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Bifunctional Calix[4]arene Sensor for Pb(II) and $Cr_2O_7^{2-}$ Ions

Mansoor Ahmed Qazi · Ümmühan Ocak · Miraç Ocak ·
Shahabuddin Memon · Imam Bakhsh Solangi

Abstract A readily available chromionophore 5,11,17,23-tetra-*tert*-butyl-25,27-bis(hydrazidecarbonylmethoxy)-26,28-dihydroxycalix[4]arene (HCC**4**) was employed as a chromogenic sensing probe selective for Pb(II) and $Cr_2O_7^{2-}$ ions among a series of various ions such as Li(I), Na(I), K(I), Rb(I), Ba(II), Sr(II), Al(III), Cd(II), Co(II), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II) as well as $Cr_2O_7^{2-}$, $CH_3CO_2^-$, Br^-, Cl^-, F^-, I^-, ClO_4^- and NO_3^- that have been examined by UV-visible and fluorescence spectroscopic techniques. The HCC**4** in DCM-MeCN system forms 2:1 (ligand-metal) complex with Pb(II). It also shows 2:1 stoichiometry with $Cr_2O_7^{2-}$. The complexation phenomenon has been confirmed by FTIR spectroscopy that favors the selective nature of HCC**4** with Pb(II) and $Cr_2O_7^{2-}$. Thermal gravimetric analysis (TGA) also supports its utility in drastic conditions.

Keywords Chromoionophore · Complexometric titration · Anions · Non-covalent chemistry · Fluorescence

Introduction

Design and development of macromolecular hosts for cation and anion guests is the exciting topic of coordination chemistry because of their extreme importance in biological processes involving molecular recognition of cationic and anionic species. The field of supramolecular chemistry has advanced comprehensively in recent years and as such there is now a superfluous of literature regarding the design, synthesis and study of chromoionophores for metal ion binding [1]. Although the beginnings of anion recognition can be traced to the same period as that of their cation counterparts, the last 20 years have seen remarkable advances in the construction of supramolecular hosts for such guests [2–4].

Toxic heavy metals like Cd(II), Hg(II) and Pb(II) etc. in high concentration can have a severe impact on the aqueous environment, animals, and humans. Among them, detection and sensation of Pb(II) ion from environmental or biomedical applications has gain intense attraction because this lethal metal is widely dispersed in the environment, and on exposure, it can lead to a number of adverse health effects like anemia, kidney damage, a disorder of the blood, memory loss, muscle paralysis and mental retardation due to Pb(II) poisoning [5].

On the other hand, a great deal of devotion has recently been focused on the selective sensing of anions by means of synthetic receptors due to anionic biological and environmental significance [6]. Cations are usually discriminated on the basis of charge and size whereas, anions of interest, for example; oxoanions are often multiatomic structures with a delocalization of the negative charge over a rather complex molecular geometry. This complexity and varied physical properties of anions such as larger size, being spherical; linear, planar, tetrahedral or octahedral geometry, they have to be taken into account for the design of molecular systems to selectively recognize an anion via the introduction of specific binding sites [7].

Oxoanions like dichromate are considered to be very noxious, carcinogenic to human beings [8–11]. Wastewater generated by industries contains chromium and its derivatives either in hexavalent Cr(VI) or trivalent Cr(III) form and it is a renowned fact that the hexavalent form of

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

Ü. Ocak · M. Ocak
Department of Chemistry, Faculty of Arts and Sciences,
Karadeniz Technical University, 61080 Trabzon, Turkey

chromium is very dangerous for human health [12]. Hexavalent chromium compounds CrO_4^{2-} or $Cr_2O_7^{2-}$ are known as human carcinogens, being both mutagenic and genotoxic [13, 14] In general, anion binding by neutral receptors is achieved by usage of hydrogen bond formed by amide [15, 16], urea [17–19], thiourea [20, 21] and hydroxyl groups [22, 23] or amino moiety [24, 25].

Calixarenes, cyclic oligomers of phenolic units linked by methylene bridges through the ortho positions are a fascinating class of macrocycles. Chemical modification of the upper or lower rim has made this class of synthetic ionophores effective complexing and sensing agents for the detection of anionic and cationic guest molecules [26, 27]. The importance of favorable amine, amide, or imide hydrogen bonding interactions for anion binding has recently been exploited in the design of calix[4]arene anion receptors, because of their stable aromatic core structure against oxidation and suitability for extraction due to exclusive characteristics of hydrogen bonding, π–π interactions, electrostatic interactions, and dipole-dipole moments [28, 29]. Although such host molecules are still relatively rare. In recent years, some calix[4]arene-based receptors have been reported possessing effective anion binding ability. This feature can be useful for multiple applications such as laboratory, clinical, environmental and industrial process analyses [30, 31]. Although several works regarding the synthesis and complexation of metal cations and toxic anions with calix[4]arene derivatives have been reported [32–34]. However, according to the best of our knowledge there is no other published study on chromogenic/fluorescent sensing of $Cr_2O_7^{2-}$. Therefore, this work aims to expand the study and provide a new path way for the design and development of bifunctional ligand that could bind both metal and dichromate anions, which can be detected by means of UV-visible and fluorescent methods. Thus, in connection with our efforts for the development of different sensing derivatives [35–39], herein we report the binding and sensing behavior of a calix[4]arene derivative, i.e. HCC**4** toward a series of selected alkali, alkaline earth and transition metal ions such as Li(I), Na(I), K(I), Rb(I), Ba(II), Sr(II), Al(III), Fe(III), Cd(II), Co(II), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II) as well as anions like $Cr_2O_7^{2-}$, $CH_3CO_2^-$, ClO_4^-, NO_3^-, Br^-, Cl^-, F^-, I^- using UV-visible, fluorescence and FT-IR spectroscopic techniques.

Experimental Section

General Experimental Information

Melting points were determined on a Gallenkamp (UK) apparatus in a sealed capillary tube. FT-IR spectroscopic measurement was carried out through Thermo Nicollet AVA-TAR 5700 using KBr pellets in a wide spectral range, i.e. 4,000–400 cm^{-1}. Whereas CHNS instrument model Flash EA 1112 elemental analyzer was used for elemental analyses.

UV-visible spectral studies of chromoionophore HCC**4** (Scheme 1) as well as its complexation investigations with metals and anions were carried on a Perkin Elmer Lambda-35, double beam spectrophotometer using standard 1.00 cm quartz cells. Fluorescence spectral studies were performed with a Photon Technologies International Quanta Master Spectrofluorimeter (model QM-4/2006). All the Reagents and solvents purchased from Merck, Aldrich and Fluka were of analytical grade and used without further purification. Analytical TLC was performed on pre-coated silica gel plates (SiO_2, Merck PF$_{254}$).

Synthesis

Synthesis of HCC**4**

The required starting material *p-tert*-butylcalix[4]arene (**2**), Diester derivative of calix[4]arene (**3**) and HCC**4** (**4**) were prepared by earlier published procedures [40, 41].

#### Synthesis of Metal Complexes with HCC**4**

For TGA and FT-IR experiments, saturated DCM solution of receptor HCC**4** was prepared in round bottomed flask, an stoichiometric amount of Pb(II) or $Cr_2O_7^{2-}$ salts was dissolved in MeCN separately. Mixed up both the contents and stirred at room temperature for 24 h. Filtered the saturated solution and residue was washed with DCM. Finally, poured the combined filtrate and washing on a Petri dish, evaporated the entire solvent and vacuum dried the resultant crystals.

Analytical Procedure

Solvent Extraction

Pedersen's procedure was applied for liquid–liquid extraction experiments [42]. 10 ml mixture of an aqueous metal picrate solution (2.5×10^{-5} M) and HCC**4** in DCM (1×10^{-3} M) in 1:1 ratio were vigorously agitated in a Stoppard glass tube with a mechanical shaker for 2 min then magnetically stirred in a shaker at 25 °C for 1 h, and finally left standing for an additional 30 min. The picrate ion concentration before and after extraction in the aqueous phase was spectrophotometrically determined as previously published procedure [43].

Alkali metal picrates were prepared as described elsewhere [44] by gradual addition of a 2.5×10^{-5} M aqueous picric acid solution to a 0.14 M aqueous solution of metal hydroxide, until neutralization which was checked by pH control with a
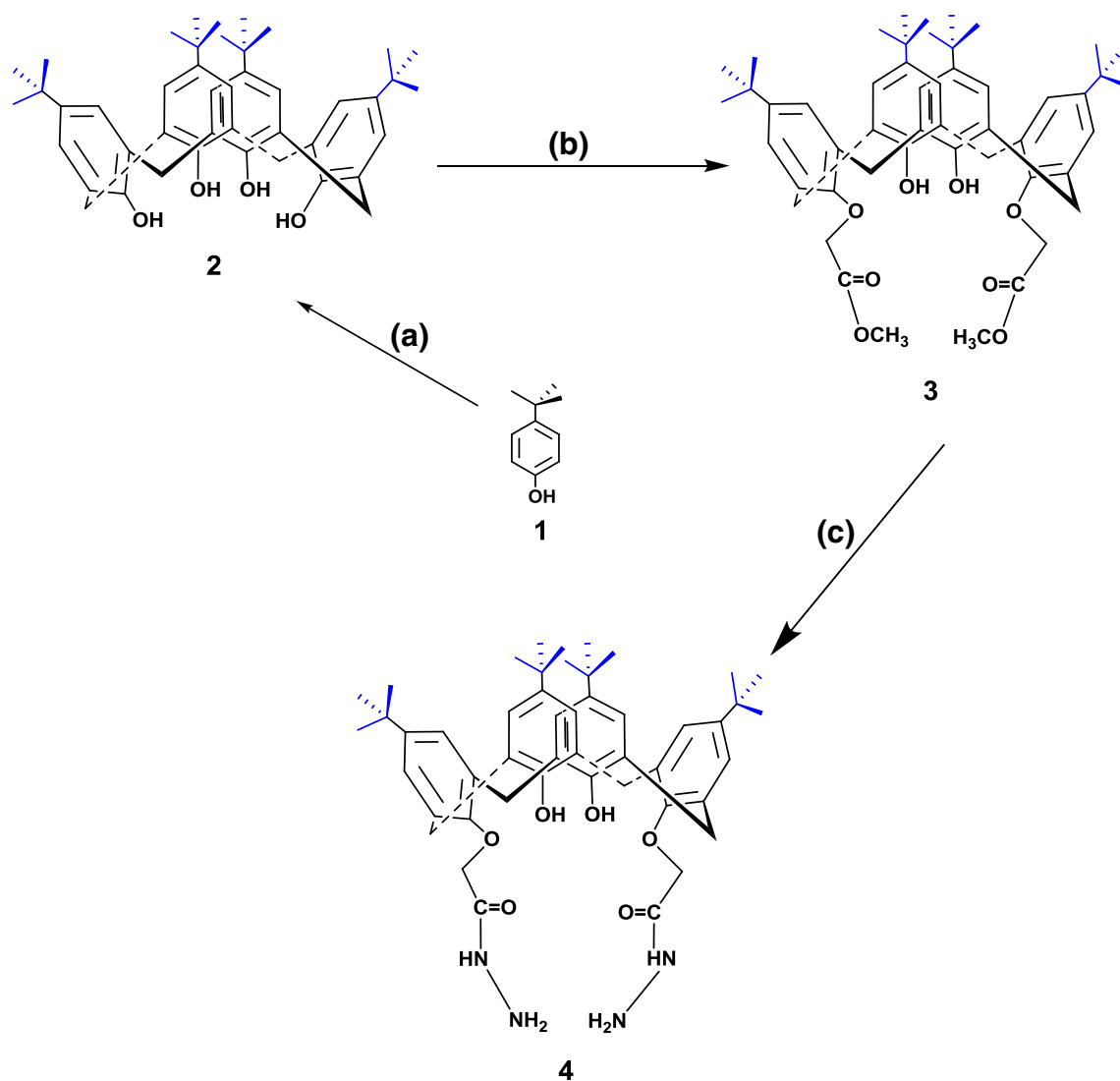
Scheme 1 Synthetic methodology for synthesis of hydrazide calix[4]arene derivative. Reagents and conditions. (a) HCHO/NaOH (b) K_2CO_3-BrCH$_2$CO$_2$Me/Acetone (dry) (c) $N_2H_4.H_2O$/CHCl$_3$-MeOH

