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Cu^{2+} and CN^{-}-selective fluorogenic sensors based on pyrene-appended thiacalix[4]arenes

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ABSTRACT

Two new fluorescent sensors **1** and **2** based on thiacalix[4]arenes bearing pyrene moieties have been synthesized in cone conformation. The binding abilities of these sensors towards different cations such as lithium, sodium, potassium, nickel, cadmium, copper, zinc, lead, silver, mercury and anions like fluoride, chloride, bromide, iodide, cyanide, acetate, hydrogen sulfate and nitrate have been examined by UV–vis and fluorescence spectroscopies. These receptors show pronounced selectivity for copper and cyanide ions. In CH_2Cl_2/CH_3CN (1:1), the presence of Cu(II) ion induces the formation of 1:1 (H/G) complex with receptor **1** and 1:2 (H/G) complex with receptor **2**. The cyanide ions form a 1:1 (H/G) complex with both receptors.

1. Introduction

Selective signalling of soft transition-metal ions and anions has potential analytical applications in many fields like chemistry, medicine, biology and environment.[1,2] In fact, a variety of effective fluorescent chemosensors for alkali and alkaline earth metal[1a,2] ions have already been developed. The development of chemosensors for soft transition-metal ions particularly needs attention because of their toxic impact on our environments.[3] Among the soft metal ions, copper is the third most abundant essential heavy metal ion (after Fe^{2+} and Zn^{2+}) present in human body. It plays an important role in fundamental physiological processes in organisms ranging from bacteria to mammals.[4] 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.[5] On the other hand, CN^{-} ion is among the most toxic inorganic anions.[6] It strongly interacts with active site of cytochrome a_3[7] and inhibits the cellular respiration in mammalian cells, as a result even its small amount is very lethal to human body.[8] Unfortunately, cyanide does not easily decompose in the environment.[9] Therefore the accidental spillage of this toxic chemical from industrial plants or its intentional release can contaminate drinking water and become a serious threat to human health. Despite its acute toxicity, cyanide or hydrogen cyanide are used in many industries like synthetic fibres and resins, herbicides, gold extraction, etc.[10] Thus, the diversity of their functions, both beneficial and otherwise, makes the detection of copper and cyanide ions important. The detection and monitoring of cations and anions by methods, which allow the development of selective and sensitive assays are in great demand. Fluorescence signalling is one of the first choices due to its high detection sensitivity and simplicity.[1a,2c,11] Thus, designing fluorescent sensors for copper[12] and cyanide[13] ions has recently drawn worldwide attention. Basically, fluorescent chemosensors consist of ion recognition unit (ionophore) attached with a fluorogenic unit (fluorophore),[2b,14] which convert binding signal of ionophore unit into a highly sensitive light signal. Thus, while designing sensors the recognition unit linked to fluorophore should be carefully examined because the recognition unit is responsible for the selectivity and binding efficiency of the chemosensor. Calixarene[15] scaffold with appropriate binding sites has been utilized for recognition of cations[16] and anions.[17] Kim and Quang[18] have recently reported calix[4]arene derived fluorescent probes highlighting the importance of fluorescent chemosensors. Recently, thiacalixarene[19] has also been used for recognition of cations[20] and anions[21] but to a limited extent in comparison to conventional calix[4]arene. For the selective binding of copper, nitrogen and sulfur, binding sites are desirable as is well exemplified by copper proteins plastocyanin, rusticyanin and cytochrome *c* oxidase.[22] Thus, a suitably decorated thiacalix[4]arene with nitrogen binding sites might be a good candidate. On the other hand, it is known that amide groups complex anions through hydrogen bonding between anions and amide N–H.[23] Thus, we envisaged that derivatizing thaicalix[4]arene framework with amide group possessing suitable signalling unit should give a host capable of interacting with both cations and

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anions. Among the different fluorogenic units, pyrene is most useful because of its efficient and sensitive monomer emission at 370–430 nm and excimer emission around 480 nm.[2c,24] The intensity ratio of excimer to monomer emission (I_E/I_M) is very sensitive to conformational change and guest ion (cation and anion) concentration,[1,24b,25] hence it is very informative tool used in sensing systems.

