

Calix[4]arene Based Highly Efficient Fluorescent Sensor for Au³⁺ and I⁻

Shahabuddin Memon¹ · Ashfaque Ali Bhatti¹ · Asif Ali Bhatti¹ · Ümmühan Ocak² · Miraç Ocak²

Received: 28 March 2015 / Accepted: 6 August 2015 / Published online: 20 August 2015
© Springer Science+Business Media New York 2015

Abstract This approach disclose the selective fluorogenic ion sensing ability of 5,11,17,23-tetraterbutyl-25,27-bis((2-hydroxy-naphthylimino)-1,2-ethylenediaminecarbonylmethoxy)-2,6,28-dihydroxycalix[4]arene (**C4NSB**). Binding property of receptor probed by using selected various cations and anions with conferring of results that demonstrates ‘turn-off’ fluorescence response and significantly high chromogenic selectivity toward Au³⁺ and I⁻. Furthermore, selective nature of receptor was investigated in the presence of different co-existing competing ions. The limit of detection (LOD) for Au³⁺ and I⁻ was determined as 1.5×10^{-5} and 4.5×10^{-6} M respectively. Receptor **C4NSB** form (1:1) stoichiometric complex with both ions and their binding constants were calculated as 8.0×10^2 for Au³⁺ and 15.6×10^2 M⁻¹ for I⁻. Complexes were also characterized through FT-IR spectroscopy.

Keywords Calix[4]arene · Fluorescent · LOD · Complex · FT-IR spectroscopy

Introduction

Selective and sensitive determination of biologically and environmentally relevant cations and anions by chemosensors

has remained in keen interest because they controls important functions in living systems and have an extremely toxic impact on the environment [1–5]. Gold ions are known as inhibitors of macrophages and polymorphonuclear leucocytes [6] and to suppress inflammation in rheumatic joints [7]. Au³⁺ has highly toxic effects to DNA and the nervous system [8] and subsequently damages DNA via catalytic cleavage [9].

On the other hand I⁻ is biologically important anion and is significant micronutrient which plays a key role in many physiological activities such as brain development, metabolism, neurological functions and thyroid gland activity [10]. It is essential element for life and biosynthesize thyroid hormones which is necessary for metabolism and mental growth [11]. However, its deficiency leads severe delays in neurological development, cretinism and endemic goiter while an excessive ingestion can also cause hyperthyroidism [12]. Accordingly, selective sensing of these ions would be very useful for the development of cellular imaging probes and other purposes in various biological and environmental fields. Molecular recognition is a crucial process in biological systems, such as enzymes, antibodies or genes and is fundamental to supramolecular chemistry [13–15]. The development of powerful and highly selective chemosensors for the detection of ions have continuously been charming zone of supramolecular chemistry [16–18]. Among them fluorescent chemosensors are very important due to instantaneous, remote and constant analytical measurements, allowing increased sensitivity and selectivity against competing analytes, reduced instrumental drift and miniaturization capabilities which are reliable and low cost [19]. It is one of the most promptly emerging fields in biology and medicine, which opens the door for molecular probes in vitro and in vivo monitoring of biologically relevant analytes [20]. This method of detection requires fluoroionophores, which are composed of an ion recognition unit, known as ionophore, and a fluorogenic unit as a

✉ Shahabuddin Memon
shahabuddinmemon@yahoo.com

¹ National Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan

² Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, Trabzon 61080, Turkey

probe, the photophysical property of which perturbs during the recognition process producing changes in luminescent emission [21]. Recently there has been momentous advancement in exploitation of supramolecules for the development of novel fluorescent sensors. Calix[4]arene has been widely employed as the basic molecular scaffold for the development of many fluorescent chemosensors. Their macrocyclic core being accessible in a variety of sizes, easily pre-organised into a number of flexible three dimensional topographies and readily selectively functionalized for the introduction of ionpores make them perfect structural platforms for molecular design to generate fluorescent receptors [22]. These metacyclophanes are versatile ionophores, which provide a platform for attachment of convergent binding groups to develop complexing host molecules primarily for cations, anions and small molecules [23–29].

Moreover, presence of ligating groups determines their selective nature for efficient recognition of cations and anions. The introduction of signaling functionality such as ether, amide, Urea, Thiourea, Schiff bases and also pyrene, anthracene, naphthalene and dansyl as fluorophores that selectively recognize both metals and anions [30–36]. Significant research has devoted for the development of selective fluorescent chemosensors of Au^{3+} and Γ^- [37–45]. But calix[4]arene based fluorescent chemosensors are rare. Keeping in view the above approaches and in continuation of our efforts for the exploration of calix[4]arenes as selective and efficient sensors [46–51]. Herein we report the newly synthesized 2-hydroxynaphthaldehyde functionalized calix[4]arene Schiff base (**C4NSB**) as fluorescent sensor Au^{3+} and Γ^- .

Experimental

Chemicals

All reagents and solvents of standard analytical grade were purchased from Alfa Aesar (Germany), Merck (Darmstadt, Germany) and were used without further purification. Standard salt solutions of metals were purchased from Sigma and Aldrich. All aqueous solutions were prepared with deionized water that was passed through a milli pore milli Q Plus water purification system.

Instrumentation

Melting points were determined on a Gallenkamp (UK) apparatus in a sealed capillary tube. Elemental analyses (CHNS) were performed using Flash EA 1112 elemental analyzer. NMR spectra were recorded with an Agilent 400 MHz spectrometer in DMSO using tetramethylsilane (TMS) as an

internal standard at room temperature. Thermo Nicolet AV-ATAR 5700 FT-IR spectrometer was used for recording IR spectra within a spectral range from 4000 to 400 cm^{-1} . Analytical TLC was performed on pre-coated silica gel plates (SiO_2 , Merck PF_{254}). Absorption spectral investigation of **C4NSB** and its complexes were performed on a Perkin Elmer Lambda-35 double beam spectrophotometer using standard 1.00 cm quartz cells whereas emission spectra were recorded on a Photon Technologies International Quanta Master Spectrofluorimeter (model QM-4/2006).