glass electrode. Finally, they were rapidly washed with ethanol and ether before being dried in vacuum for 24 h. 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 Determination of Complexes

Method of continuous variation, i.e. Job's method [45] was applied for the determination of stoichiometry of HCC**4** with cations and anions for their complexation in DCM-MeCN as binary solutions. For Pb(II), the equimolar solutions (1.25×10^{-5} M) of both components, i.e. ligand and metal were mixed under the condition that sum of the ligand-metal concentration remains constant. The absorbance was measured at 230 nm. Moreover, same procedure was applied for HCC**4**-Cr$_2$O$_7^{2-}$ stoichiometry, however; absorbance was measured at 272 nm.

*Fluorescence Emission Measurement of HCC**4***
and Its Complexes

Emission intensities of HCC**4** (1.25×10^{-5} M) excited at 300 nm were measured in DCM-MeCN at room temperature. Titration experiment was performed by placing 50 µl of HCC**4** into a cuvette, adding appropriate aliquot (2 equvi.) of each metal and anion stock, followed by dilution with DCM-MeCN up to 4 ml. Same equivalents (2 equvi.) were taken for the interference study of foreign ions into the solution of HCC**4** with metal and anion complexes. For all measurements, excitation was 300 nm; excitation and emission slits widths were both 5 nm each.

Result and Discussion

The *p-tert*-butylcalix[4]arene (**2**), Diester derivative of calix[4]arene (**3**) and HCC4 (**4**) were prepared by previously published procedures [40, 41]. The synthetic pathway is illustrated in Scheme 1. 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

Solvatochromic properties of a compound in various solvent systems are generally as a result of differential solvation in ground/first excited state of molecule. Thus, with increasing solvents polarities, better stabilization by the solvation of the molecule in the first excited state compare to the ground state will lead to positive solvatochromism *(red shift)* and vice versa is true for negative solvatochromism.

In pursuit of all these factor, HCC4 was dissolved in various solvent like acetone (ACO), chloroform (CF), 1,4-dioxane, dichloromethane (DCM), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) with optimized fixed concentration of 1.25×10^{-5} M. UV-visible spectral data of compound HCC4 in different solvents are shown in Fig. 1a and b. After comprehensive analysis of a number of annotations, we can precise the following main remarks: for each solvent used, In case of DCM and CF the absorption spectra of receptor HCC4 obtained is characterized by the presence two absorption bands, with λ_{max} at 230–240 and 282 nm respectively. The effect of solvents polarity on the absorption spectrum was revealed by a blue shift for the first band (230 nm) for 1, 4-dioxane, DCM, CF is more remarkable as compare to DMF and DMSO. These results indicate that the spectrum of HCC4 in these media is characterized by two electronic transitions, of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions arising from solvent polarity. DMF and DMSO shows devoidness of previously mentioned band at

230 nm and possess only weak shoulder at 280 nm. Hypsochromic shifting with well-defined bands of HCC4 in less polar solvents like 1,4-dioxane, DCM, CF may be ascribed to the presence of four intermediate nature bearing nitrogen atoms. That's why it gives blue shifting (i.e. negative solvatochromism) in less polar solvents. However, in DMF and DMSO, presence of a distinctive transition in these solvents series may be justified only by the overlapping of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands which are very close in energy.

Attempts have been made to observe the solvatochromic behavior of HCC4 in MEOH, ACO and MeCN even at low concentration; but due to partial solubility, aggregation and too much noise in the spectra, all of them have been discarded.

Analytical Perspectives of HCC4 as Chromogenic Sensor

By keeping view of our previous investigations [35–39], Hydrazine derived calix[4]arene amide derivative have been chosen for synthesis and complexation study. Presence of amide functionality provides selectivity to this bi-functional receptor for simultaneous detection of cations as well as anions. Thus, with ease of two step synthetic route, possessing soft nature (borderline) of nitrogen donor atom along with macrocyclic effect, all these features makes these derivatives might be a promising candidate for stronger complex formation and selective sensing with soft/borderline amino/thiophilic metal cations such as Cu(II), Hg(II) and Pb(II) etc. we have carried out various titration experiments go investigate the selective complexation affinity with cations and anions and therefore several analytical parameter have been examined in this regard. Cationic and anionic properties of HCC4 were investigated and confirmed by UV-visible, fluorescence, TGA, FT-IR spectroscopies.

With careful analysis of solvatochromic spectral features of HCC4 as mentioned above, DCM-MeCN was selected as binary solvent system for complexation studies on the basis of solubility of metal perchlorate and tetrabutylammonium
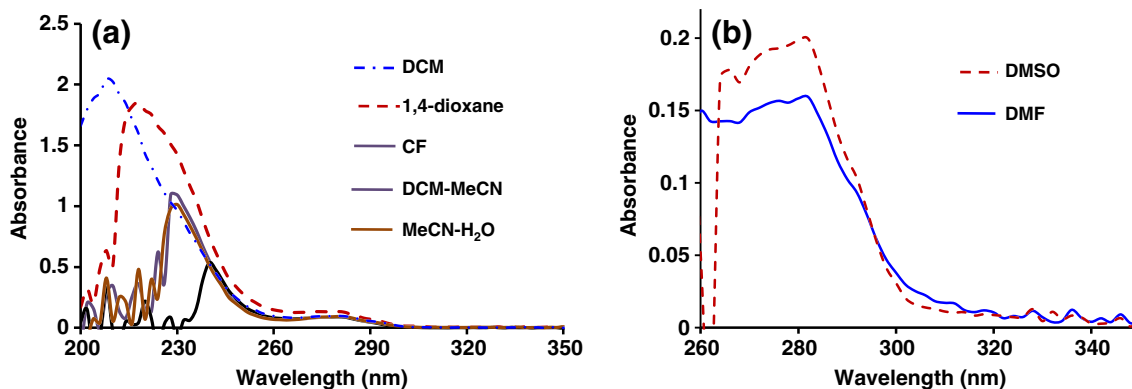

Fig. 1 Absorption spectral behavior of HCC4 in different solvents (1.25×10^{-5} M)

salts, less toxicity effects, no aggregation, maximum number of bands with in standard absorption limits and well-defined spectral properties in aforementioned binary solvents. However, we also investigate the complexation properties of HCC4 in other binary solvents such as methanol, THF, 1,4-dioxane, isopropanol alone or with DCM at different concentrations but significant complexation properties was observed with DCM-MeCN.

Complexation Affinity of HCC4

UV-Visible Study

For complexation study, all of the titration experiments were performed in DCM-MeCN by adding aliquots (2 eq) of different guests (cation and anion). The UV-visible absorption spectrum of the HCC4 exhibits strong absorption band at 230 nm and comparatively weak absorption at 282 nm. These two absorption may be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively (Fig. 2). On addition of tested metal ions representative of Li(I), Na(I), K(I), Rb(I), Ba(II), Sr(II), Al(III), Cd(II), Co(II), Cu(II), Hg(II), Ni(II), Pb(II), Zn(II) ions were added (2equiv.) to the solution (1.25×10^{-5} M) of

HCC4 (Fig. 2a, b), only pronounced response has been found for Pb(II). The band intensity at 230 nm was surprisingly increased from 1.0 to 1.6 followed by disappearance of shoulder at 382 nm in case of Pb(II) ions (Fig. 2c).

The electronic spectra of these complexes observed at 230 and 282 nm could be assigned to π-electrons of carbonyl group and nitrogen/oxygen-metal charge transfer absorption upon complexation with metal [46]. However, similar titration experiment carried out for other metal ions even border line metal ions such as Cu(II), Ni(II), Co(II), Hg(II) and Zn(II), causes only a minimal enhancement in the absorption intensities which implies the selective response of HCC4 towards Pb(II). This remarkable complexation affinity towards Pb(II) ion proved that besides the soft nature of ligand or metal ion, thermodynamic stability, ionic radii, cavity size as well as geometry of ligand and metal ion are also important aspects for specificity which confers the affinity of ligand toward a metal ion.