Recently, we reported a ratiometric[26a] fluorescent sensor for copper based on thiacalix[4]arene of cone conformation possessing dansyl moieties, which exhibits the increasing emission at 433 nm at the expense of the fluorescent emission centred at 504 nm. In continuation of our research programme for design, synthesis and evaluation of calix[4]arene and thiacalix[4]arene based receptors selective for soft metal ions[26] and anions,[27] we have now designed fluorescent chemosensors **1** and **2** based on thiacalix[4]arene framework possessing pyrene moieties, which can be used for the selective detection of Cu^{2+} and CN^- ions. The capture of Cu^{2+} by the receptor resulted in reverse photoinduced electron transfer from pyrene to electron deficient amide nitrogen. The fluorescence emission is also considerably quenched in the presence of CN^- ions. Recently, Kim et al.[28] reported *N*-methylpyrene amide appended thiacalix[4]arene derivative having crown-6 ring, which selectively interacts with Pb^{2+}. The oxygen atoms of the crown ring play very important role in achieving high selectivity for Pb^{2+}. On the other hand, *N*-methylpyrene amide appended calix[4]arene derivative having two propyl groups instead of a crown ring exhibited no selectivity for specific metal ions. Based on these reports we planned to change the coordination environment by employing thiacalix[4]arene **3** and dipropoxythiacalix[4]arene **4** of cone conformations as molecular scaffolds for the preparation of thiacalix[4]arene derivatives **1** and **2**, respectively. Preliminary studies on the complexation abilities of these thiacalix[4]arene derivatives have shown that the modification actually changes the coordination sites and that thiacalix[4]arene derivatives **1** and **2** of cone conformations have selective fluorescent quenching in the presence of Cu^{2+} and CN^- ions. To the best of our knowledge this is the first report where thiacalix[4]arene scaffold has been combined with pyrene moieties to prepare fluorescent sensors for copper and cyanide ions. While this work was in progress, Xie et al. reported[29] fluorescent sensors for Cu(II) based on sugar-aza-crown ethers, however, in this case the binding process of Cu^{2+} ions to sugar-aza-crown ethers was quite slow as it required 3 h to reach the equilibrium and the titration solutions were prepared 1 day in advance while in present investigation the binding process of Cu(II) towards thiacalix[4]arene derivatives **1** and **2** is very fast. In addition, during the preparation of this manuscript, Huang et al. reported[30] a fluorescent sensor for Cu^{2+} ions based on calix[4]arene where the binding of copper results in fluorescence enhancement while in the present investigation the thiacalix[4]arene derivative **2** shows ratiometric sensing for copper. Ratiometric fluorescent probes have the important feature of permitting signal rationing and thus increase the dynamic range and provide built in correction for environmental effects.

2. Results and discussion

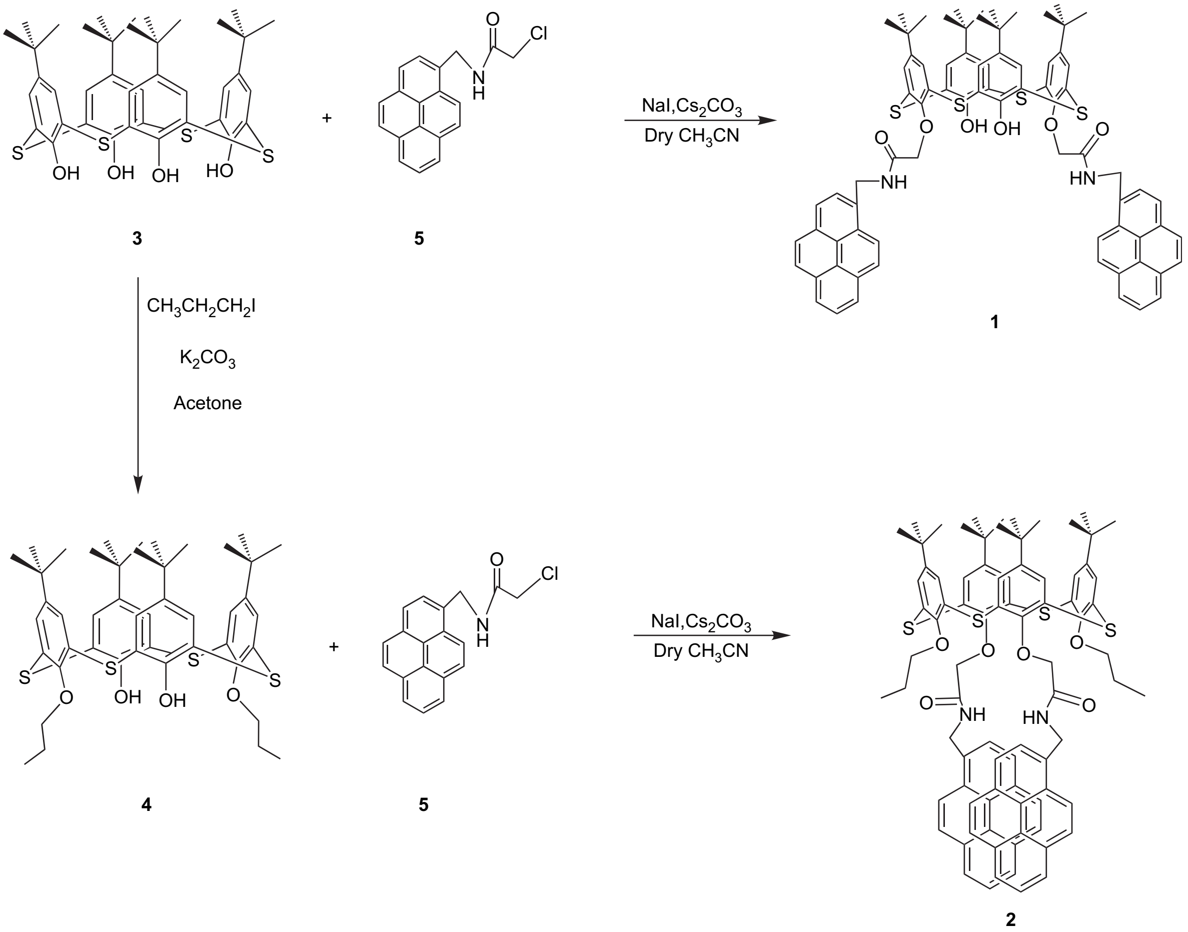
The reaction of *p*-*tert*-butylthiacalix[4]arene **3** with 2.2 mol equiv of *N*-(1-pyrenylmethyl)chloroacetamide **5**[31] in the presence of 1.0 mol equiv of Cs_2CO_3 and catalytic amount of NaI in dry CH_3CN afforded 25,27-bis[(*N*-(1-pyrenylmethyl)aminocarbonyl)-methoxy]-5,11,17,23-tetra-*tert*-butyl-26,28-dihydroxythiacalix[4]-arene **1** in 27% yield (Scheme 1). Under the same conditions as used above for the preparation of compound **1** the reaction of 25,27-dipropoxythiacalix[4]arene **4**[32] with 2.2 mol equiv of *N*-(1-pyrenylmethyl)chloroacetamide **5**[31] afforded 25,27-bis[(*N*-(1-pyrenylmethyl)aminocarbonyl)methoxy]-5,11,17,23-tetra-*tert*-butyl-26,28-dipropoxythiacalix[4]arene **2** in 73% yield (Scheme 1). The structures of compounds **1** and **2** were confirmed from their spectroscopic and analytical data. The IR spectra of compounds **1** and **2** showed a stretching band at 1663 cm^{-1} and 1660 cm^{-1} due to –NHC=O groups. In general, the ^1H NMR spectra of compounds **1** and **2** showed two singlets (18H each) for *tert*-butyl protons, one singlet for OCH_2 protons, one doublet for NCH_2 protons, two singlets (4H each) for aromatic protons, one multiplet (18H each) for pyrene protons and one broad signal for NH protons, the magnetic equivalences of pyrene-appended thiacalix[4]arene derivatives **1** and **2** suggesting C_{2v}-symmetric structure that is in cone conformation.