Synthesis of 5,11,17,23-tetratertbutyl-25,27-bis((2-hydroxynaphthylimino)1,2-ethylenediaminecarbonylmethoxy)-26,28 dihydroxycalix[4]arene (C4NSB)

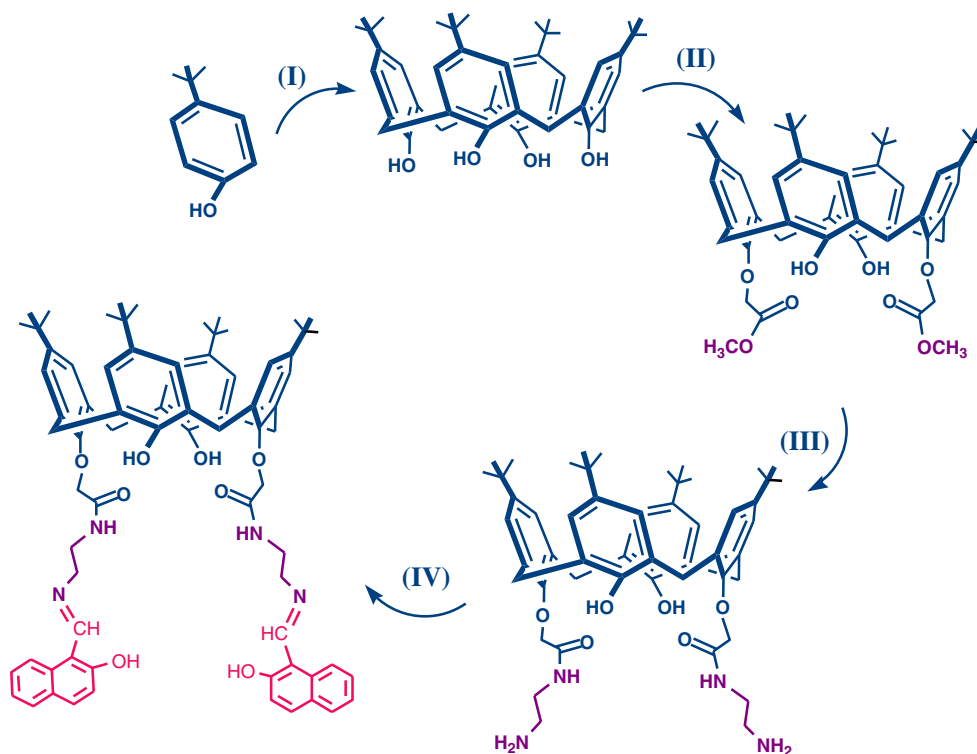
Synthesis of compounds **1**, **2** and **3** is depicted in Scheme 1 was carried out by following reported procedures [52–54] and finally receptor **C4NSB** was synthesized by treating (0.087 g, 0.50 mmol) solution of 2-hydroxynaphthaldehyde in absolute ethanol and was added drop wise into a stirring solution of calix[4]arene (**3**) (0.30 g, 0.252 mmol) in ethanol (30 ml). The reaction contents were allowed to stirring for overnight at room temperature followed by continuous refluxing for 78 h. The reaction was monitored by TLC and FT-IR. The precipitate was filtered off and filtrate was concentrated at reduced pressure to yellow solid powder. The solid masses were washed with ethanol and the residue obtained was further recrystallized from THF to furnish compound **C4NSB**. Yield (0.150 g, 0.121 mmol, 67 %); m.p. $395\text{ }^\circ\text{C}$, FT-IR (KBr): 3360 cm^{-1} (OH), 1635 (CO-NH) , 1615 (C=N) , 1483 , 1426 , 1364 , 1315 , 1246 , 1200 and 1190 cm^{-1} (C-O), and (C-N); $^1\text{H NMR}$ (400 MHz, DMSO, TMS, ppm): δH : 1.02 (18 H, s, t-Bu), 1.26 (18 H, s, t-Bu), 3.65 (4H, d, $J=13.2\text{ Hz}$, $\text{ArCH}_2\text{-Ar}$), 3.90 (4 H, m, $\text{NHCH}_2\text{CH}_2\text{NHCOTio}$), 4.20 (4H, m, $\text{NHCH}_2\text{CH}_2\text{NHCOTio}$), 4.40 (4H, s, OCH_2CO), 4.49 (4H, d, $J=13.2\text{ Hz}$, ArCH_2Ar), 5.5 (2H, s, Ar-OH), 7.08 (4H, s, ArH), 7.12 (4H, s, ArH), 7.20 (2H, s, Ar-OH), 7.21 (2H, t, Ar naphth), 7.26 (2H, d, Ar naphth), 7.30 (2 H, t, Ar naphth), 7.59 (2 H, t, Ar naphth), 7.63 (2 H, m, Ar naphth), 7.86 (2 H, d, Ar naphth), 8.11 (2H, s, N=CH), 8.29 (4H, s, NH), 30.3, 31.6, 32.8, 39.9, 40.6, 48.1, 55.9, 112.4, 119.2, 122.6, 124.6, 126.5, 128.0, 129.2, 129.7, 132.1, 138.8, 148.3, 158.4, 160.6, 164.1, ESI-MS (m/z): 1187.6 [$(\text{M}+1)^+$], Anal. Calc. for $\text{C}_{70}\text{H}_{80}\text{N}_4\text{O}_6$; C, 70.82; H, 6.74; N, 4.72; Found: C, 70.38; H, 6.71; N, 4.69 %.

Synthesis of Complexes with C4NSB

Solid state complexes of **C4NSB** with Au^{3+} and Γ^- were synthesized in the same molar ratio determined by job's plot. Saturated solutions of **C4NSB** in ethanol were prepared in

Scheme 1 Synthesis of **C4NSB**

(I) HCHO/NaOH (II)
 BrCH₂COOCH₃/K₂CO₃ (III)
 NH₂C₂H₄NH₂ (IV) 2-
 hydroxynaphthaldehyde



round bottom flasks separately. Stoichiometric amount of Au³⁺ and I⁻ were added into each respective reaction flask. The mixture was stirred at room temperature for 24 h. Solution was filtered off and volume was abridged to small at reduced pressure. The mixture was poured on petri dish to dry at room temperature. The resultant crystals were dried in vacuum oven and used for characterization.

UV-visible and Fluorescence Procedure

Sensing ability and selectivity of **C4NSB** toward different metals and anions were monitored by using UV-visible and fluorometer. Stock solution of ligand (2.6×10^{-3} M) was prepared in 25 mL of ethanol and followed by dilution to (2.6×10^{-5} M) into 100 ml. emission response of receptor **C4NSB** was estimated through titration experiments in a binary solvent system of Et-OH+H₂O (1:1 v/v). In 10 ml test tubes, 2 ml of ligand (2.6×10^{-5} M) and 2 ml of metal salts (2.6×10^{-4} M) were mixed together. Final concentration of both receptor and metals in 4 ml of mixture was calculated as (1.3×10^{-5} and 1.3×10^{-4} M) respectively. Four milliliters of mixture containing 10 M equivalents of each metal and absorbance was measured using a 1 cm absorption cell. Emission intensities of **C4NSB** were measured at excitation wavelength 330 nm for metals and anions at room temperature. Interference study of co-existing ions was carried out by using 10 equivalents (1.3×10^{-4} M) of all ions mixed into **C4NSB** complexes solution as described above.

