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PAPER

Thiacalix[4]arene-cinnamaldehyde derivative: ICT-induced preferential nanomolar detection of Ag^+ among different transition metal ions†

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A new thiacalix[4]arene-cinnamaldehyde derivative **3**, which undergoes red shift in the fluorescence spectrum in the presence of Ag^+ ions, has been synthesized. This emission shift is attributed to the intramolecular charge transfer process in the presence of Ag^+ ions with a detection limit in the nanomolar range.

Introduction

Silver, because of its toxic effects, is an important metal ion among various heavy transition-metal ions.[1] The use of silver in the electrical, photographic imaging, and pharmaceutical industries results in contamination of the environment.[2] Silver ions also have a negative effect in biological systems, such as interacting with vital enzymes which results in inactivation of these enzymes,[3] interacting with cell membranes,[4] and interfering with electron transport.[5] Irreversible darkening of the skin and mucous membrane is a side effect originating from prolonged use of silver .[6] Thus, keeping in view the role played by silver in day to day life, simple and rapid sensing of silver in biological and environmental systems is very important. Many approaches such as atomic absorption, inductively coupled plasma-mass atomic emission, fluorescence, and UV-vis absorption spectroscopy have been widely employed to quantify trace amounts of silver ions.[7] Among these methodologies, fluorescence signalling is one of the first choices as it is highly sensitive and simple which translates binding events into tangible fluorescence signals.[8] More importantly, most fluorescent sensors can be used as cellular imaging reagents which make the fluorescence approach superior to other analytical methods. Therefore, much effort has been devoted to design fluorescent sensors for versatile objectives. A number of photophysical processes can be exploited to yield visible parameters which can be correlated to analyte concentration.[9] For high sensitivity and simplicity, a significant spectral shift in either the absorption or emission spectra becomes very important. However, the success of fluorescence enhancement with spectral shift for detecting silver ions[10] has been limited till now because silver ions usually quench fluorescence emission *via* electron transfer and intersystem crossing processes.[11] Thus, it is extremely advantageous to propose a novel sensor with spectral shifts for silver ions. In this regard, sensors based on metal-induced changes in fluorescence are particularly attractive as they offer significant spectral shifts. The most fundamental way to assure such a spectral change is to design a molecule exhibiting intramolecular charge transfer (ICT) mechanism which involves the observation of changes in the ratio of the intensities of the absorption or the emission at two wavelengths.[12]

Our research involves the design, synthesis and evaluation of (thia)calix[4]arene based receptors for selective sensing of soft metal ions, anions and evaluation of their switching behaviour.[13] A number of molecular switches based on thiacalix[4]arenes have been reported in the past by our research group.[14] Recently, we have reported a thiacalix[4]arene based chemosensor bearing two pyrene groups which demonstrates ratiometric sensing with Ag^+ and fluorescence quenching with Fe^{3+} ions in mixed aqueous media.[15] Now, we have designed and synthesized a receptor, **3**, based on 1,3-alternate conformation of thiacalix[4]arene bearing dimethyliminocinnamaldehyde moieties. The chemosensor **3** shows a strong fluorescence attributed to the excited state redistribution of charge which makes a twisted intramolecular charge transfer (TICT) state.[16] Out of the various transition and alkali metal ions, only in the presence of Ag^+ ions, the chemosensor **3** displays a selective spectral shift in fluorescence emission as a consequence of intramolecular charge transfer (ICT), which involves electron transfer from the nitrogen atom of the dimethylamino moiety to the imino nitrogen, of which the electron density is diminished on interaction with Ag^+ ions. The addition of other transition metal ions like Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} shows linear decrease of the emission, while the addition of Ba^{2+}, Mg^{2+}, K^+, Li^+, Na^+, Ni^{2+}, Co^{2+} did not alter the fluorescence emission of receptor **3**.