The cation binding properties of compounds **1** and **2** were investigated by UV–vis absorption and fluorescence spectroscopies while anion binding properties were investigated by fluorescence and NMR spectroscopies. All the titration experiments were carried out in CH_2Cl_2/CH_3CN (1:1, v/v) by adding aliquots of different guests (cation and anion). The UV–vis absorption spectra of the compounds **1** and **2** exhibit typical pyrene absorption bands at λ 330 nm and 347 nm for compound **1** (Fig. 1) and at λ 328 nm and 344 nm for compound **2** (Fig. 2). The addition of increasing amounts of Cu^{2+} ions from 6.0 μM to 600 μM (1.0–100 equiv) resulted in a decrease in absorption at 330 nm or 328 nm and 347 or 344 nm and formation of a new red shifted broad band (Figs. 1 and 2), which indicates that the interaction of Cu^{2+} is occurring through nitrogen atoms of the amide groups. The capture of Cu^{2+} ion by the receptor results in reduction of electron donating ability of N atom, which causes red shift in absorbance spectra (Figs. 1 and 2).[33] This red shift is attributed to a photoinduced charge transfer mechanism.[2b,16e,17d,e,33b,34] Leblanc et al.[33a] previously reported PCT-based peptidyl fluorescent chemosensors for the detection of Cu^{2+} in which it was observed a UV band shift of the ligand resulting from $N\cdots Cu^{2+}$ binding. There was no change in absorption spectrum when titrations with other metal ions were carried out.

The fluorescence spectrum of compound **1** gave typical monomer emission of pyrene group at 377 nm (Fig. 3) and there was no band due to excimer emission, which means that the two pyrene units are not in stacked conformation. Upon addition of Cu^{2+} ions (6.0–600 μM) to the solution of compound **1**, a significant quenching in the fluorescence emission, which was attributed to **1**/Cu^{2+} complex was observed (Fig. 3). This remarkable fluorescence quenching induced by Cu^{2+} is ascribed to reverse PET from pyrene units to the nitrogen atom of which the electron density is diminished by metal complexation. Under the same conditions as used above for Cu^{2+}, we also tested the fluorescence response of **1** to other metal ions such as Li^+, Na^+, K^+, Ni^+, Zn^{2+}, Cd^{2+}, Ag^+, Hg^{2+}, Pb^{2+} besides Cu^{2+}, as shown in Figure 4, no significant fluorescence change of **1** occurred in the presence of (60 μM) of these metal ions.

In order to determine the stoichiometry of the **1**/Cu^{2+} complex, the method of continuous variation (Job's plot) was also used. The total concentration of the compound **1** and Cu^{2+} was constant (3.33×10^{-6} M), with a continuous variable molar fraction of guest ($[Cu^{2+}]/[\mathbf{1}]+[Cu^{2+}]$). Figure 5 shows the Job plot of compound **1** with Cu^{2+} ion. The **1**/Cu^{2+} complex concentration approaches a maximum when the molar fraction of Cu^{2+} is 0.5, which means **1** and Cu^{2+} formed a 1:1 complex (Fig. 5). The association constant ($\log\beta$) of compound **1** for Cu^{2+} ions was calculated from fluorescence titration experiments by means of SPECFIT programme (global analysis system V3.0 for 32-bit Window system), which uses singular value decomposition and non-linear regression modelling by the Leverberg–Marquardt method[35] and was found to be 4.939+/−0.0973 M^{-1}.

The photophysical properties of compound **2** were different from those of compound **1**. The excitation of compound **2** at 342 nm gave weak monomer and strong excimer emissions at 375 nm and 467 nm, respectively (Fig. 6). The formation of excimer band at



Scheme 1.