Results and Discussion**UV-visible Study**

Selective nature of receptor for particular ion makes it a robust chemosensor. In this regard the absorptive and fluorescent behavior of receptor was examined upon addition of various metal ions. To examine the chromogenic behavior and selectivity of **C4NSB** titration experiments were carried out in Et-OH+H₂O system for selected series of mono, di and tri valent cations such as Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ag⁺, Ba²⁺, Ca²⁺, Mn²⁺, Mg²⁺, Sr²⁺, Ni²⁺, Cd²⁺, Co²⁺, Cu²⁺, Hg²⁺, Pb²⁺, Zn²⁺, Pd²⁺, Fe²⁺, Fe³⁺, Cr³⁺, As³⁺, Sb³⁺, Au³⁺, Tl³⁺, V³⁺ and W³⁺. Preliminary examinations reveal that free ligand **C4NSB** exhibit three less intensive characteristics bands at 318, 375, 420 nm. These absorption bands ascribe to the π - π^* and n- π^* transitions respectively due to the excitation of lone pair and aromatic π electrons (Fig. 1). There was minimal variations occurring and only a slight enhancement in the absorption intensity of **C4NSB** was observed upon addition of different metal ions except W³⁺ which also brought about very minimal change in it's behavior. Contrary to this, a prominent change was observed in the absorption behavior of **C4NSB** by the addition of Au³⁺. The band at 420 nm completely disappeared and the bands at 318, 375 nm merged together to a single sharp higher absorption intensity band at 325 nm. Consequently the band at 318 nm red shifted to 325 nm (Fig. 1). These spectral changes of **C4NSB**-Au³⁺

complex from 290 to 400 nm could be assigned due to the involvement of π -electrons of (C=N) imine aromatic rings and lone pair of electrons present on oxygen/nitrogen with Au^{3+} and O/N to metal charge transfer took place when Au^{3+} contacts with 2-hydroxynaphthalimide moiety of **C4NSB** [55].

Characteristics binding ability of **C4NSB** for different anions like of F^- , Cl^- , Br^- , I^- , CO_3^{2-} , HCO_3^- , CH_3CO_2^- , SO_4^{2-} , HSO_4^- , CN^- , SCN^- , NO_3^- , ClO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and $\text{S}_2\text{O}_7^{2-}$ also investigated under same conditions (Fig. 2). The distinctive UV-visible absorption changes were recorded upon the addition of anions into **C4NSB** (1.3×10^{-5} M). Different anions produce slight variations in spectral properties of receptor. However, a dramatic change was observed in spectral response of **C4NSB** on addition of I^- which caused emergence of two new bands at 296 and 366 nm in the visible region. While hyper chromic effect along with blue shift was observed in the bands at 318, 375 and 420 nm. These bands shifted ≈ 23 and 9 nm to shorter wavelength region respectively. This mode of interaction of **C4NSB**- I^- complex can be explained by the hydrogen bonded interaction between hydroxyl protons ($-\text{OH}$) of **C4NSB** and I^- . This response suggests very strong and selective affinity of **C4NSB** toward Au^{3+} and I^- . Correspondence of functional groups along with thermodynamic stability, ionic radii, cavity size as well as geometry of ligand and ions are also important aspects for specificity which confers the affinity of receptor toward a both Au^{3+} and I^- .

Fluorescence Study

Fluorescence sensing ability of **C4NSB** toward aforementioned different biological crucial and noxious metals was investigated under similar conditions at excitation wavelength of 330 nm as shown in (Fig. 3). Fluorescence response of receptor **C4NSB** did not produce any significant distinctions upon interaction with different metals. However receptor demonstrated prominent change in fluorescence intensity on interaction with Au^{3+} that causes quenching in its response.

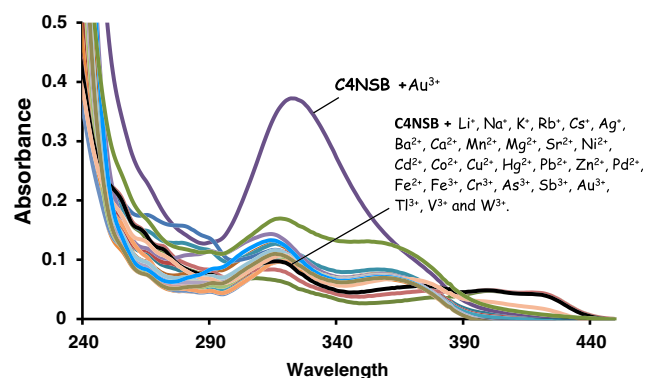


Fig. 1 Absorption spectra of **C4NSB** (1.3×10^{-5} M) with different metals (10 eq.) in Et-OH+ H_2O (1:1 v/v)

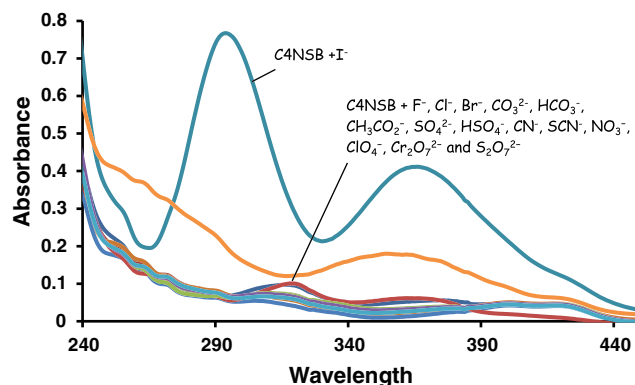


Fig. 2 Absorption spectra of **C4NSB** (2.6×10^{-5} M) and **C4NSB** with different anions (10 eq.) in Et-OH+ H_2O (1:1 v/v)

The emission intensity remarkable quenched up to 59 fold (Fig. 3). This distinctive result obtained after Au^{3+} addition among series of various cations confirms the **C4NSB** as Au^{3+} selective potential probe. The decrease in fluorescence intensity during complexation is attributed to deactivation of ICT process occurring between the 2-hydroxy naphthalene moiety and the imine functional group site. Upon contact of Au^{3+} within **C4NSB** cavity O and N drift their electrons to Au^{3+} and thus diminish ICT process by reducing the delocalization into naphthalene ring.