Furthermore, we have also examined the anion binding studies of HCC4 with different anions like of F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$, NO_3^-, ClO_4^- and $Cr_2O_7^{2-}$ as their tetrabutylammonium salt under same conditions (Fig. 3). The characteristic UV-visible absorption changes have been
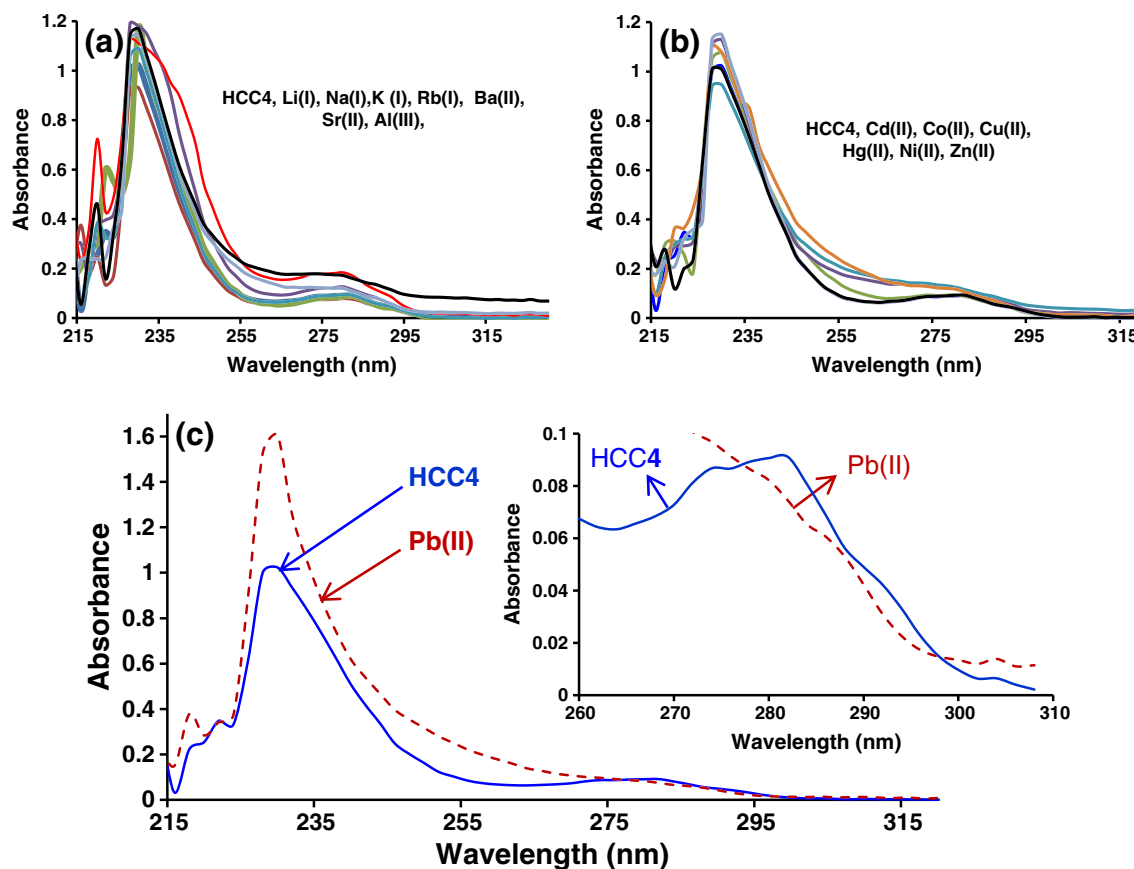
Fig. 2 Absorption spectra of HCC4 (1.25×10^{-5} M) and its complexes with various (**a**) Alkali and alkaline earth metal ions (2equvi.) (**b**) Transition metal ions (2equvi.) (**c**) With Pb(II)ion
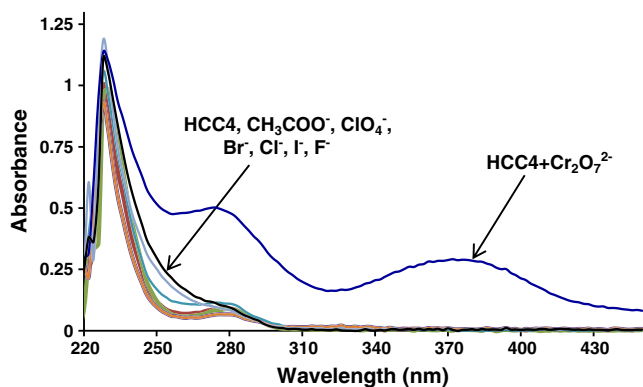
Fig. 3 Absorption spectra of HCC4 (1.25×10^{-5}M) and its complexes with different anions (2equvi.)

recorded upon the addition of tetrabutylammonium salts to a solution of HCC4 (1.25×10^{-5}M). Among the anions tested, HCC4 selectively bind $Cr_2O_7^{2-}$ anion. The absorption spectrum shows that upon addition of $Cr_2O_7^{2-}$ ion, not only strong absorption in the region 250–300 nm takes place but also a formation of new band in the visible region at 380–430 nm is the informative sign of complex formation. HCC4-$Cr_2O_7^{2-}$ selective complexation can be explained by the hydrogen bonded interaction between $Cr_2O_7^{2-}$ and hydrazide protons (–NH) of HCC4.

The absorption change (A_0-A) and ratiometric behavior (A/A_0) of **4** in the presence of guest ion (cation or anion) also supports the pronounced Pb(II) and $Cr_2O_7^{2-}$ selectivity of HCC4. From the bargraph representative of absorption change (A_0-A), Only Pb(II) and $Cr_2O_7^{2-}$ shows remarkable changes from HCC4 among rest of ions (Fig. 4a–d).

Pb(II) quantitative binding characteristics of HCC4 was determined by gradual increment of these metal ion concentrations into the solution of HCC4. Investigation of UV-visible spectral variation shows linear relationship between absorption intensity to Pb(II) ion concentration (Fig. 5a).

By plotting the changes in HCC4 in the absorbance intensity at 230 nm as a function of Pb(II) concentrations, Hoerl curve was obtained as shown in inset of Fig. 5a. From the inset, the inflection point was determined as 2.0 for ([Pb(II)]/[HCC4]) which explores 1:2 (ligand: metal) stoichiometry of complex.
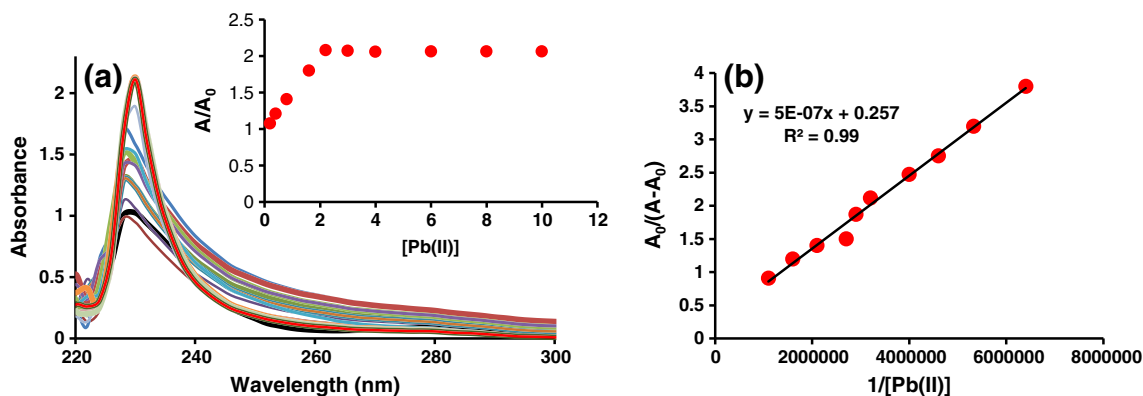
Association constant for Pb(II) was also calculated from Benesi-Hildebrand equations for UV-visible spectroscopic titration [47, 48].

For 1:2 (host: guest) stoichiometry:

$$\frac{A_0}{A - A_0} = \left(\frac{\varepsilon_0}{\varepsilon_0 - \varepsilon}\right)\left(\frac{1}{K_B[Guest]}^2 + 1\right)$$
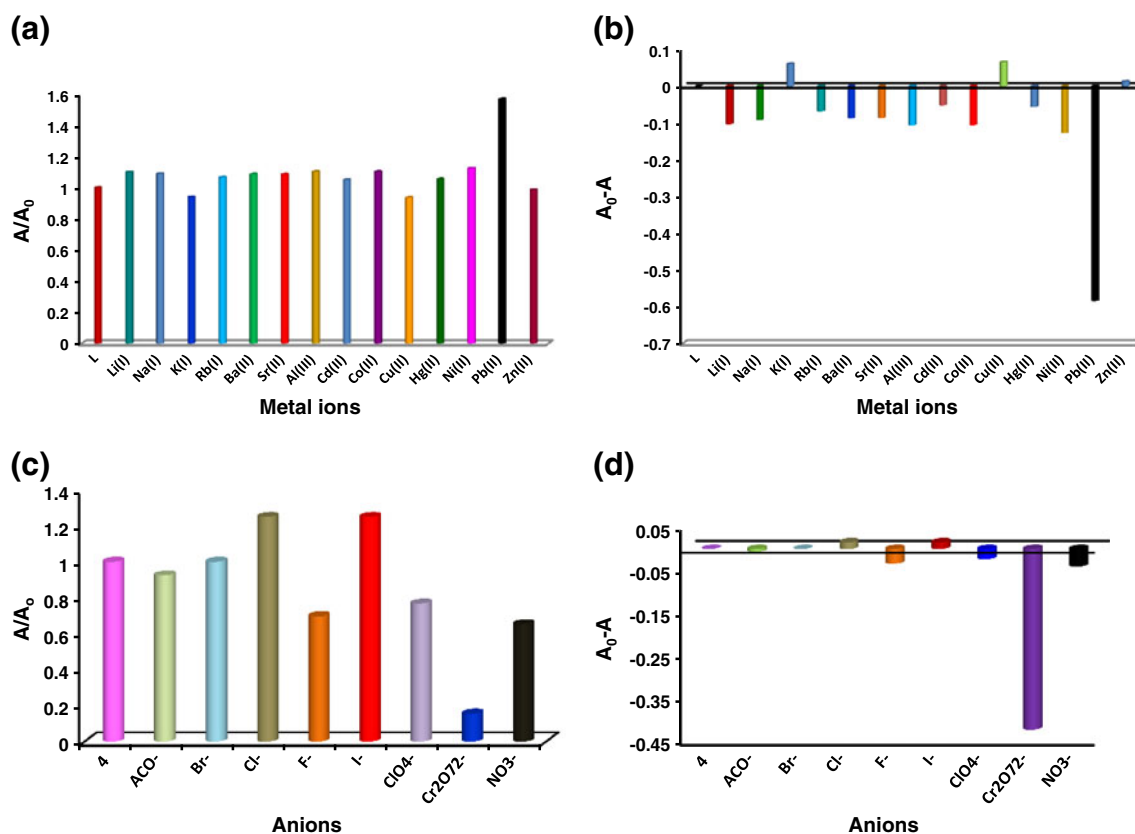
Fig. 4 UV-visible ratiometric behavior (A/A_0) and absorption change (A_0-A) of HCC4 (**L**) with various ions (**a,b**) cations (**c,d**) anions

Fig. 5 (a) Influence of the addition of increasing amounts (0.2→10 eq.) of Pb(II) on the absorption spectra of HCC**4** (1.25×10^{-5} M) in DCM-MeCN (b) A graph of $A_0/A-A_0$ versus 1/[Pb(II)] for the determination of association constant

Where A_0 and A represents the absorbance of HCC**4** measured before and after the addition of cations, respectively; ε_0 and ε are the corresponding molar extinction coefficients of HCC**4** in the absence and presence of the cations, respectively. [Guest] is the concentration of the titrants and K_B represents the association constant of host-guest complexation.