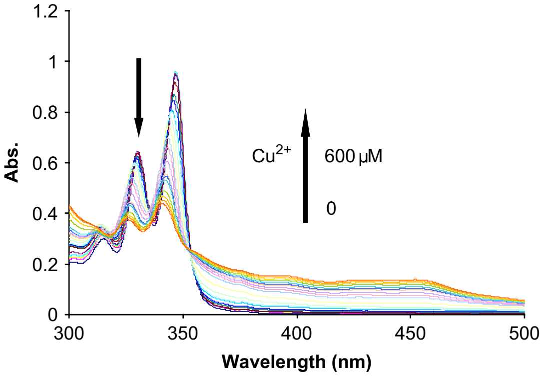


Figure 1. Absorption spectra of compound **1** (6.0 μM) on addition of Cu^{2+} (0–100 equiv, 0–600 μM) in CH_2Cl_2/CH_3CN (1:1, v/v).

467 nm indicates that there was strong face to face π-stacking between two pyrene units. There was no change in the intensity ratio of excimer to monomer (I_E/I_M) of **2** in the concentration range 10^{-7}–10^{-4} M, which indicates that excimer emission at 467 nm is from intramolecular interaction and not from an intermolecular interaction.

The fluorescence titration profile of **2** with Cu^{2+} showed ratiometric response with monomer enhancement and excimer quenching upon addition of 60 μM (10 equiv) of Cu^{2+} ions (Fig. 6). The relative intensity ratio of monomer to excimer emission (I_M/I_E) of free ligand was 0.47 and it increases by 11.7-fold to 5.52 (Fig. 7) with addition of 60 μM (10 equiv) of Cu^{2+} ion. Under the same conditions as used above for Cu^{2+}, we also tested the fluorescence response of **2** to other metal ions such as Li^{+}, Na^{+}, K^{+}, Ni^{+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Hg^{2+}, Pb^{2+} besides Cu^{2+}, as shown in Figure 7, no significant fluorescence change of **2** occurred in the presence of (60 μM) of these metal ions.

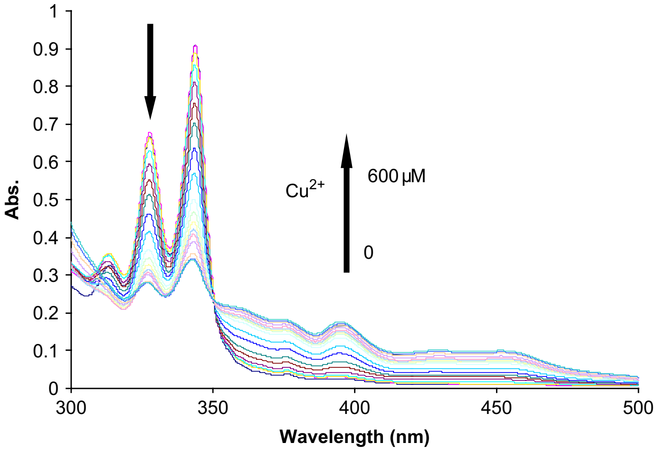


Figure 2. Absorption spectra of compound **2** (6.0 μM) on addition of Cu^{2+} (0–100 equiv, 0–600 μM) in CH_2Cl_2/CH_3CN (1:1, v/v).

The stoichiometry of the complex formed between compound **2** and Cu^{2+} ion was evaluated by the method of continuous variation (Job's plot, Fig. 8) and it was found to be 1:2 (H/G), which indicated that the two Cu^{2+} ions were interacting with receptor **2**. The

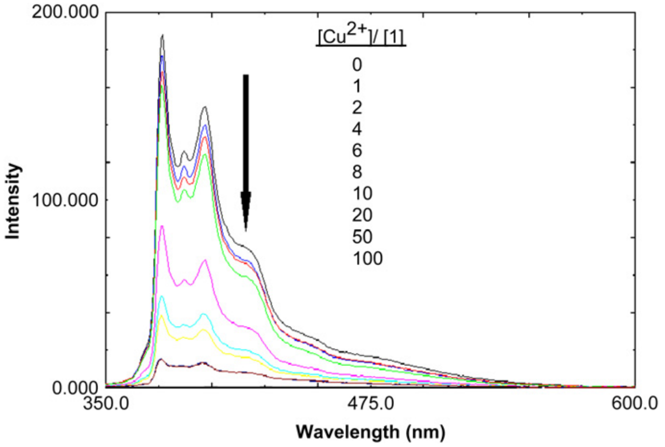


Figure 3. Fluorescence emission spectra of **1** (6.0 μM) upon various addition of Cu^{2+} (0–100 equiv, 0–600 μM) in CH_2Cl_2/CH_3CN (1:1, v/v).

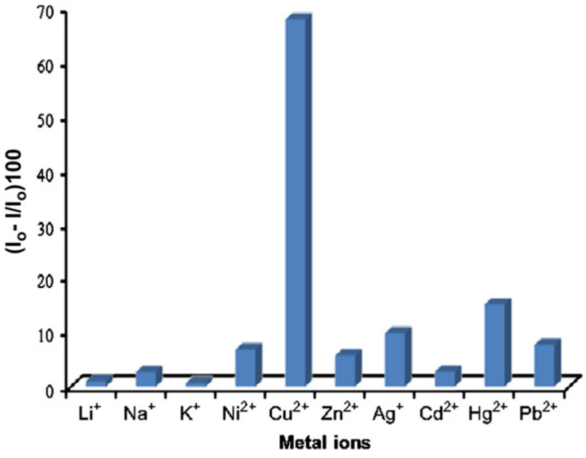


Figure 4. Fluorescence quenching ratio $[(I_o-I/I_o)\times 100]$ of **1** (6.0 μM) at 377 nm upon addition of different metal ions (10 equiv, 60 μM) in CH_2Cl_2/CH_3CN (1:1, v/v).