Similarly more investigations were also carried out to evaluate fluorogenic selectivity of **C4NSB** toward I^- . Fluorescence ability of receptor for aforementioned anions were scrutinized and resultantly no any prominent changes in the fluorescent spectra of receptor were noticed on titration with different anions except I^- that caused quenching in fluorescence response. Discriminating response of **C4NSB** for I^- was reflected by prominent fluorescent changes in the behavior of receptor as the strong emission band at 360 nm was effectively quenched upon addition of (10 eq.) of I^- , i.e. considerable reduction in the emission intensity up to 95 fold followed which was ascribed to **C4NSB**- I^- complex (Fig. 4).

Since receptor **C4NSB** contains 2-hydroxy naphthalene and phenyl fluorophore rings along with imine functional

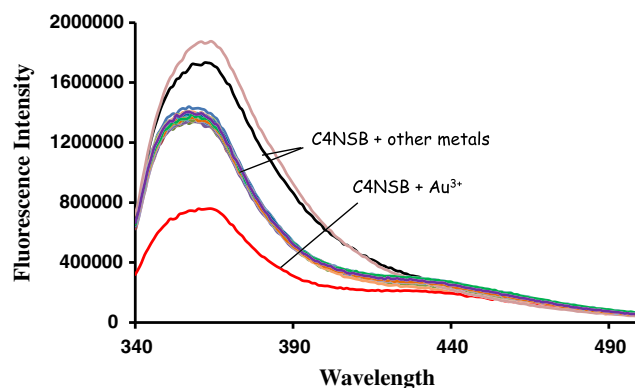


Fig. 3 Fluorescence spectra of **C4NSB** (1.3×10^{-5} M) and with different metals (10 eq.) in Et-OH+ H_2O (1:1 v/v)

group having N and O electron donating atoms that exhibit strong fluorescence intensity at 360 nm. The higher intensive response is due to the fact of Au^{3+} that is a heavy metal ion or the C=N isomerization and ICT effect in **C4NSB** may be inhibited upon coordination of receptor with Au^{3+} . Fluorescence quenching of receptor may be recognized due to the enhancement of spin-orbit coupling on interaction with Au^{3+} ion [56, 57]. The heteroatoms (N, O) share their electrons toward Au^{3+} and decrease the electronic density into naphthaldehyde rings and thus weaken the ICT mechanism over C=N imine group. This quenching effect demonstrates effective on–off fluorescent behavior. While in the case of Γ^- large fluorescence quenching was observed that is distinguishing feature of **C4NSB** for the fluorometric sensing of Γ^- among rest of the anions. The hydroxyl protons engaged in hydrogen bonding with Γ^- . Such interaction increases the electron density on hydroxyl oxygen atom and increase electronic charge within fluorophore rings. Consequently enhanced fluorescence intensity of **C4NSB** is drastically quenched on interaction with Γ^- .

Further investigation about quantitative analytical measurement of **C4NSB** was executed as a function of emission profiles on increasing ions concentration. There were spectral variations noticed by the gradual increment of Au^{3+} and Γ^- concentration. Increasing concentration of metal ion up to 10 equivalents to receptor (1.3×10^{-4} M) caused gradual quenching in fluorescence intensity of **C4NSB** at 360 nm for Au^{3+} (Fig. 5). Similarly in the case of Γ^- fluorescence emission intensity of receptor also quenched with respect to increasing molar concentration that caused stable decrease in emission intensity (Fig. 6). This quenching effect of complexes is due to the strong interaction of **C4NSB** with Au^{3+} as well as Γ^- and subsequently decrease ICT on coordination. Thus **C4NSB** demonstrates clear ‘turn-off’ fluorescence response and significantly high chromogenic selectivity toward Au^{3+} and Γ^- . Detection limit and limit of quantification was calculated from the

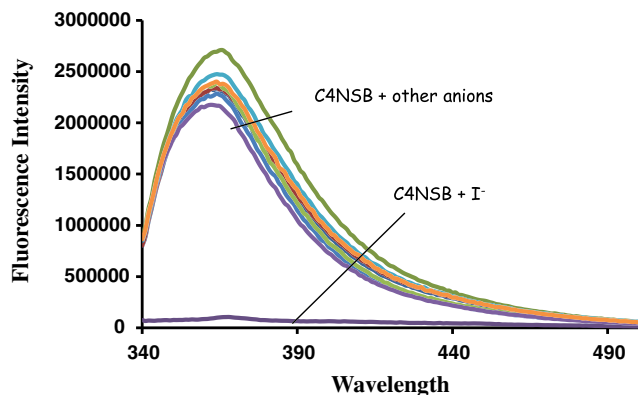


Fig. 4 Fluorescence spectra of **C4NSB** (1.3×10^{-5} M) and with different anions (10 eq.) in Et-OH+H₂O (1:1 v/v)

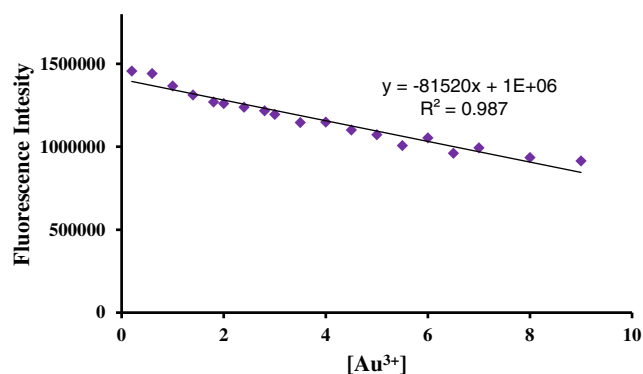


Fig. 5 Calibration Plot of quenching behavior of **C4NSB** (1.3×10^{-5} M) versus increasing amounts (0→10 eq.) of Au^{3+} in Et-OH+H₂O (1:1 v/v)

fluorescence intensity as a function of concentration added and was found as 1.5×10^{-5} , 5.2×10^{-5} for Au^{3+} and 1.3×10^{-6} , 4.5×10^{-6} for Γ^- respectively. This sufficiently low detection limit of these ions is helpful for determination in many chemical systems. The association constant K_a of **C4NSB** for Au^{3+} and Γ^- was calculated on the basis of the Benesi–Hilderbrand plot [58]. It was found to be 8.0×10^2 for Au^{3+} and $15.6 \times 10^2 \text{ M}^{-1}$ for Γ^- . The stoichiometric ratio of the complexes was determined by Job’s plot [59] at 360 nm and it was found to be 1:1 for both **C4NSB**- Au^{3+} and Γ^- complexes (Fig. 7a and b). Hence, all of these results confirmed that **C4NSB** has remarkably high selectivity and sensitivity towards Au^{3+} and Γ^- ions.

