}^{2+}$  has a particularly high thermodynamic affinity for typical N-chelating ligands and fast metal to ligand binding kinetics. Thus, 4 may be used as a potential  $\text{Cu}^{2+}$  selective chromoionophore.

#### FT-IR Study

For FT-IR experiments, 4 with a nitrate salt of Copper and KBR were mixed and then ground to powder form in an agate mortar. The resulting mixture was kept in oven at  $115^\circ\text{C}$  for 1 h and then pressed to form pellets [32].

The reactions of compound 4 with  $\text{Cu}^{2+}$  give product with metal/ligand ratio of 1:1. FT-IR spectroscopic technique also provides strong evidence of complexation of 4 with  $\text{Cu}^{2+}$ . Figure 15 clearly gives the stronger evidence for complexation as shifting in various frequencies of specific functional groups occurred as a result of introduction  $\text{Cu}^{2+}$  into receptor cavity. For example complexation caused  $\nu(\text{C-N})$  tertiary peak which appear at  $1,220\text{ cm}^{-1}$  becomes greatly reduced furthermore, the band around at  $3,400\text{ cm}^{-1}$  that appears as weak overtone due to overlapping of N-H and O-H stretching was then found as proper/prominent band after complexation at  $3,452\text{ cm}^{-1}$  and this reveals that N-donor atom is now no longer available due to interaction with  $\text{Cu}^{2+}$ . Other prominent bands at 1482, 1392 for  $\delta_{as}(\text{CH}_3)$  and  $\delta_s(\text{CH}_3)$  respectively, 1362 for  $\delta(\text{O-H})$ , 1293 for (C-N), and  $1200\text{ }\nu(\text{C-O})\text{ cm}^{-1}$ . On complexation, all these bands were replaced with single distinctive band at  $1,384\text{ cm}^{-1}$  [14]. Band at  $1,608\text{ cm}^{-1}$  for  $\nu(\text{C=C})$  was also displaced to  $1,591\text{ cm}^{-1}$  which give informative sign for changing in the geometry of 4 after complexation.

#### Conclusions

As a part of research study, Complexation ability of tetra-aminoethyl derivative of calix[4]arene was done by using UV-visible, Fluorescence and FT-IR spectroscopic techniques. It has been revealed from the experimental evidences that 4 exhibits significant selective nature towards  $\text{Cu}^{2+}$  ions among the series of selected transition metals. The geometry of binding series of 4, comprising four donor nitrogen donor atoms are seems to be ideal in terms of size and arrangement and accommodation of  $\text{Cu}^{2+}$  ion, which imparts the importance of pre-organization in designing the supramolecule. From the results, it may be concluded that being soft nature of both ligand and metal, the study may be treated as a test for the detection of  $\text{Cu}^{2+}$  ions.

**Acknowledgements** We thank the National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro/Pakistan for the financial support of this work.