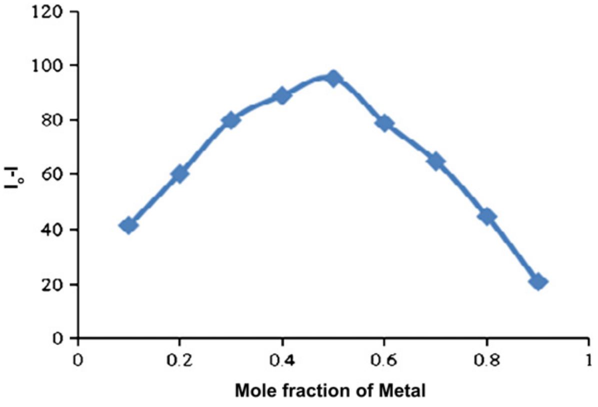


Figure 5. Job's plot for **1** and Cu^{2+} $[\mathbf{1}+Cu^{2+}]=3.33\times 10^{-6}$ M in CH_2Cl_2/CH_3CN (1:1, v/v).

association constant ($\log \beta$) of compound **2** with Cu^{2+} ions was calculated from fluorescence titration experiments by means of SPECFIT programme (global analysis system V3.0 for 32-bit Window system), which uses singular value decomposition and non-linear regression modelling by the Leverberg–Marquardt method[35] and was found to be 10.3086+/−0.62078 M^{-1}. The global analysis

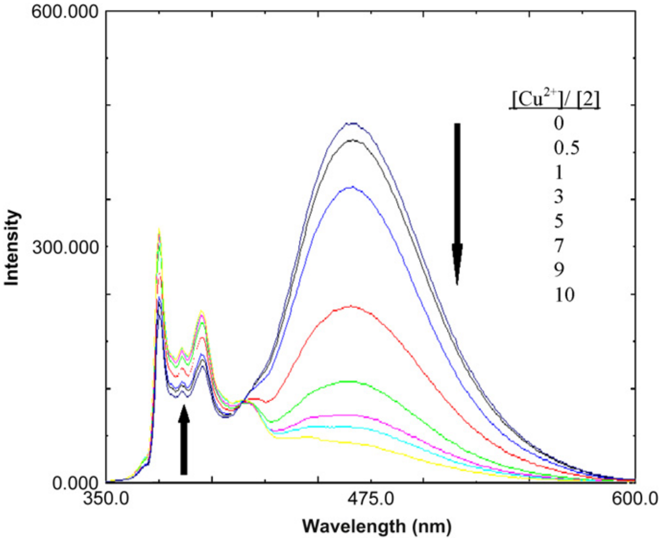


Figure 6. Fluorescence emission spectra of **2** (6.0 μM) upon various addition of Cu^{2+} (0–10 equiv, 0–60 μM) in CH_2Cl_2/CH_3CN (1:1, v/v).

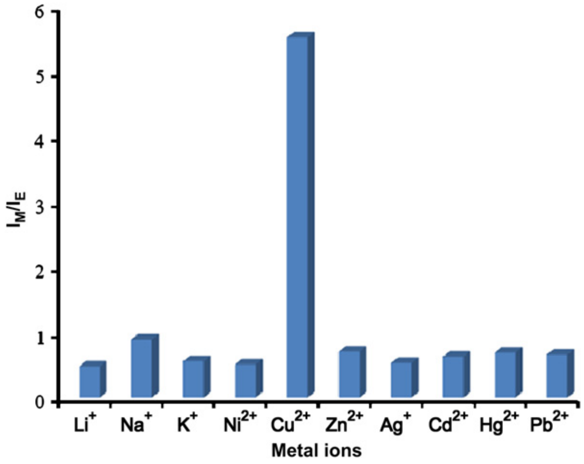


Figure 7. Ratiometric (I_M/I_E) selectivity of compound **2** (6.0 μM) upon addition of different cations (60 μM).

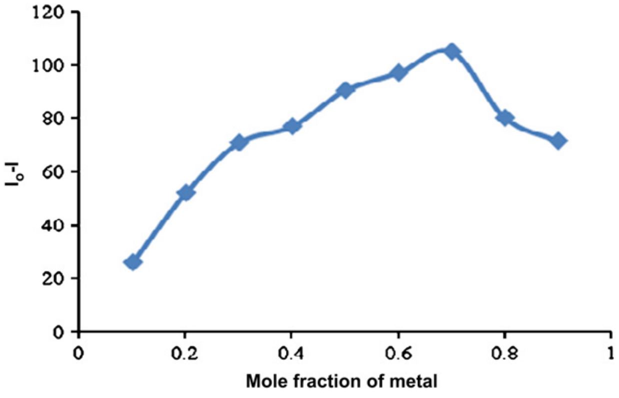


Figure 8. Job's plot for **2** and Cu^{2+} $[\mathbf{2}+Cu^{2+}]=3.33\times 10^{-6}$ M in CH_2Cl_2/CH_3CN (1:1, v/v).

showed that the titration curves were consistent with the formation of 1:2 (H/G) complex.