Efficient and selective sensing property of **C4NSB** was further explored by examining the effect of co-existing ions. Competitive experiments were carried out with 10 equivalents of other different metal and anions mixed with complexes solution of same concentration. The fluorescence responses of **C4NSB**- Au^{3+} and Γ^- complexes remained same in comparison to other metal ions and did not cause any disturbances in their fluorescence response. Interference study of complexes was further visualized by using ratiometric fluorescence behavior (I/I_0) as shown in (Fig. 8). Selective

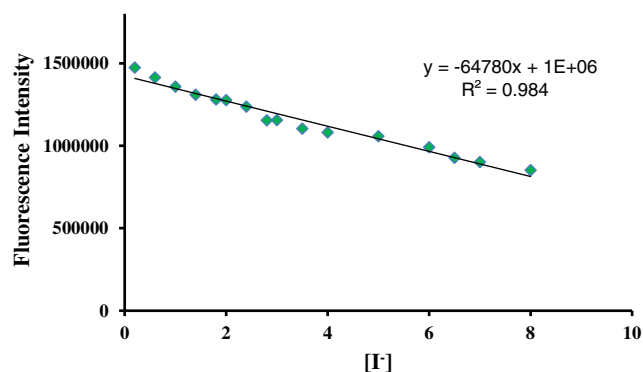


Fig. 6 Calibration Plot of quenching behavior of **C4NSB** (1.3×10^{-5} M) versus increasing amounts (0→10 eq.) of Γ^- in Et-OH+H₂O (1:1 v/v)

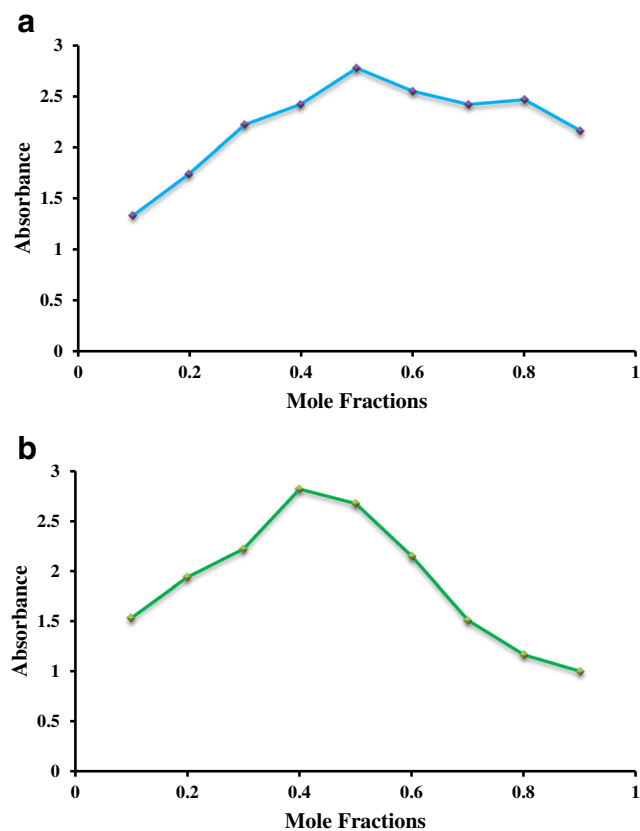


Fig. 7 a Job's Plot of C4NSB-Au^{3+} complex b C4NSB-I^-

nature of **C4NSB** toward Au^{3+} and I^- was remained almost same by the involvement of other co-existing ions and these findings confirmed the remarkable selective nature of **C4NSB** for Au^{3+} and I^- .

Sterne Volmer Analysis

The quenching nature of the complexes was further probed by using SterneVolmer plots [46]. Sterne

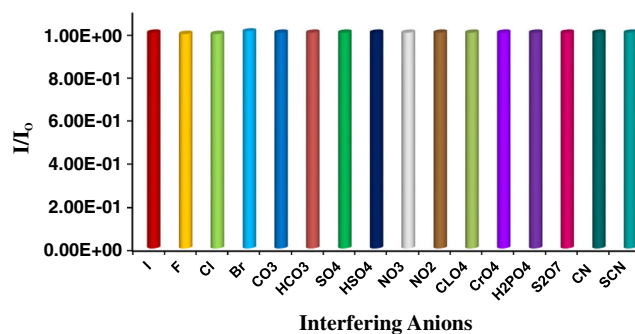


Fig. 9 Fluorescence intensities change ratio $[I/I_0]$ of C4NSB-I^- (1.3×10^{-5} M) at 330 nm upon addition of different metal ions (10.0 eq.) in $\text{Et-OH+H}_2\text{O}$ (1:1, v/v)

Volmer plots are a useful method of presenting data on emission quenching. Plotting relative emission intensities (I_0/I) against quencher concentration (metals) yields a linear Sterne Volmer plot for a static quenching process. These results are consistent with static quenching. The static quenching constants (K_{sv}) were found as 8.3×10^2 , 1.3×10^2 for Au^{3+} and I^- (Fig. 9).

Proposed Interaction

Since the receptor **C4NSB** containing O and N present in hydroxyl, amide and imine functionality as soft binding site that donate their electron pair to soft acid, i.e. Au^{3+} and hydroxyl protons share hydrogen bonding with I^- . These interactions help to accommodate guest ions into receptor's cavity. Furthermore, thermodynamic stability, ionic radii, cavity size as well as geometry of receptor are central features for selective affinity of **C4NSB** for both ions. On this basis proposed binding mode of **C4NSB** for Au^{3+} and I^- is shown in (Fig. 10).