By plotting the ratio of $A_0/(A-A_0)$ plotted versus 1/[Pb(II)] as in Fig. 5(b), the value of log K was 5.71 (R^2=0.99) for HCC**4**-Pb(II) complex.

Same spectral behavior was obtained for $Cr_2O_7^{2-}$ ions as absorption profile of absorbance intensity versus $Cr_2O_7^{2-}$ ion concentration shows linearity (Fig. 6a). The log K value was found to 6.27 (R^2=0.99) for HCC**4**-$Cr_2O_7^{2-}$ (Fig. 6b) with the inflection point 2.0 ($[Cr_2O_7^{2-}]$/[HCC**4**]) which reveals the 1:2 (ligand:anion) stoichiometry of HCC**4**-$Cr_2O_7^{2-}$ complex (Table 1).

The stoichiometry of these complexes was evaluated by the method of continuous variation (Job's plot). Figure 7a represents the typical Job's plots of HCC**4**-Pb(II) complexation at

Fig. 6 (a) Influence of the addition of increasing amounts (0.2→10 eq.) of $Cr_2O_7^{2-}$ on the absorption spectra of HCC**4** (1.25×10^{-5} M) in DCM-MeCN (b) A graph of $A_0/A-A_0$ versus 1/[$Cr_2O_7^{2-}$] for the determination of association constant
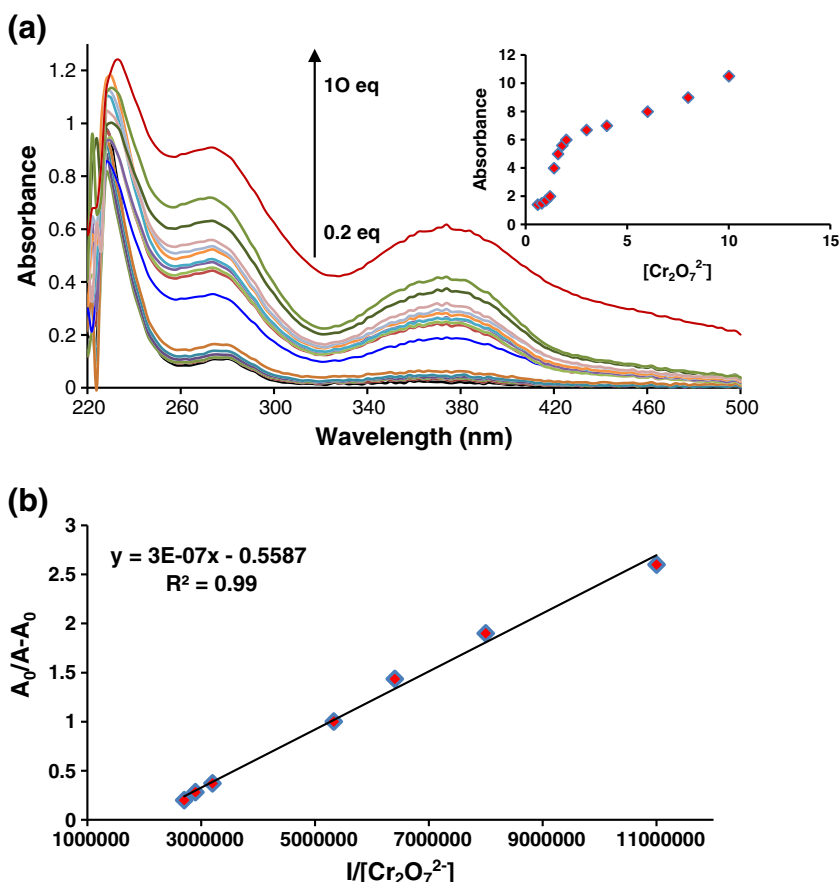
Table 1 Association constants of different ions

Stability constants							
Cations							
Li(I)	Na(I)	K(I)	Rb(I)	Ba(II)	Sr(II)	Al(III)	Cd(II)
n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Co(II)	Cu(II)	Hg(II)	Ni(II)	Pb(II)	Zn(II)		
n/a	n/a	n/a	n/a	5.71	n/a		
Anions							
$CH_3CO_2^-$	Br^-	Cl^-	F^-	I^-	ClO_4^-	$Cr_2O_7^{2-}$	NO_3^-
n/a	n/a	n/a	n/a	n/a	n/a	6.27	n/a

n/a Not available because of minor spectral changes

230 nm, a plot of absorbance versus mole fraction shows that the value goes through a maximum at a molar fraction of 0.67 indicating a 1:2 stoichiometry in the complex which indicated that two Pb(II) ions were interacting with receptor HCC**4**.

Job's plot experiment regarding stoichiometric determination between HCC**4** and $Cr_2O_7^{2-}$ at 272 nm shows 1:2 ratio, i.e. two dichromate ions coordinate ($Cr_2O_7^{2-}$) with HCC**4** (Fig. 7b).

Stability determination of chromogenic sensor as well as its complexes with respect to time is the zealous area of study; since it provide important information that our compound which is selective to particular ion make stable complex with the passage of time in a specific solvent.

In order to examine the stability of chromogenic sensor as well its complexes with Pb(II) and $Cr_2O_7^{2-}$ the absorption spectra of HCC**4** as well as its complexes in DCM-MeCN were instantly acquired (Fig. 8a–c) after continuous UV irradiation with the passage of 0, 50, 100, 150, 200, 250, 300, 350, 400 and 450 min [49].

On addition of $Pb(ClO_4)_2$ $3H_2O$, HCC**4** responds very fastly with significant enhancement in absorption intensity of a band at 230 nm followed by disappearance of another band 280 nm occurs very fast within 1 min: which remains constant for more than a week (Fig. 8b).

However, treatment with tetrabutylammoniumdichromate [$\{(CH_3CH_2CH_2CH_2)_4N\}_2$ Cr_2O_7] shows distinctive behavior

causes appearance of new band in the visible region. This anion complex also found to be stable even after 3 days (Fig. 8c).

Foreign ion Effect

The effect of foreign ion is an important parameter in complexation study since its tell us about strong or weaker complexation nature of ligand towards particular ions. The interference effect of some alkali (Li (I), Na(I), K(I)), Rb(I)) alkaline-earth (Ba(II), Sr(II)) and transiton metal ions as well as anions $CH_3CO_2^-$, F^-, Cl^-, Br^-, I^-, ClO_4^-, and NO_3^- during sensing of Pb(II) and $Cr_2O_7^{2-}$ respectively, was investigated. The competitive experiments were carried out at fixed concentration of these ions at 1.25×10^{-5} mol L^{-1} and then recording the change of the absorption intensity before and after adding the interferent (2 equiv. each) into the Pb(II) and $Cr_2O_7^{2-}$ solutions. The UV-visible spectra show that no any other ions except Hg(II) caused significant variation in the absorption spectra of HCC**4**-Pb(II) complex (Fig. 9a). These results reveal that HCC**4** showed high affinity towards Pb(II).

Moreover, the results obtained from the study regarding interfering effect of afformentioned anions also confirms the $Cr_2O_7^{2-}$ selective nature of HCC**4** sensor as except slight inference from I^-, no other ion causes signifcant variations in the UV-visible spectra of HCC**4**-$Cr_2O_7^{2-}$ (Fig. 9b).
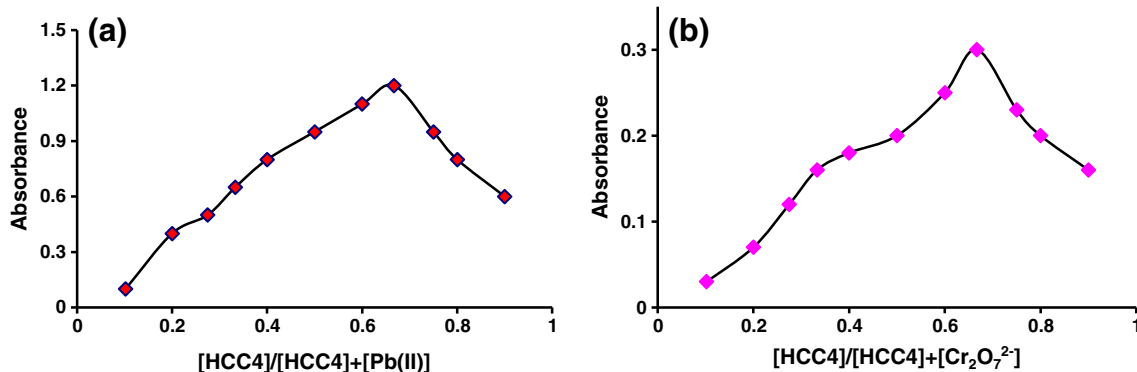
Fig. 7 Job's plot determination of complexes of HCC4 (1.25×10^{-5} M) (a) Pb(II) (b) $Cr_2O_7^{2-}$
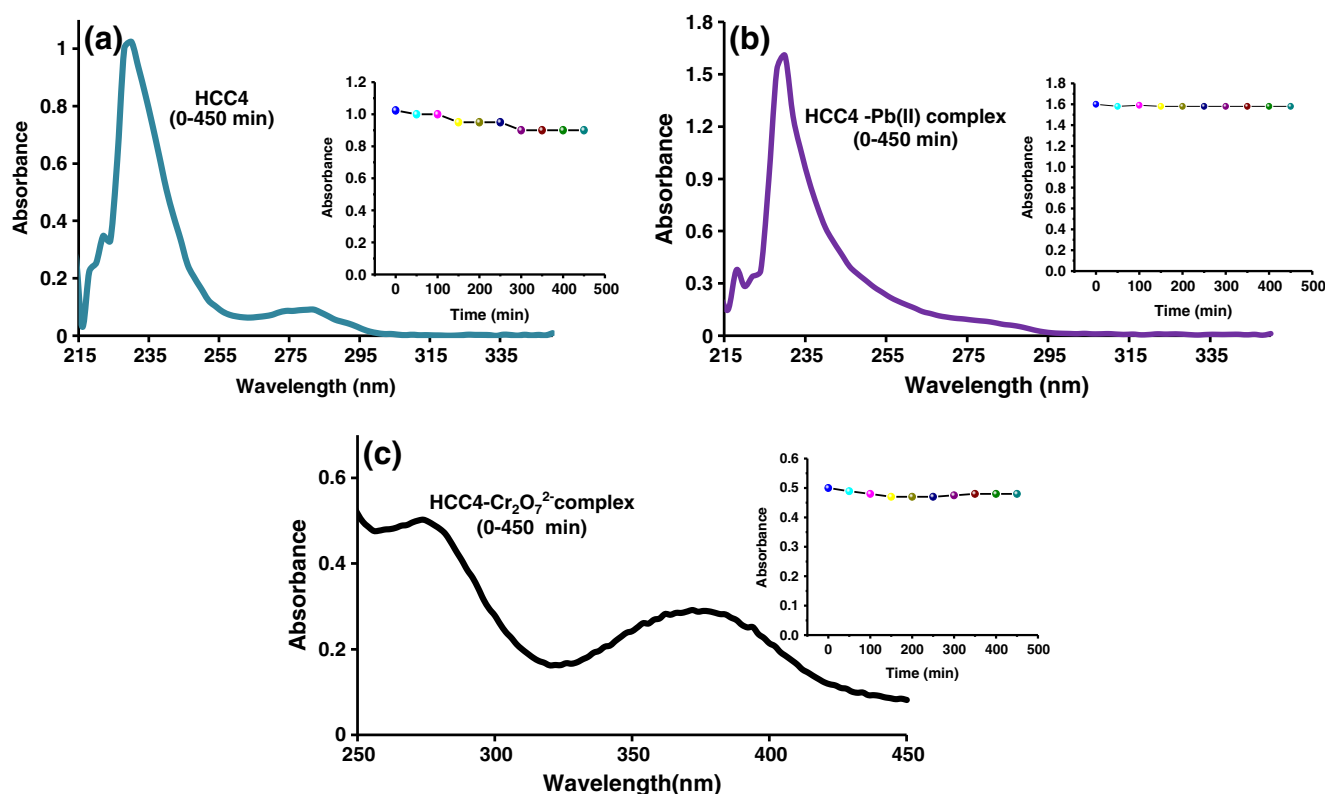
Fig. 8 Time-dependent absorption spectra of (**a**) HCC4 (**b**) HCC4-Pb(II) complex (**c**) HCC4-$Cr_2O_7^{2-}$ at 1.25×10^{-5}M in DCM-MeCN upon irradiation of UV light; (inset) graphs showed stability of HCC4 and its complexes with respect to time