To test the practical applicability of compounds **1** and **2** as Cu^{2+} selective fluorescent sensor, competitive experiments were carried

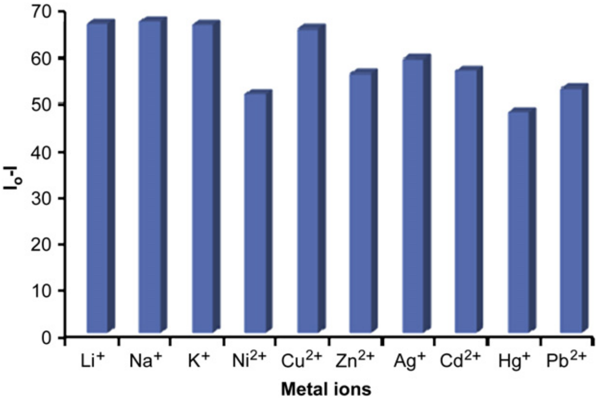


Figure 9. Competitive selectivity of compound **1** (6.0 μM) towards Cu^{2+} (10 equiv, 60 μM) in the presence of other metal ions (10 equiv, 60 μM).

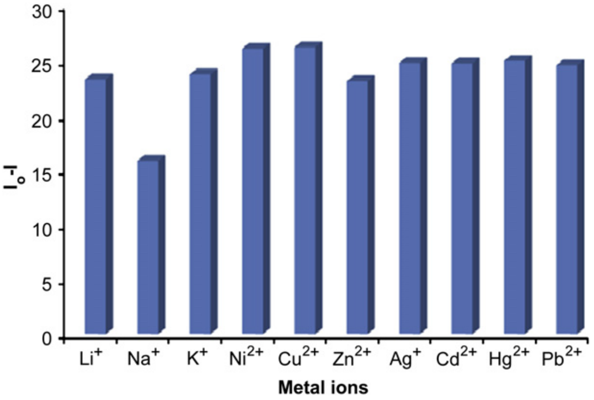


Figure 10. Competitive selectivity of compound **2** (6.0 μM) towards Cu^{2+} (10 equiv, 60 μM) in the presence of other metal ions (10 equiv, 60 μM).

out in the presence of Cu^{2+} at 60 μM mixed with Na^{+}, K^{+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Hg^{2+}, Pb^{2+} at 60 μM, as shown in Figures 9 and 10, no significant variation in fluorescence intensity change (I_o−I) was found by comparison with or without the other metal ions besides Cu^{2+} ion except for Ni^{2+} and Hg^{2+}, which interfere with the detection of Cu^{2+} ions with compound **1** and Na^{+}, which interfere with the detection of Cu^{2+} ions with compound **2**. These results suggest that compounds **1** and **2** may be used as potential Cu^{2+} selective fluorescent chemosensors.

Table 1
Fluorescence change (I–I_o)[a] for compounds **1** and **2** upon addition of various tetrabutylammonium anions

Ligand	λ (nm)	F$^-$	Cl$^-$	Br$^-$	I$^-$	CN$^-$	OAc$^-$	HSO$_4^-$	NO$_3^-$
1	377	−15.0	−22.49	−14.9	−22.17	−41.23	−14.98	−11.48	−14.97
2	375	−18.77	−18.77	−11.38	−13.22	−65.65	−12.21	−21.18	−9.32
	467	−3.96	−7.19	−10.76	−12.94	−85.27	−9.32	−5.91	−11.43

[a] Conditions: **1** and **2**, 6.0 μM in CH$_2$Cl$_2$/CH$_3$CN (1:1, v/v), excitation at 342 nm; anions, 60 μM in CH$_2$Cl$_2$/CH$_3$CN (1:1, v/v); I_o, fluorescence emission intensity of free ligand; I, fluorescence emission intensity of anion complexed.

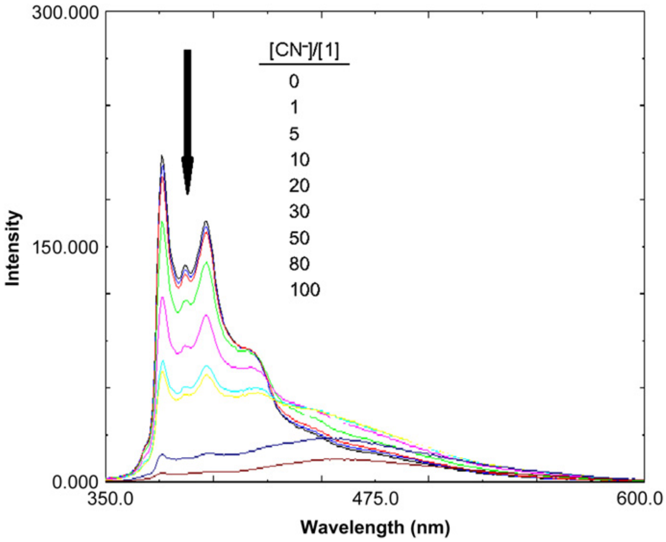


Figure 11. Fluorescence emission spectra of compound **1** (6.0 μM) upon various addition of CN$^-$ (0–100 equiv, 0–600 μM) in CH$_2$Cl$_2$/CH$_3$CN (1:1, v/v).