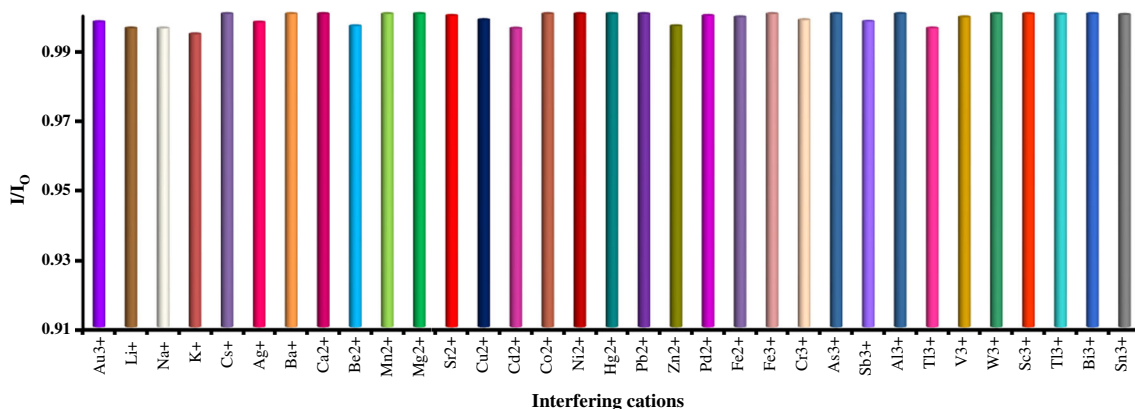


Fig. 8 Fluorescence intensity change ratio $[I/I_0]$ of C4NSB-Au^{3+} (1.3×10^{-5} M) at 330 nm upon addition of different metal ions (10.0 eq.) in $\text{Et-OH+H}_2\text{O}$ (1:1, v/v)

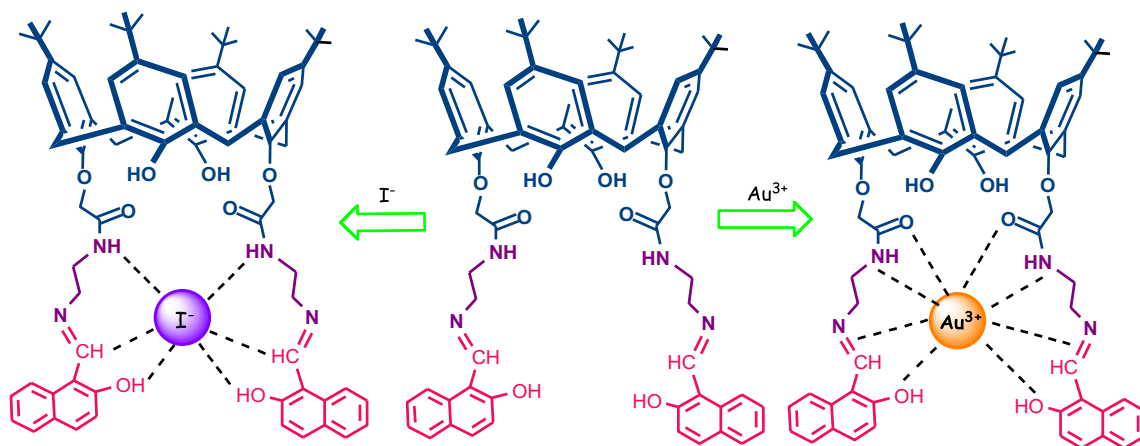


Fig. 10 Proposed structure of complexes

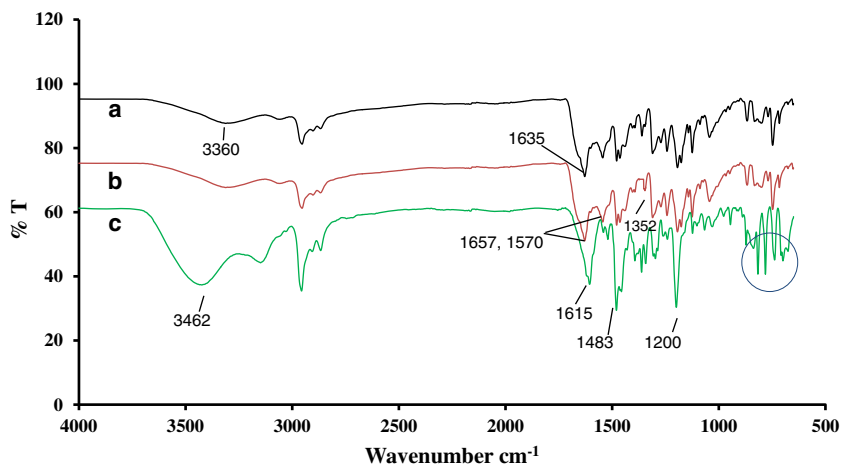
FT-IR Study

FT-IR helps to deeply understand the interaction modes between different functional groups. Selectivity of **C4NSB** toward toxic Au³⁺ and I⁻ was characterized by using FT-IR spectroscopy. Receptor **C4NSB** shows various characteristic stretching and bending bands as shown in (Fig. 11a). The bands indicate the existence of various functional groups in calix[4]arene moiety such as 3360 cm⁻¹ for O-H, 1635, 1552 and 1615 cm⁻¹ are stretching bands for carbonyl (amide) and C=N (imine) functionalities respectively. 1483, and 1426 cm⁻¹ implies to C-O-H and 1364 cm⁻¹ C-N, 1315, 1304 and 1246 cm⁻¹ represents C-N, C-O, 1200, 1190 cm⁻¹ C-N, 1127, 1050 and 873, 865, 830, 775 cm⁻¹ for C-O-C of calix[4]arene rings.

After complexation with Au³⁺ carbonyl bands at 1635, 1552 cm⁻¹ is slightly blue shifted to 1657, 1570 cm⁻¹ respectively. Beside this, the band at 1364 cm⁻¹ decrease in intensity along with red shifted to 1352 cm⁻¹. These changes are informative sign due

to metal-nitrogen/oxygen stretching and bending vibrations give clear indication for involvement of nitrogen oxygen and π electrons with Au³⁺. While on complexation I⁻ some evidences also suggest strong host-guest interaction (Fig. 11b). Similarly after complexation there was a broad band observed from 3740 to 3300 cm⁻¹ because of hydroxyl protons make hydrogen bonding with I⁻. Moreover, the band position at 3360 shifted to 3462 cm⁻¹. Carbonyl band at 1635 cm⁻¹ changed its position to 1615 cm⁻¹ besides this intensity of bands at 1504, 1200 increased along with blue shifted to 1483 and bands at 1246, 1127 become less intensive. Furthermore new bands appeared at 1525, 1395, 948, 818 and 783 cm⁻¹ as result of strong interaction with I⁻ (Fig. 11c). These spectral changes strongly support the formation **C4NSB**-I⁻ complex. The selective sensing response of **C4NSB** for Au³⁺ and I⁻ is significantly demonstrated by disappearance and appearance of new bands of specific functional groups occurred as a result of guests' introduction into receptor's cavity.

Fig. 11 FT-IR spectra of a) **C4NSB** b) **C4NSB**-Au³⁺ c) **C4NSB**-I⁻



Conclusion

A fluorescence and chromogenic sensing ability of newly synthesized receptor, i.e. **C4NSB** was explored for efficient, rapid and selective sensing of Au^{3+} and Γ^- . Receptor exhibited a high affinity and selectivity for Au^{3+} and Γ^- relative to most of the other competent co-existing ions by remarkable change in spectral response. Moreover complexes of **C4NSB** with Au^{3+} and Γ^- were characterized by using FT-IR spectroscopy. Since the geometry and ideal binding sites containing N, O and C=N in **C4NSB** possessing conformity in size, nature, and lodging helps to accommodate both ions. We expect that present strategy and photo physical properties of this fluorescent chemosensor will help to extend applications for both Au^{3+} and Γ^- .