Same trend can been seen from absorption change (A_0-A) and ratiometric behaviors (A/A_0) of metal and anion complexes of HCC**4** (Fig. 10 a–d).

Liquid–Liquid Extraction Study

In order to further verify the Pb(II) selective complexation of HCC**4**, liquid–liquid extraction procedure was applied to evaluate the cation binding affinity of HCC4 in transferring different metals, such as, alkali (Li(I), Na(I), K(I)), Rb(I)), alkaline earth (Ba(II), Sr(II)) and transition metals (Al(III), Cd(II), Co(II), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II)) from

aqueous to organic medium (Fig. 11a), i.e. DCM. The extraction efficiency (%E) of HCC4 toward all aforementioned metal picrates is given in Fig. 12a and Table 2. As seen from Table 2, extraction ranges of HCC**4** towards all the metal cations between 10 % and 96.4 % using DCM as organic solvent. Among the metal cations, it has been observed that HCC**4** shows greater extraction ability toward Pb(II) as compared to parent compound **1**, i.e. 94 %. However, the %E value for Hg(II) ion was found to be 47 % which may be ascribed to the borderline nature of Hg(II) as well as HCC4 which possess borderline nitrogen donor atom binding functionality therefore, it may coordinate with
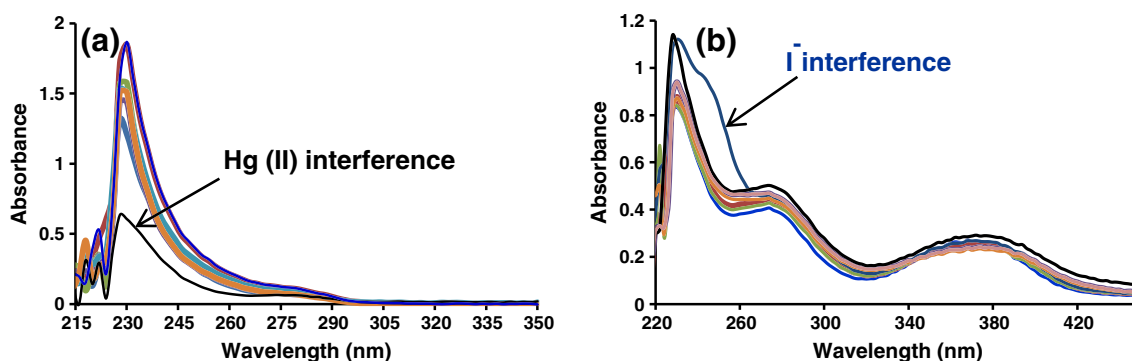
Fig. 9 Absorption response of HCC4 (1.25×10^{-5}M) in DCM-MeCN upon addition of various metal ions into the solution of (**a**) HCC4-Pb(II) complex (**b**) HCC4-$Cr_2O_7^{2-}$ complex
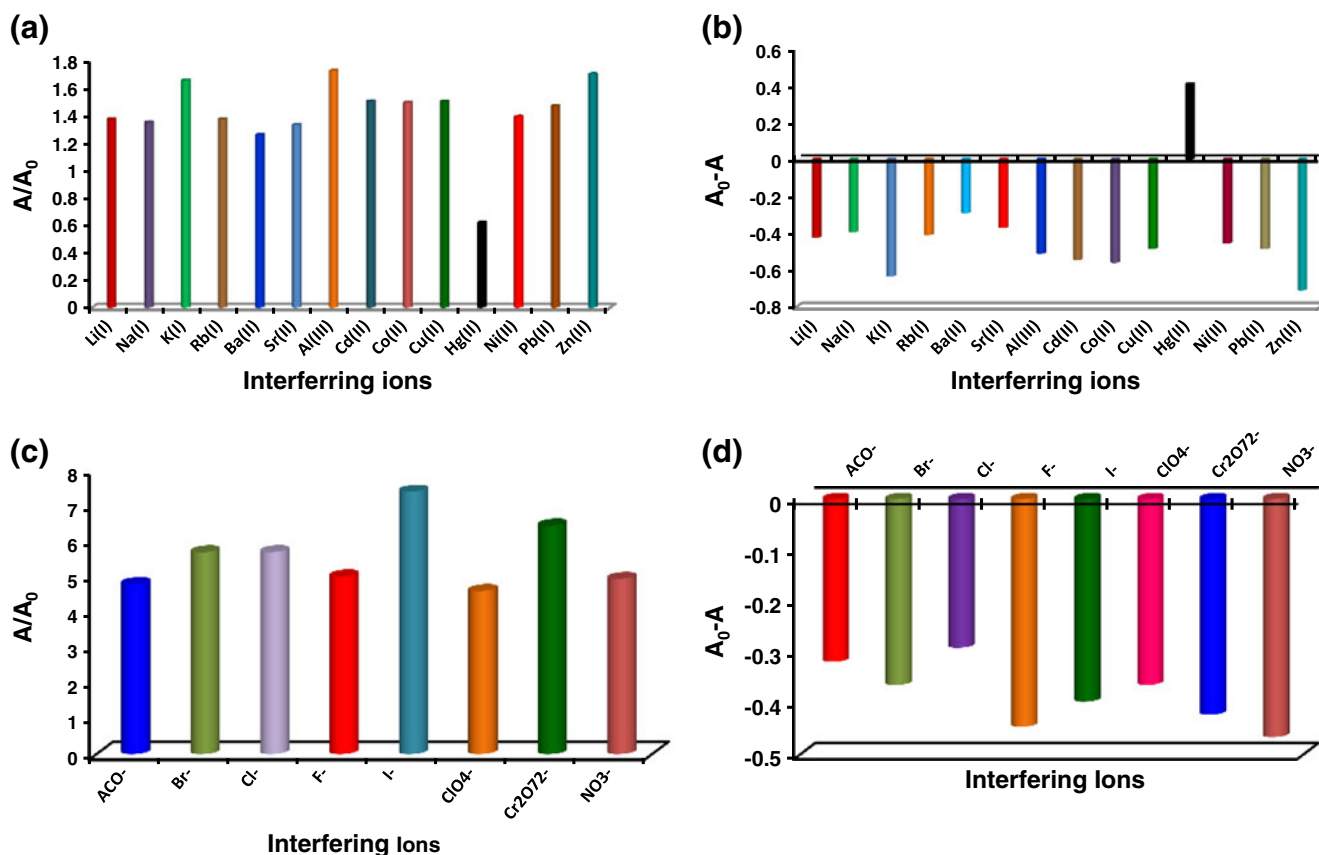
Fig. 10 Ratiometric and absorption response of HCC4 towards interfering ions in the presence of (**a,b**) Pb(II) (**c,d**) $Cr_2O_7^{2-}$

borderline cations, Fe(II), Co(II), Ni(II). The trend of extraction ability of HCC4 toward the metal ions was found in the order: Pb(II)>Hg(II)>K(I)>Cu(II)>Ni(II)>Zn(II)>Cd(II)>Co(II)>Na(I)>Al(III)>Ba(II)>Rb(I)>Sr(II)>Li(I). These enhanced extraction ability of HCC4 for Pb(II) may be due to the arrangement of its amide binding functionalities according to the geometries of these metal ions, as well as the compatibility between the ionic radii and cavity size

of HCC4. These features enhance the utility of HCC4 in various fields such as environmental chemistry, membrane technology, and ion selective electrodes technology and phase-transfer reactions.