We also investigated anion binding studies of compounds **1** and **2** with different anions like F$^-$, Cl$^-$, Br$^-$, I$^-$, CN$^-$, OAc$^-$, HSO$_4^-$ and NO$_3^-$ as their tetrabutylammonium salt. The fluorescence intensity changes (I–I_o) of compounds **1** and **2** on addition of different anions are presented in Table 1. From these results it can be concluded that cyanide ion has preferential interaction with the compounds **1** and **2**. Upon addition of CN$^-$ (6.0 μM–600 μM) to the solution of compound **1**, a significant quenching in the monomer emission was observed (Fig. 11). Likewise, there was complete quenching in both monomer and excimer emission when CN$^-$ ions (6.0–1200 μM) were added to solution of compound **2** (Fig. 12). Similar results were obtained when strong base such as Bu$_4$NOH was specifically employed. Thus, we propose that the fluorescence quenching of compounds **1** and **2** on addition of cyanide ions probably occurs by the deprotonation of the amide moiety, which results in the formation of an anion, which then transfers electron to the pyrene moiety. To confirm this assumption and evaluate the intermolecular interactions between the compound **1** and cyanide ions, we also carried out ^{1}H NMR titrations in CDCl$_3$. It was found that on addition of small amounts of tetrabutylammonium cyanide to a solution of compound **1** in CDCl$_3$, the weakening of signal due to NH protons takes place, which indicates that interaction of these protons is taking place with cyanide ions but there is no change in the chemical shift of NH protons, which means there is no hydrogen bonding between cyanide and NH protons. On adding 0.3 equiv of CN$^-$ ion, the NH protons completely disappeared, which indicates

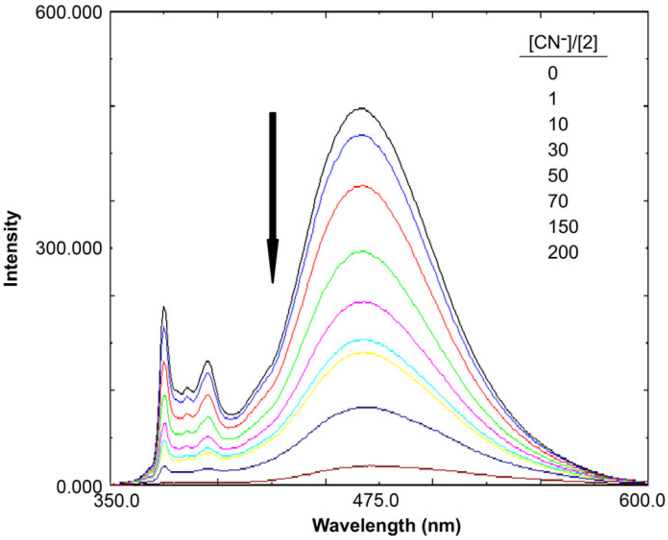


Figure 12. Fluorescence emission spectra of compound **2** (6.0 μM) upon various addition of CN$^-$ (0–200 equiv, 0–1200 μM) in CH$_2$Cl$_2$/CH$_3$CN (1:1, v/v).

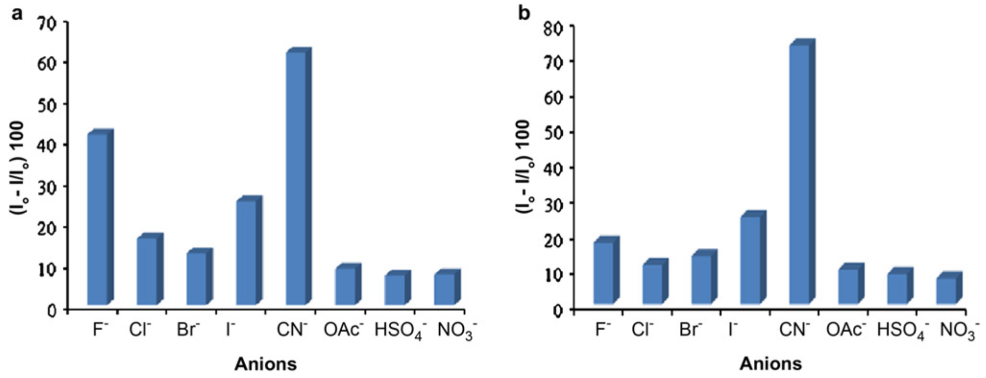


Figure 13. Fluorescence quenching ratio [$(I_o-I/I_o)\times100$] of (a) compound **1** (6.0 μM) and (b) compound **2** (6.0 μM) upon addition of different anions (100 equiv, 600 μM) in CH_2Cl_2/CH_3CN (1:1, v/v).

that the deprotonation of the NH protons is taking place in the presence of cyanide ions. The deprotonation is further supported by the fact that the –CONHC*H*$_2$ protons, which appear as a doublet in the absence of CN^- appear as singlet in the presence of CN^- ions. The deprotonation of the NH proton in amide or thiourea was believed to be the basis of fluoride sensing in recent research.[36,37]

We also tested the fluorescence response of compounds **1** and **2** in the presence of other anions like F^-, Cl^-, Br^-, I^-, OAc^-, HSO_4^-, NO_3^- besides CN^-, as shown in Figure 13a and b, no significant fluorescence change of compounds **1** and **2** occurred in the presence of (600 μM) of these anions except F^-, which quenches the fluorescence of compound **1** to some extent.

3. Conclusion

In conclusion, we developed selective fluorescent sensors **1** and **2** for Cu^{2+} and CN^- based on thiacalix[4]arene armed with pyrene moieties. The recognition of Cu^{2+} resulted in significant quenching in monomer emission of compound **1** and ratiometric response with monomer enhancement and excimer quenching of compound **2**. Thus, compounds **1** and **2** may be considered as a potential bifunctional fluorescent chemosensors for Cu^{2+} and CN^- ions. Work is in progress to explore sensors for other heavy metal ions and anions based on thiacalix[4]arenes/calix[4]arenes armed with different fluorophores.