Acknowledgments We thank the National Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro/Pakistan and Scientific and Technological Research Council of Turkey (TUBITAK, B.02.1.TBT.0.06.01-216.01/895-6391) for the financial support of this work.

References

- Czarnik AW (1993) Fluorescent chemosensors for ion and molecule recognition. American Chemical Society, Washington, DC
- De Silva AP, Fox DB, Huxley AJM, Moody TS (2000) Combining luminescence, coordination and electron transfer for signaling purposes. *Coord Chem Rev* 205:41–57
- De Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, Rice TE (1997) Signaling recognition events with fluorescent sensors and switches. *Chem Rev* 97: 1515–1566
- Desvergne JP, Czarnik AW (1997) Chemosensors of ion and molecule recognition. Kluwer, Dordrecht
- Tchounwou PB, Ayensu WK, Ninashvili N, Sutton D (2003) Environmental exposure to mercury and its toxicopathologic implications for public health. *Environ Toxicol* 18:149–175
- Fleming CJ, Salisbury EL, Kirwan P, Painter DM, Barnetson RS (1996) Chrysiasis after low-dose gold and UV light exposure. *J Am Acad Dermatol* 34:349–351
- American Rheumatism Association (1973) A controlled trial of gold salt therapy in rheumatoid arthritis. *Arthritis Rheum* 16:353–358
- Block WD, Knapp EL (1945) Metabolism, toxicity, and manner of action of gold compounds in the treatment of arthritis: vii. The effect of various gold compounds on the oxygen consumption of rat tissues. *J Pharmacol Exp Ther* 83:275–278
- Goodman CM, McCusker CD, Yilmaz T, Rotello VM (2004) Toxicity of gold nanoparticles functionalized with cationic and anionic side chains. *Bioconjug Chem* 15:897–900
- Michael GH, Robert SG (1968) Modern nutrition in health and disease, 4th edn. Lea and Febiger, Philadelphia
- Dai G, Levy O, Carrasco N (1996) Cloning and characterization of the thyroid iodide transporter. *Nature* 379:458–460
- Pearce EN (2012) Iodine-induced thyroid dysfunction: Comment on “Association between iodinated contrast media exposure and incident hyperthyroidism and hypothyroidism”. *Arch Intern Med* 172:159–161
- Steed JW, Atwood JL (2000) Supramolecular chemistry. John Wiley and Sons, Chichester
- Schneider HJ, Yatsimirsky A (2000) Principles and methods in supramolecular chemistry. John Wiley and Sons, Chichester
- Wang R, Bu J, Liu J, Liao S (2008) Calix[4]arene based selective fluorescent chemosensor for organic acid recognition. *Front Chem Chin* 3:348–352
- Czarnik AW (1992) Fluorescent chemosensors for ion and molecule recognition; ACS Symposium Series 538. American Chemical Society, Washington, DC
- De Silva AP, Gunnlaugsson T, McCoy CP (1997) Photoionic supermolecules: mobilizing the charge and light bridges. *J Chem Educ* 74:53–58
- Bodenant B, Weil T, Businelli-Pourcel M, Fages F, Barbe B, Pianet I, Laguerre M (1999) Synthesis and solution structure analysis of a bispyrenyl bishydroxamate calix[4]arene-based receptor, a fluorescent chemosensor for Cu^{2+} and Ni^{2+} metal ions. *J Org Chem* 64: 7034–7039
- Park SM, Kim MH, Choe JI, No KT, Chang SK (2007) Cyclams bearing diametrically disubstituted pyrenes as Cu^{2+} and Hg^{2+} selective fluoroionophores. *J Org Chem* 72:3550–3553
- Bonacchi S, Genovese D, Juris R, Montalti M, Prodi L, Rampazzo E, Sgarzi M, Zaccheroni N (2011) Luminescent chemosensors based on silica nanoparticles. *Top Curr Chem* 300:93–138
- Subrata P, Ravi G, Lo R, Suresh E, Bishwajit G, Parimal P (2012) Cation-induced fluorescent excimer emission in calix[4]arene-chemosensors bearing quinoline as a fluorogenic unit: experimental, molecular modeling and crystallographic studies. *New J Chem* 36:988–1002
- Gutsche CD (1989) Calixarenes. The Royal Society of Chemistry, Cambridge
- An WT, Jiao Y, Sun XH, Zhang XL, Dong C, Shuang SM, Xia PF, Wong MS (2009) Synthesis and binding properties of carboxylphenyl-modified calix[4]arenes and cytochrome c. *Talanta* 79:54–61
- Matthews SE, Beer PD (2005) Calixarene-based anion receptors. *Supramol Chem* 17:411–435
- Tabakci M, Tabakci B, Yilmaz M (2005) Design and synthesis of new chiral calix[4]arenes as liquid phase extraction agents for α -amino acid methylesters and chiral α -amines. *J Incl Phenom Macrocycl Chem* 53:51–56
- Tabakci B, Beduk AD, Tabakci M, Yilmaz M (2006) Synthesis and binding properties of two polymeric Thiocalix[4]arenes. *React Funct Polym* 66:379–386
- Yilmaz A, Tabakci B, Tabakci M (2009) New diamino derivatives of p-tert-butylcalix[4]arene for oxyanion recognition: synthesis and complexation studies. *Supramol Chem* 21:435–441
- Yilmaz A, Tabakci B, Akceylan E, Yilmaz M (2007) Synthesis and dichromate anion extraction ability of p-tert-butylcalix[4]arene diamide derivatives with different binding sites. *Tetrahedron* 63: 5000–5005
- Mathew VJ, Khopkar SM (1997) Hexaacetato calix(6)arene as the novel extractant for palladium. *Talanta* 44:1699–1703
- Sirit A, Karakucuk A, Memon S, Kocabas E, Yilmaz M (2004) Synthesis and characterization of a novel chiral chromogenic calix[4](azoxa)crown-7. *Tetrahedron Asymmetry* 15: 3595–3600
- Bozkurt S, Karakucuk A, Sirit A, Yilmaz M (2005) Synthesis of two calix[4]arene diamide derivatives for extraction of chromium(VI). *Tetrahedron* 61:10443–10448
- Vázquez M, Fabbrizzi L, Taglietti A, Pedrido RM, González-Noya AM, Bermejo MR (2004) A colorimetric approach to anion sensing: a selective chemosensor of fluoride ions, in which color is generated by anion-enhanced π delocalization. *Angew Chem Int Ed* 43:1962–1965