#### References

- Solomon EI, Chen P, Metz M, Lee S-K, Palmer AE (2001) *Angew Chem Int Ed* 40:4570
- Mirica LM, Ottenwaelder X, Stack TDP (2004) *Chem Rev* 104:1013
- Klinman JP (1996) *Chem Rev* 96:2541
- Kumar R, Bhalla V, Kumar M (2008) *Tetrahedron* 64:8095
- Linder MC, H-Azam M (1996) *Am J Clin Nutr* 63:797S
- Uauy R, Olivares M, Gonzalez M (1998) *Am J Clin Nutr* 67:952S
- Harris ZL, Gitlin JD (1996) *Am J Clin Nutr* 63:836S
- Scheinberga IH, Sternlieb I (1996) *Am J Clin Nutr* 63:842S
- Inoue Y, Gokel GW (1990) Cation binding by macrocycles: Complexation of cationic species by crown ethers. M. Dekker, New York
- De Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, Rice TE (1997) *Chem Rev* 97:1515
- Ma QL, Ma HM, Wang ZH, Su MH, Xiao HZ, Liang SC (2001) *Chem Lett* 2:100
- Szymanowski J (1993) *Hydroxyoximes and Copper Hydrometallurgy*. CRC Press, Boca Raton
- Guha AK, Yun CH, Basu R, Sirkar KK (1994) *Alche J* 40:1223
- Bogacki M (1997) *Solv Extr Ion Exch* 15:731
- Gutsche CD, Stoddart JF (eds) (1998) *Calixarenes revisited: Monographs in Supramolecular chemistry*. The Royal Society of Chemistry, Cambridge, UK
- Asfari Z, Bohmer V, Harrowfield J, Vicens J (2001) *Calixarenes* (2001). Kluwer, Dordrecht, The Netherlands
- Deligöz H (2006) *J Incl Phenom Macrocycl Chem* 55:197
- Ludwig R, Dzung NTK (2002) *Sensors* 2:397
- Shimizu H, Iwamoto K, Fujimoto K, Shinkai S (1991) *Chem Lett* 2:2147
- Yamamoto H, Ueda K, Sandanayake KRAS, Shinkai S (1995) *Chem Lett* 24:497
- King MA, Moore CP, Sandanayake KRAS, Sutherland IO (1992) *J Chem Soc Chem Commun* 7:582
- Gordon JL, Böhmer V, Vogt W (1995) *Tetrahedron Lett* 36:2445
- McCarrick M, Wu B, Harris SJ, Diamond D, Barrett G, McKervey MA (1992) *J Chem Soc Chem Commun* 18:1287
- Kubo Y, Hamaguchi S, Yoshida AKN, Tokita SJ, J Chem Soc Chem Commun (1993) 3
- Kubo Y, Maeda S, Tokita S, Kubo M (1996) *Nature* 382:522
- Chawla HM, Srinivas K (1994) *J Chem Soc Chem Commun* 22:2593
- Yilmaz M, Memon S, Tabacki M, Bartsch RA (2006) Design of polymer appended calixarenes ion carriers new frontiers in polymer research. Nova Science Publisher, Hauppauge, New York, pp 125–172
- Deligöz H, Erdem E (1997) *Sol Extr Ion Exch* 15:811
- Gutsche CD, Iqbal M, Stewart D (1986) *J Org Chem* 51:742
- Gutsche CD, Lin L-G (1986) *Tetrahedron* 42:1633
- Gutsche CD, Nam KC (1988) *J Am Chem Soc* 110:6153
- Lim SF, Zheng Y-M, Zou S-W, Chen JP (2008) *Envirom Sci Technol* 42:2551
- Harris DC, *Quantitative Chemical Analysis*, (fourth ed.) 1995, pp. 529
- Pedersen CJ (1968) *Fed Proc Fed Am Soc Exp Biol* 27:1305



35. Deligöz H, Yilmaz M (1995) *Solvent Extr Ion Exch* 13:19
36. Harikrishnan U, Menon SK (2008) *Dyes Pigm* 77:462
37. Shirshov YM, Zynio SA, Matsas EP, Beketov GV, Prokhorovich AV, Venger EF (1997) *Supramol Sci* 4:491
38. Máté SK, Bitter I, Grün A, Nagy G, Kollár L (2002) *Anal Chim Acta* 461:273
39. Carroli FI, Solti A (1973) *J Am Chem Soc* 95:8512
40. Liang Z, Liu Z, Gao Y (2007) *Spectrochim Acta A* 68:1231
41. Verlag der Zeitschrift für Naturforschung, Tübingen! <http://www.znaturforsch.com>.
42. Gutsche CD (1998) *Calixarenes Revisited*. The Royal Society of Chemistry, Cambridge
43. Asfari Z, Bohmer V, Harrowfield J, Vincens J (2001) *Calixarenes* 2001. Kluwer Academic Publishers, Dordrecht
44. Vicens J, Bohmer V (1991) *Calixarenes: A versatile class of macrocyclic compounds; Topics in inclusion science*. Kluwer Academic Publishers, Dordrecht
45. Roundhill DM (1995) *Prog Inorg Chem* 43:533
46. Pearson RG, Ho TL (1975) *Chem Rev* 75:1
47. Bartsch RA, Way JD (1996) *Chemical Separations with Liquid Membranes ACS Symposium Series, No. 462*. American Chemical Society, Washington
48. Memon S, Yilmaz M (2000) *React Funct Polymers* 44:227
49. Kao TL, Wang CC, Pan YT, Shiao YJ, Yen JY, Shu CM, Lee GH, Peng SM, Chaung WS (2005) *J Org Chem* 70:2912
50. Kram TC, Lurie IS (1992) *Forensic Sci Int* 55:131
51. Chow CF, Lam MHW, Wong WY (2004) *Inorg Chem* 43:8387