4. Experimental section

4.1. General

The ^1H and ^{13}C NMR spectra were recorded on JEOL 300 MHz spectrometer using TMS as internal standard and $CDCl_3$ as solvent. FAB Mass spectra were recorded on JEOL XS102/DA-6000 mass spectrometer using xenon (6 kV, 10 mA) as FAB gas. Infrared spectra were recorded on a Pye Unicam SP3-3 Infrared spectrophotometer. UV/vis and fluorescence spectra were recorded with Shimdzu UV-1601 spectrophotometer and Shimadzu RF-5301(PC) spectrofluorophotometer, respectively. Elemental analysis was done at Department of Chemistry, Guru Nanak Dev University, Amritsar, India, using Flash EA 1112 CHNS-O analyzer of Thermo Electron Corporation. Stock solutions (0.1 M) of metal perchlorate salts and tetrabutylammonium salts were prepared in CH_2Cl_2/CH_3CN (1:1, v/v). Stock solutions (0.01 mM) of compounds **1** and **2** were prepared in CH_2Cl_2/CH_3CN (1:1, v/v). For all measurements of fluorescence spectra, excitation wavelength was at 342 nm and slit width at 3.0 nm. UV/vis and fluorescence spectra were performed by using 6.0 μM of compounds **1** and **2** in CH_2Cl_2/CH_3CN (1:1, v/v) and varying concentration of guests (cation or anion).

4.2. Synthesis of 1

To a mixture of thiacalix[4]arene **3** (0.10 g, 0.139 mmol) and *N*-(1-pyrenylmethyl)chloroacetamide **5** (0.105 g, 0.305 mmol) in 30 ml of dry CH_3CN, anhydrous Cs_2CO_3 (0.045 g, 0.139 mmol) and a catalytic amount of NaI were added. The reaction mixture was refluxed for 48 h. The solvent was removed in vacuo after completion of reaction. The resulting solid was dissolved in CH_2Cl_2 (100 ml) and the organic layer was washed thrice with water (50 ml). The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give crude product, which was purified by column chromatography from ethyl acetate/hexane (7:3, v/v) to give 0.05 g (27%) of **1** as dirty white solid. Mp 325–328 °C, IR (KBr pellet, cm^{-1}) 1663, 3432; ^1H NMR (300 MHz, $CDCl_3$): δ 0.71 (18H, s, $C(CH_3)_3\times2$), 0.99 (18H, s, $C(CH_3)_3\times2$), 4.34 (4H, s, $CH_2\times2$), 5.49 (4H, d, J=3.3 Hz, $NCH_2\times2$), 6.04 (2H, s, $OH\times2$), 6.77 (4H, s, $ArH\times4$), 6.84 (4H, s, $ArH\times4$), 7.70–8.38 (18H, m, $ArH\times18$, pyrene), 8.81(2H, br, $NH\times2$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 31.6, 32.1, 34.4, 40.6, 70.7, 119.8, 122.8, 124.1, 125.4, 126.5, 127.3, 127.8, 127.9, 128.5, 130.3, 131.5, 132.6, 143.8, 145.7, 147.2, 155.9, 166.7, 168.2; FABMS: *m*/*z* 1261 (M^+-1). Anal. Calcd for $C_{78}H_{74}N_2O_6S_4$: C, 74.16; H, 5.86. Found: C, 73.97; H, 5.56.

4.3. Synthesis of 2

To a solution of dipropyloxythiacalix[4]arene **4** (0.10 g, 0.124 mmol) and Cs_2CO_3 (0.04 g, 0.124 mmol) in 30 ml of dry CH_3CN, *N*-(1-pyrenylmethyl)chloroacetamide **5** (0.094 g, 0.274 mmol) and catalytic amount of NaI were added. The reaction mixture was refluxed for 40 h. After completion of reaction (TLC), solvent was removed in vacuo. To the resulting product, 1 N HCl (50 ml) and CH_2Cl_2 (100 ml) were added. The organic layer was washed three times with water and dried over $MgSO_4$ to get crude solid. Recrystallization from CH_2Cl_2/CH_3OH (8:2, v/v) gave 0.13 g (73%) of **2** as white solid. Mp>330 °C, IR (KBr pellet, cm^{-1}) 1660, 3345; ^1H NMR (300 MHz, $CDCl_3$): δ 0.69–0.77 (24H, m, $C(CH_3)_3\times2$, $CH_3\times2$), 1.08–1.20 (4H, m, $CH_2\times2$), 1.24(18H, s, $C(CH_3)_3\times2$), 3.72 (4H, t, J=8.4 Hz, $OCH_2\times2$), 4.25 (4H, s, $OCH_2\times2$), 5.08 (4H, d, J=6.0 Hz, $NCH_2\times2$), 7.15 (4H, s, $ArH\times4$), 7.46 (4H, s, $ArH\times4$), 7.92–8.23 (20H, m, $ArH\times18$, pyrene, $NH\times2$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 9.94, 21.9, 30.6, 31.1, 40.8, 70.6, 71.7, 122.8, 124.8, 125.1, 125.8, 126.2, 127.1, 127.4, 127.8, 128.7, 130.8, 131.2, 132.1, 142.8, 145.9, 147.0, 156.9, 167.9, 168.8; FABMS: *m*/*z* 1348 (M^++2). Anal. Calcd for $C_{84}H_{86}N_2O_6S_4$: C, 74.88; H, 6.39. Found: C, 74.57; H, 6.36.

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