33. Ediz O, Tabakci M, Memon S, Yilmaz M, Roundhill DM (2004) A convenient approach towards the synthesis of a “proton switchable” chromium(vi) extractant based on calix4arene. *Supramol Chem* 16: 199–204
34. Ocak U, Ocak M, Surowiec K, Bartsch RA, Gorbunova MG, Tu C, Surowiec MA (2009) Metal ion complexation in acetonitrile by di-ionized calix[4]arenes bearing two dansyl fluorophores. *J Incl Phenom Macrocycl Chem* 63:131–139
35. Hu J, Yu Y, Brooks JC, Godwin LA, Somasundaram S, Torabinejad F, Kim J, Shannon C, Easley CJ (2014) A reusable electrochemical proximity assay for highly selective, real-time protein quantitation in biological matrices. *J Am Chem Soc* 136:8467–8474
36. Hu J, Wang T, Kim J, Shannon C, Easley CJ (2012) Quantitation of femtomolar protein levels via direct readout with the electrochemical proximity assay. *J Am Chem Soc* 134:7066–7072
37. Li X, Yu M, Yang F, Liu X, Wei L, Li Z (2013) A dual-model and on-off fluorescent Al³⁺/Cu²⁺ chemosensor and the detection of F/Al³⁺ with ‘in situ’ prepared Al³⁺/Cu²⁺ complexes. *New J Chem* 37:2257–2260
38. Jou MJ, Chen X, Swamy KMK, Kim HN, Kim HJ, Lee S, Yoon J (2009) Highly selective fluorescent probe for Au³⁺ based on cyclization of propargylamide. *Chem Commun* 46:7218–7220
39. Dong M, Wang YW, Peng Y (2010) Highly selective ratiometric fluorescent sensing for Hg²⁺ and Au³⁺ respectively, in aqueous media. *Org Lett* 12:5310–5313
40. Egorova OA, Seo H, Chatterjee A, Ahn KH (2010) Reaction-based fluorescent sensing of Au(I)/Au(III) species: mechanistic implications on vinyl gold intermediates. *Org Lett* 12:401–403
41. Song Z, Xiao C, Dai Y, Fei Q, Huan Y, Feng G (2012) Fluorescence quenching amplification in silica nanosensors for Au³⁺. *Nanotechnology* 23:425501
42. Çubuk S, Kahraman MV, Yetimoğlu EK, Kenan S (2014) Photocured thiol-ene based optical fluorescence sensor for determination of gold (III). *Anal Chim Acta* 812:215–221
43. Joseph R, Chinta JP, Rao CP (2010) Benzothiazole appended lower rim 1,3-di-amido-derivative of calix[4]arene: synthesis, structure, receptor properties towards Cu²⁺, iodide recognition and computational modeling. *Inorg Chim Acta* 363:2833–2839
44. Kim JS, Park SY, Kim SH, Thuéry P, Souane R, Matthews SE, Vicens J (2010) A pyrenyl-appended triazole-based calix[4]arene as a fluorescent sensor for iodide ion. *Bull Kor Chem Soc* 31:624–629
45. Joseph R, Gupta A, Ali A, Rao CP (2007) Fluorescent and absorption studies on the selective recognition of iodide by lower rim 1,3-bis(aminoethoxy)-p-tert-butylcalix[4]arene derivative. *Indian J Chem* 46:1095–1100
46. Ocak Ü, Ocak M, Surowiec K, Liu X, Bartsch RA (2009) Metal ion complexation in acetonitrile by upper-rim allyl-substituted, di-ionized calix[4]arenes bearing two dansyl fluorophores. *Tetrahedron* 65:7038–7047
47. Qazi MA, Ocak Ü, Ocak M, Memon S (2013) An excellent copper selective chemosensor based on calix [4] arene framework. *Anal Chim Acta* 761:157–168
48. Qazi MA, Qureshi I, Memon S (2011) Analytical evaluation of Cu²⁺ selective behavior of calix [4] arene derivative. *J Fluoresc* 21:1703–1711
49. Solangi IB, Bhatti AA, Qazi MA, Memon S, Bhangar MI (2012) Selective cation recognition by p-tetranitrocalix [4] arene. *Pak J Anal Environ Chem* 13:129–136
50. Qazi MA, Qureshi I, Memon S (2011) Hg(II) selective complexation by chromoionophoric calix[4]arene derivative. *J Fluoresc* 21: 1231–1238
51. Qazi MA, Ocak Ü, Ocak M, Memon S, Solangi IB (2013) Bifunctional calix [4] arene sensor for Pb(II) and Cr₂O₇²⁻ ions. *J Fluoresc* 23:575–590
52. Gutsche CD, Iqbal M, Stewart D (1986) Calixarenes. 19. Syntheses procedures for p-tert-butylcalix[4]arene. *J Org Chem* 51:742–745
53. Maity D, Chakraborty A, Gunupuru R, Paul P (2011) Calix[4]arene based molecular sensors with pyrene as fluoregenic unit: effect of solvent in ion selectivity and colorimetric detection of fluoride. *Inorg Chim Acta* 372:126–135
54. Chen X, Dings RPM, Nesmelova I, Debbert S, Haseman JR, Maxwell J, Hoye TR, Mayo KH (2006) Topomimetics of amphipathic α -sheet and helix-forming bactericidal peptides neutralize lipopolysaccharide endotoxins. *J Med Chem* 49:7754–7765
55. Liang Z, Liu Z, Gao Y (2007) Synthesis, characterization and photochromic studies of three novel calix[4]arene–Schiff bases. *Spectrochim Acta A Mol Biomol Spectrosc* 68:1231–1235
56. Izatt RM, Bradshaw JS, Nielsen SA, Lamb JD, Christian JJ, Sen D (1985) Thermodynamic and kinetic data for cation-macrocycle interaction. *Chem Rev* 85:271–339
57. Izatt RM, Bradshaw JS, Pawlak K, Bradshaw JS, Bruening RL (1991) Thermodynamic and kinetic data for macrocycle interactions with cations and anions. *Chem Rev* 91:1721–2085
58. Benesi HA, Hildebrand JH (1949) A spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons. *J Am Chem Soc* 71:2703–2707
59. Harris DC (1995) *Quantitative Chemical Analysis* 4th edn. W.H. Freeman & Company, New York