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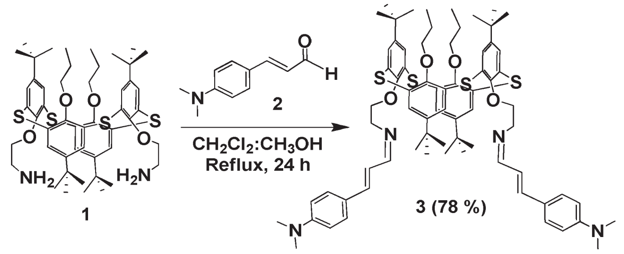

Scheme 1 Synthesis of **3**.

Results and discussion

The condensation of diamine **1**[17] with *N*,*N*-dimethylaminocinnamaldehyde **2** furnished compound **3** in 78% yield (Scheme 1). The structure of compound **3** was confirmed from its spectroscopic and analytical data. The IR spectrum of compound **3** showed a C=N stretching band at 1602 cm^{-1} (see ESI S12†). There is no absorption band corresponding to free aldehyde and amino groups, which indicates that the condensation has taken place. The ^1H NMR spectrum (see ESI S7 and S8†) of compound **3** showed four triplets (6, 4, 4 and 4H) at 0.62, 3.05, 3.82 and 4.14 ppm corresponding to the CH_3, NCH_2, OCH_2 and OCH_2 protons, three multiplets (4, 8 and 8H) at 1.02–1.09, 6.63–6.74 and 7.31–7.34 ppm corresponding to the methylene, aromatic and CH protons, four singlets (18, 18, 12 and 4H) at 1.26, 1.28, 2.99 and 7.41 ppm corresponding to the *tert*-butyl, NCH_3 and aromatic protons, and a doublet (2H) at 7.87 ppm corresponding to the imino protons. The mass spectrum showed a parent ion peak at *m*/*z* 1205.6 corresponding to the compound **3** (see ESI S10†). These spectroscopic data corroborate the structure **3** for this compound.

The binding behaviour of compound **3** towards different cations (Ag^+, Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Ba^{2+}, Mg^{2+}, K^+, Li^+ and Na^+) as their perchlorate salts was studied by UV-vis and fluorescence spectroscopy. The titration experiments were carried out in dry THF by adding aliquots of different metal ions. The absorption spectrum of **3** (10.0 μM) is characterized by typical absorption bands of dimethyliminocinnamaldehyde moiety at 265 and 352 nm (Fig. 1A) assigned to the transition from S_0 to S_2 and S_1 states respectively.[16] A low energy absorption at 352 nm indicates that this is a π–π^* type of transition. Addition of Ag^+ ions up to one equivalent resulted in a red shift of the band centered at 352 nm to 396 nm with an isosbestic point at 370 nm (Fig. 1A). The formation of a new band at 396 nm is due to the interaction of Ag^+ ions with imino nitrogen atoms leading to weak intramolecular charge transfer (ICT) from the nitrogen atom of the dimethylamino moiety to the imino nitrogen atom. On further addition of Ag^+ ions (1–100 equiv) the absorption band at 396 nm decreases with simultaneous appearance of a new absorption band at 466 nm (Fig. 1B). The variations in the absorption bands at 396 and 466 nm on addition of Ag^+ ions led to a clear isosbestic point at 432 nm. We believe that as the amount of Ag^+ ions increases, the interaction between the Ag^+ ions and the imino nitrogen atoms induces an enhanced ICT from the nitrogen atom of the dimethylamino moiety to the imino nitrogen atom, of which the electron density is diminished on interaction with Ag^+ ions which results in a large red shift with appearance of a new band at 466 nm. In the presence of 100 equivalents of other metal ions like Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Ba^{2+} and Mg^{2+} the absorption band at 352 nm decreases accompanied by a red shift to 466 nm (Fig. 2). While the addition of K^+, Li^+ and Na^+ ions resulting in the small decrease in the absorbance at 352 nm with slight red shift (Fig. 2). The addition of just one equivalent of divalent metal ions like Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Ba^{2+} and Mg^{2+} shifted the absorption band of receptor **3** at 352 nm to 466 nm (see ESI S4†) as divalent metal ions have more affinity towards electrons, immediately inducing a strong intramolecular charge transfer in comparison to Ag^+ ions, which are of a monovalent nature. From these UV-vis studies, it is clear that compound **3** is interacting with different metal ions in the ground state. Fitting the changes in the absorbance spectra of compound **3** with different metal ions (Ag^+, Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Ba^{2+} and Mg^{2+}) that change the absorption spectrum of **3**, the nonlinear regression analysis program SPECFIT[18] demonstrated that 1 : 1 stoichiometry (host : guest) was the most stable species in solution and gave different