All these above mentioned discussion discloses that appropriate cationic size, presence of donor nitrogen atoms in the binding sites of HCC4 in a periphery, their effectiveness and aggregation, and their collective/cooperative behavior
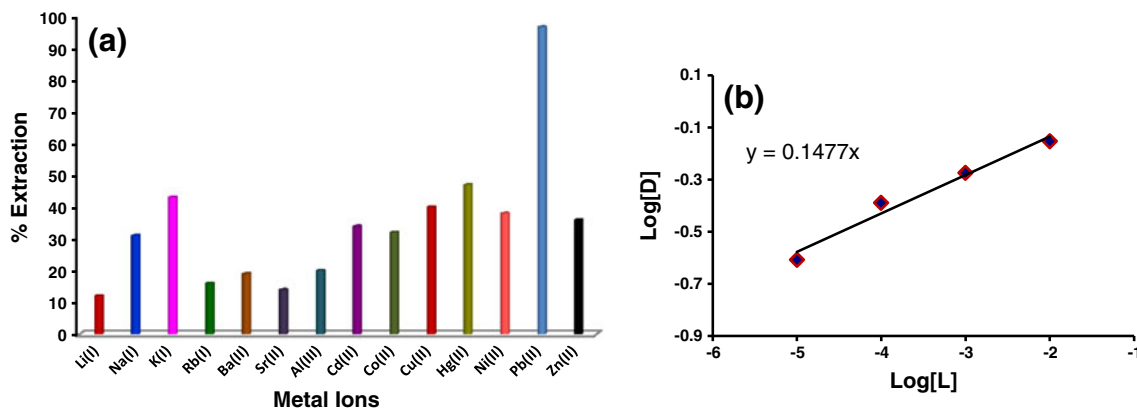
Fig. 11 (**a**) % Extraction efficiency of HCC4 towards various metal picrates. Aqueous phase, [metal picrate]=2.5×10^{-5}M; organic phase, DCM, [HCC4]=1×10^{-3}M at 25 °C for 1 h. (**b**) Log D versus log [L]

for the extraction of Pb(II) picrate by HCC4 from an aqueous phase to organic phase, i.e. DCM at 25 °C

Fig. 12 Emission spectra of HCC4 (1.25×10^{-5} M) upon addition of various (**a**) metal ions (**b**) anions (2equiv.) in DCM-MeCN; (Inset.) spectra with selected wavelength showed major changes in the fluorescent spectra HCC4 towards various ions
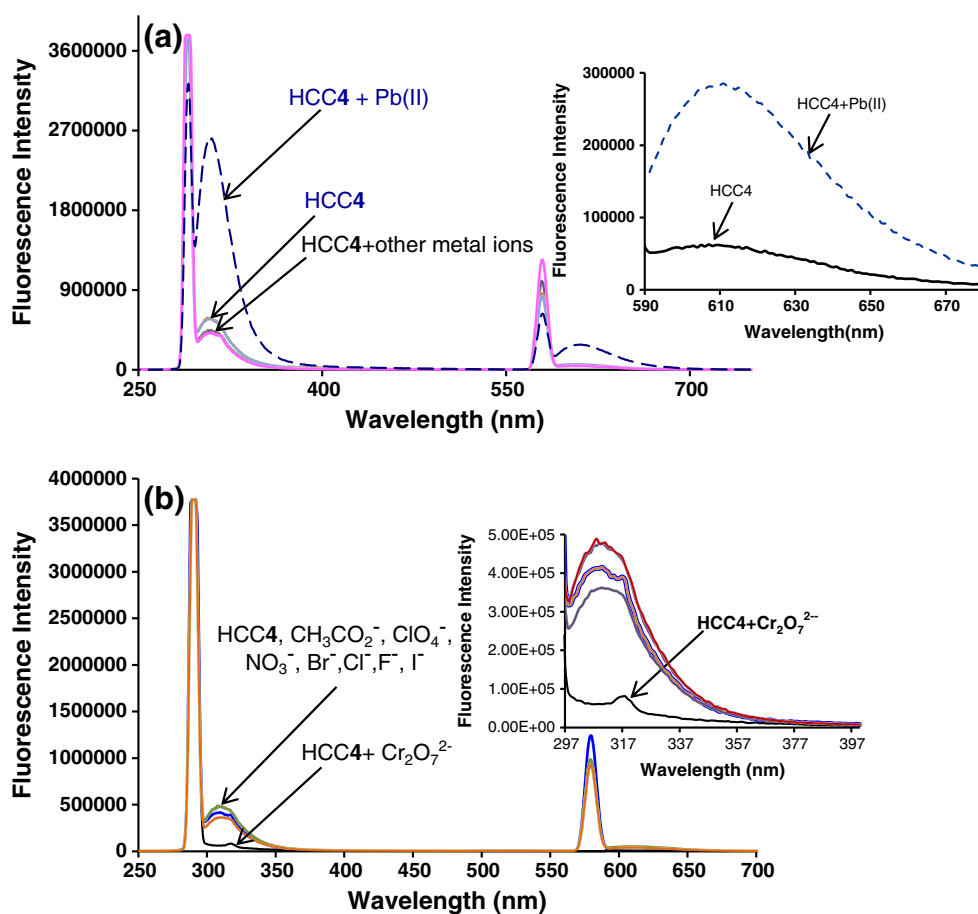

along with the size of aromatic ring play an important role in complexation phenomenon.

Log-log Plot Analysis

For the characterization extraction ability, the dependence of the distribution coefficient D of the selective metal ion between the two phases upon the calixarene concentration was examined [51]. If the general extraction equilibrium is assumed to be Eq. 1 with M^{n+} 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. When introduce the distribution coefficient

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

$$\overset{n+}{M}_{aq} + {}^{n}Pic^{-}_{aq} + x[L]_{(org)} \rightleftharpoons \left[M(pic)_n(L)_x\right]_{org} \quad (1)$$
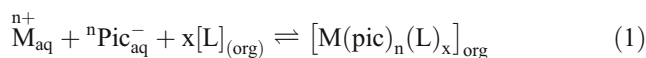
Extraction equilibrium constant is expressed as Eq. (2)

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

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

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

Table 2 Comparative (%) Extraction results of metal ions by compound **2** and HCC4

Extracted metal picrates (%)

Ligand	Li(I)	Na(I)	K(I)	Rb(I)	Ba(II)	Sr(II)	Al(III)	Cd(II)
2[a]	18.9	8.5	3.3	–	–	–	–	9.4
HCC4	12	31	43	16	19	14.8	20	34
	Co(II)	Cu(II)	Hg(II)	Ni(II)	Pb(II)	Zn(II)		
2[a]	7.9	9.9	15.5	6.3	<1	–		
HCC4	32	40	47	38	94	36		

[a]Ref. [50]

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

$$Log\,D = Log(K_{ex}(Pic^-)^n) + \times log[L] \qquad (4)$$

With these possibilities, 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 [47].

Figure 11b shows a plot of Log D versus Log [L] for the extraction of Pb(II) by HCC4. A linear relationship between Log D and -Log [L] with the slope of lines of Pb(II) roughly equal to 0.147, suggesting that HCC4 forms 2:1(M:L) complex with Pb(II).
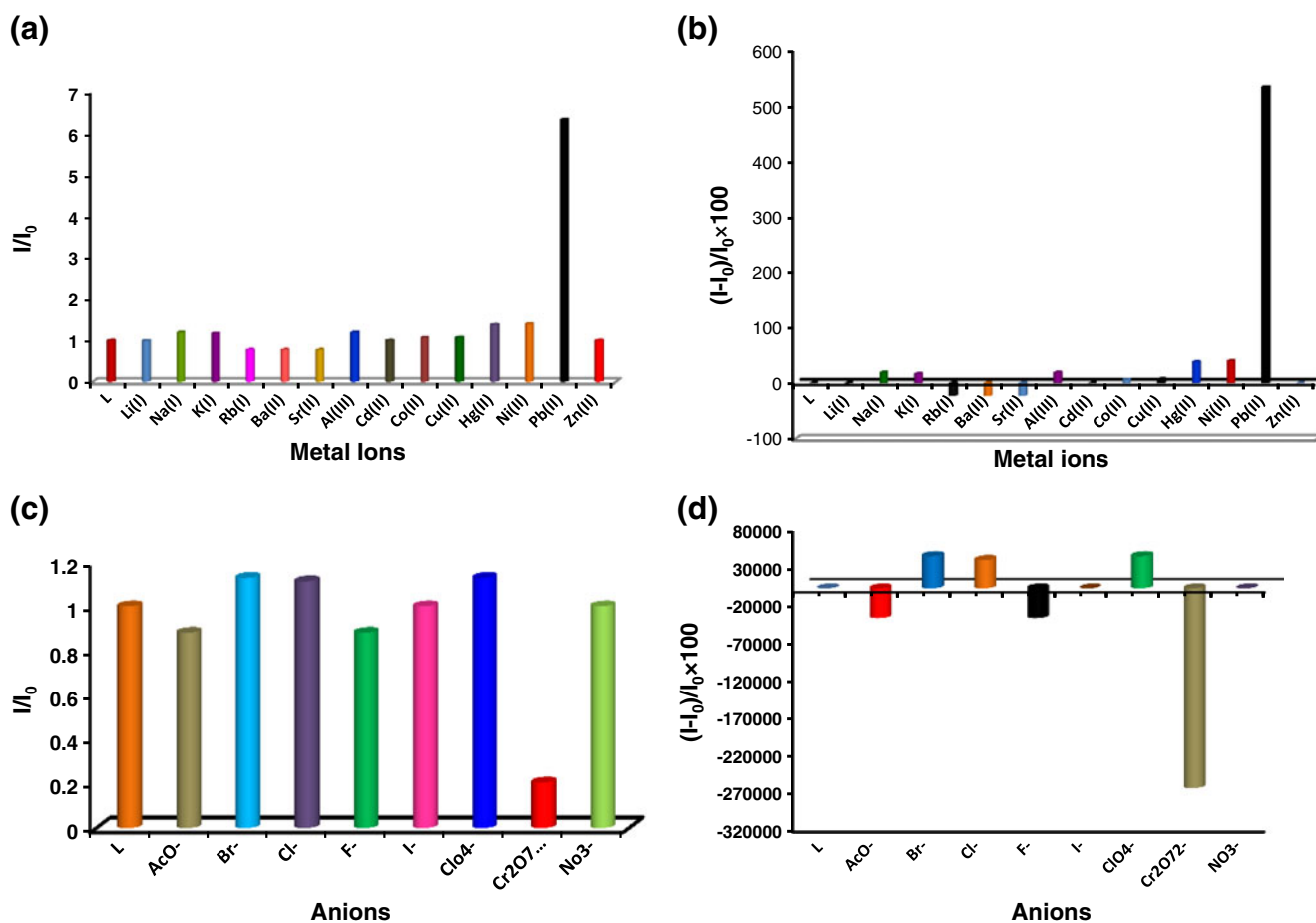
Fluorescence Study

To investigate the fluorescence behavior of HCC4 towards Pb(II) and $Cr_2O_7^{2-}$, titration experiment was performed under same condition as in UV-visible spectroscopy. In the fluorescence spectrum (Fig. 12), HCC4 exhibited a typical strong emission band at 288 nm along with two weak emissions 306, 580 nm. Upon addition of small amount
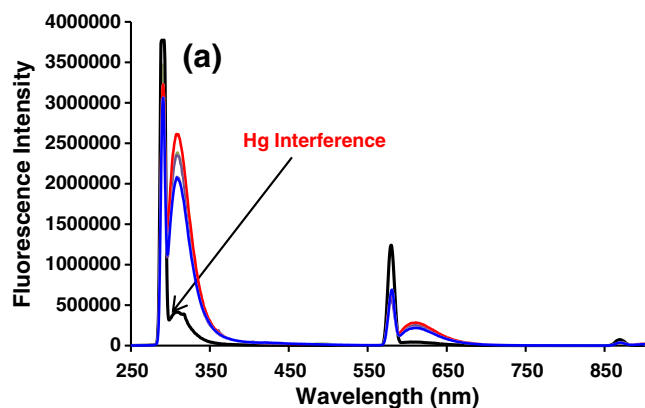
(2 eq) of Pb(II) ion into the solution of HCC4 (1.25×10^{-5} M), the emission intensity at band 306 nm was remarkably increased up to 6 fold along with formation of new band at 609 nm (inset Fig. 12a), However, rest of metal ions such as Li(I), Na(I), K(I), Rb(I), Ba (II), Sr(II) Al(III), Cd(II), Co(II), Cu(II), Hg(II), Ni(II), and Zn(II) under same aforementioned condition did not cause significant influence on the emission spectra of HCC4. These pronounced result obtained after Pb(II) addition among series of various cations confirms the HCC4 as Pb(II) selective potential probe.

Furthermore, HCC4 as a highly $Cr_2O_7^{2-}$ selective On-Off fluorescent sensor was confirmed by its fluorescence quenching nature in band intensity at 306 nm among series of other tested anions like $CH_3CO_2^-$, F^-, Cl^-, Br^-, I^-, ClO_4^-, and NO_3^- (Fig. 12b). Fluorescence quenching ratio $[(I-I_0)/I_0 \times 100]$ and emission changes (I/I_0) also reflects the strong complexation of HCC4 towards Pb(II) and $Cr_2O_7^{2-}$ ions (Fig. 13a–d).

The competition experiments were also conducted for HCC4 to observe the significant changes in the fluorescence emission of HCC4, with or without addition of Pb(II) and $Cr_2O_7^{2-}$ ions in the presence of other co-existing ions.

Fig. 13 Fluorescence quenching ratio $(I-I_0)/I_0 \times 100$ and ratiometric response (I/I_0) of HCC4 (**L**) towards various (**a,b**) cations (**c,d**) anions

Fig. 14 Fluorescence response of HCC4 (1.25×10^{-5}M) in DCM-MeCN upon addition of various metal ions into the solution of (**a**) HCC4-Pb(II) complex

When 2 equiv. of interfering ions was added into the solution of HCC4 in the presence of 2 equiv of Pb(II) ion, except Hg(II), the fluorescence spectra with other ions displayed a similar pattern at near 306 and 609 nm as compare to Pb(II) ion only (Fig. 14). However, addition of Hg(II) causes breaking of 4-Pb(II) complex and results in restoration of ligand fluorescence spectral properties.

On the other hand, addition of foreign anions into the solution of HCC4 in the presence of $Cr_2O_7^{2-}$ ions gave more or less similar response except I^- which causes slight interference. Relative fluorescence intensity (I/I_0) and fluorescence quenching ratio [$(I-I_0)/I_0 \times 100$] of Pb(II) and $Cr_2O_7^{2-}$ complexes also shows that except some interference they were not significantly affected by presence of 2 equiv. of other ions (Fig. 15a–d).

All the results obtained from UV-visible and fluorescence study shows that receptor HCC4 possess ideal geometry with maximum number of both soft/hard binding sites to accommodate Pb(II) ion. Moreover, binding possibility at narrow rim of calix[4]arene can be discarded by the presence of strong intramolecular hydrogen bonding between phenolic hydrogens.

For a molecule to be effective as an anion host, it is necessary that its structural features are compatible with those of the guest anion. The dichromate ($Cr_2O_7^{2-}$) ions are oxo/dianions with oxide functionalities at their periphery; consequently, these functionalities are potential sites for hydrogen bonding to the $Cr_2O_7^{2-}$. Therefore, receptor HCC4 that is fixed in a cone conformation carrying hydrazide binding groups at both rims is seems to be ideal in terms of $Cr_2O_7^{2-}$ binding.
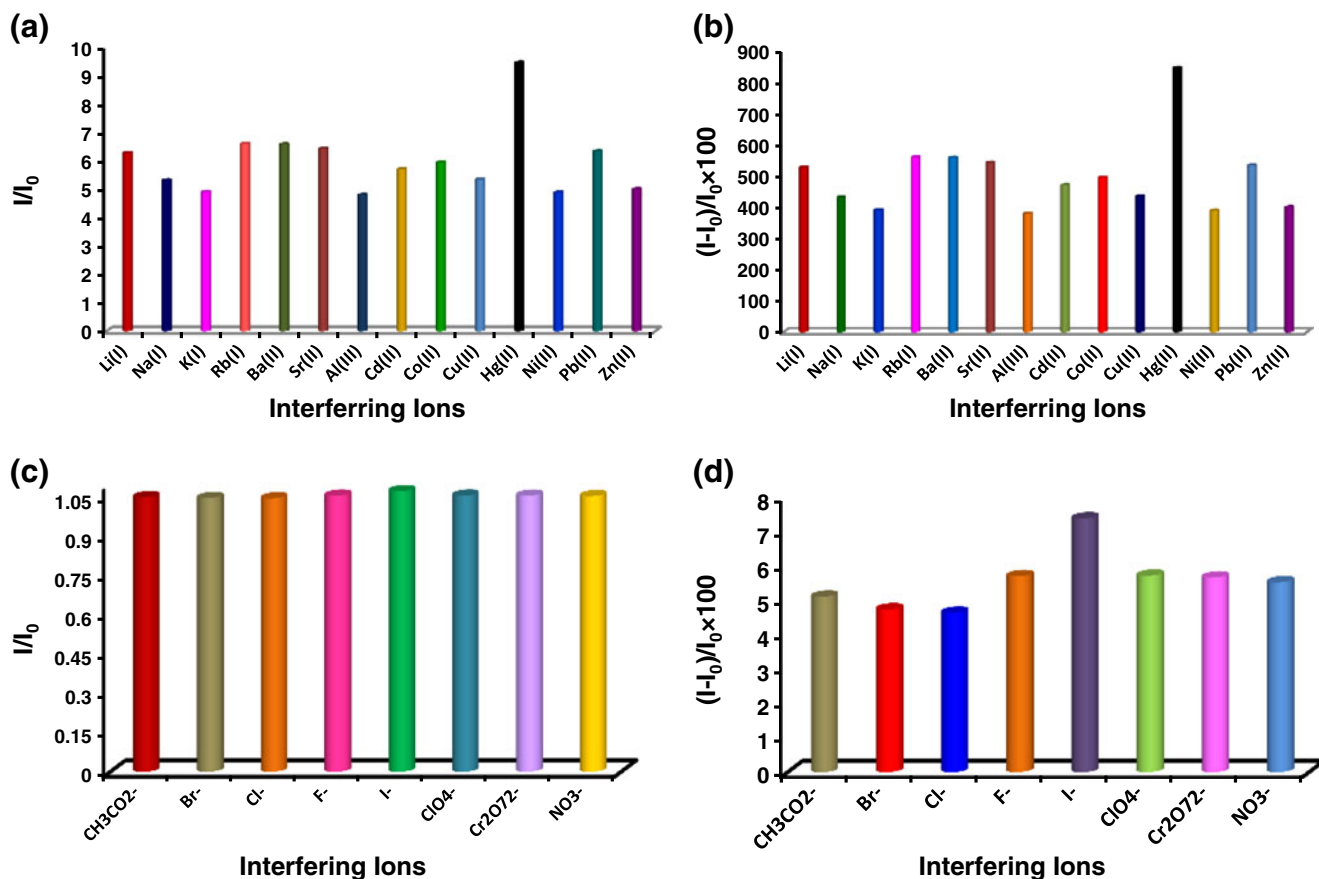
Fig. 15 Fluorescence quenching ratio $(I-I_0)/I_0 \times 100$ and relative fluorescence intensity (I/I_0) of HCC4 towards interfering ions in the presence of (**a,b**) Pb(II) (**c,d**) $Cr_2O_7^{2-}$
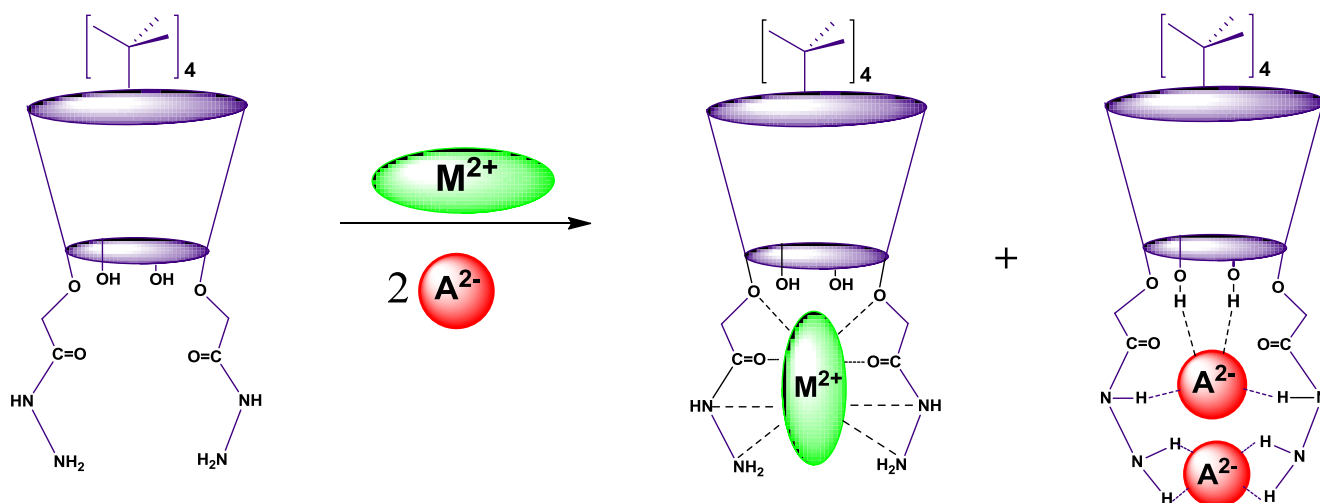
Fig. 16 Proposed interactions between receptor HCC4 and metal/anion

Thus, with reference to Jobs' plot and molar ratio stoichiometric analysis, therefore, the proposed mechanism for metal–ligand as well as anion–ligand interaction is shown in Fig. 16.

Thermal behavior

The thermo gravimetric analysis (TGA) provides us an informative sign for thermal stability, amount confirmation
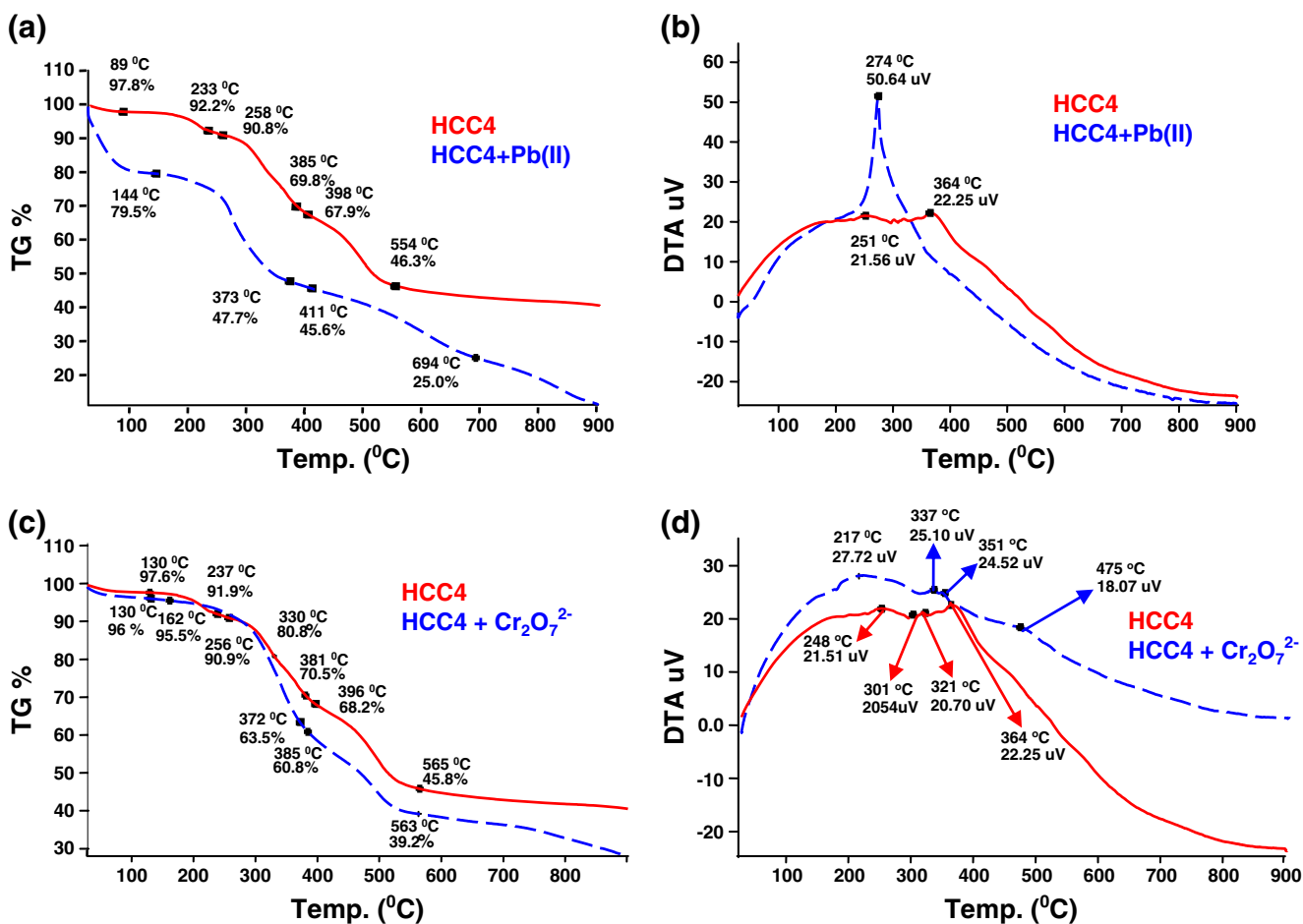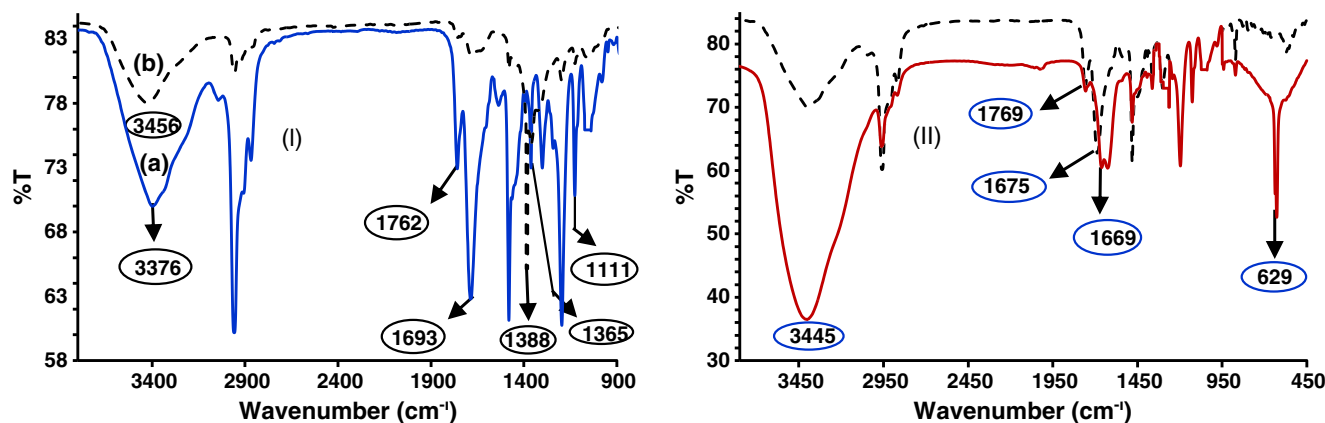

Fig. 17 The TG/DTA curves of HCC4 and its complexes with (**a,b**) Pb(II), (**c,d**) $Cr_2O_7^{2-}$ in N_2 atmosphere

Fig. 18 (I) Comparative FT-IR spectral data for [(**a**) HCC4 and (**b**) Pb(II) complex] (II) $Cr_2O_7^{2-}$-complex

and purity of the compounds. Therefore, thermal stability of the HCC4 as well as and its complexes with Pb(II) and $Cr_2O_7^{2-}$ were evaluated by thermal analysis (TG//DTA). It was found that HCC4 undergo a three-step thermal degradation (Fig. 17a–d). The first step (89–233 °C) is due to the loss of moisture, whereas the second step (258–385 °C) could be attributed to the loss of the corresponding amide functionalities of HCC4, while the third one (398–554 °C) is due to the cleavage of the calixarene backbone. TG curve of HCC4-Pb(II) complex, shows two step thermal degradation process and relatively appears to be less stable as compare to its parent molecule as it reduced to 48 % (52.3 % mass loss, 1.25 mg) in the first step up to 373 °C and finally reduced to 25 % (mass loss 75 %, 2.068 mg) at 653 °C at second step respectively whereas parent molecule was found to be stable up to this stage, i.e. 554 °C and reduced to only 46 % (54 % mass loss, 2.64 mg). The DTA result of the HCC4 showed the weight loss exothermic weight loss two exothermic peaks at 248, 301, 321 and 364 °C which becomes replaced by only one sharp hypsochromic shifted weight loss exothermic peak at temperature of 274 °C after complexation with Pb(II).

Thermal behavior of anionic complex of HCC4, i.e., HCC4-$Cr_2O_7^{2-}$ was also determined. TG curves of aforementioned complex shows two step thermal degradation process at 162–372 °C and 385–563 °C with finally reduced to 39 % (61 % total mass loss, 3.61 mg). DTA curves of HCC4-$Cr_2O_7^{2-}$ complex shows weight loss exothermic weight loss four exothermic peaks at 217, 337, 351, and 475 °C. Although thermal gravimetric analysis of all complexes shows relatively more thermal sensitivity with respect to their parent HCC4 nevertheless, this technique confirms formation of this complexes [39].

FT-IR Study

Infrared spectroscopy is considered to be the most informative method for the characterization of host–guest interactions and numerous authors reported FT-IR and FT-IR

Raman spectroscopic studies on complexation phenomena. It offers various powerful methods to obtain deeper insight into the chemical structural changes of macrocycles caused by complex formation. The potential applicability of HCC4 as Pb(II) selective sensor was further confirmed by FT-IR spectroscopic analysis and are presented in Fig. 18(I).

FT-IR spectrum of HCC4 showed distinguish bands (KBr/cm⁻¹) at 3,376 [υ(O••••H)], 1,762 and 1,693 for υ(C=O), 1,365 for υ(C–N), l511 and 1,484 for aromatic υ(C=C) and 1,200 for υ(C–O) respectively. After complexation, the spectrum of HCC4 shows distinctive variations in terms of shifting, disappearance and appearance of new bands. From the Fig. 18(I), it has been observed that the region at 3,500–3,000 cm⁻¹ shows significant differences as the band at 3,482 cm⁻¹ for υ(O••••H) was blue shifted to 3,456 cm⁻¹ clearly gives the indication for changing in the geometry of molecule as a result of introduction of Pb(II) into ligand cavity. Noticeable changes appeared at region 2,000–1,500 cm⁻¹, where two sharps peeks υ(C=O) at 1,762 and 1,693 cm⁻¹ was completely disappeared after complexation with both metal ions. Furthermore, Pb(II) complex shows remarkable red shifting of peak from 1,365 to 1,388 cm⁻¹(υ(C–N)) due to metal-nitrogen stretching vibration which gives clear indication for involvement of nitrogen donors with Pb(II) ion.

On contrary, FT-IR complexation analysis of HCC4 with $Cr_2O_7^{2-}$ also shows different spectral characteristics (Fig. 18(II)), where two sharps peaks at 1,762 and 1,693 cm⁻¹ ascribed for υ(C=O) remains present after complexation followed by disappearance of peak at 1,365 cm⁻¹ (υ(C–N)). At 629 cm⁻¹ new sharp also appears which may be attributed to the involvement of protons of amines binding sites with both $Cr_2O_7^{2-}$.

Conclusions

In summary, we show here the selective chromogenic and fluoregenic characteristics of hydrazide derived calix[4]

arene sensing derivative. HCC4 was appeared to be bifunctional potential chemosensor for Pb(II) ion. Selectivity study shows the slightly interference from foreign ions on HCC4-Pb(II) complex as the presence of soft binding sites seems to be ideal in terms of size, arrangement and accommodation of Pb(II) ions. On the other hand, we also have explored highly selective dichromate ($Cr_2O_7^{2-}$) ion selective chromogenic/fluorescent sensor first time with minor foreign ion effect as presence of protons of hydrazide moieties with in calix[4]arene frame work confers its high specificity towards $Cr_2O_7^{2-}$. All of complexation process was further verified by TGA and FT-IR and spectral analysis.

Mainly, the design approach and extraordinary photophysical properties of the sensor HCC4 would help to extend the development of fluorescent sensors for other toxic metal ions and anions.

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