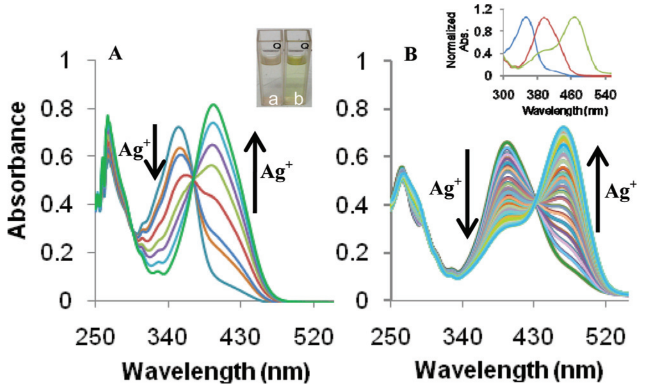

Fig. 1 UV-vis spectra of **3** (10.0 μM) with Ag^+ ions in THF; (A) in the presence of 0–1 equiv of Ag^+ ions; (B) in the presence of 1–100 equiv of Ag^+ ions; inset showing the colour change: (a) before; (b) after the addition of Ag^+ ions and normalized absorbance spectra; blue, free **3**; red, **3** + 1 equiv Ag^+ ions and green, **3** + 100 equiv Ag^+ ions.

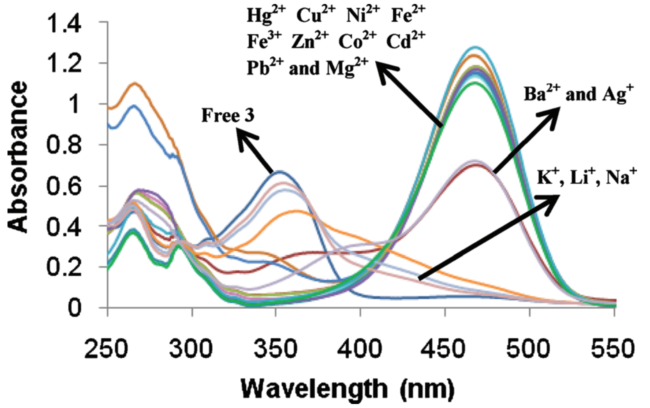

Fig. 2 UV-vis spectra of **3** (10.0 μM) with various metal ions (100 equiv each) in THF.

Table 1 Binding constants of different metal ions with compound **3**

Metal ions	log *β*	Metal ions	log *β*
$Ag+$	6.25 ± 0.23	Hg^{2+}	5.02 ± 0.44
Fe^{2+}	4.83 ± 0.07	Fe^{3+}	5.26 ± 0.08
Zn^{2+}	4.19 ± 0.32	Cu^{2+}	5.90 ± 0.23
Ni^{2+}	4.37 ± 0.06	Co^{2+}	5.47 ± 0.11
Cd^{2+}	4.52 ± 0.05	Pb^{2+}	5.33 ± 0.03
Ba^{2+}	3.34 ± 0.05	Mg^{2+}	4.80 ± 0.08

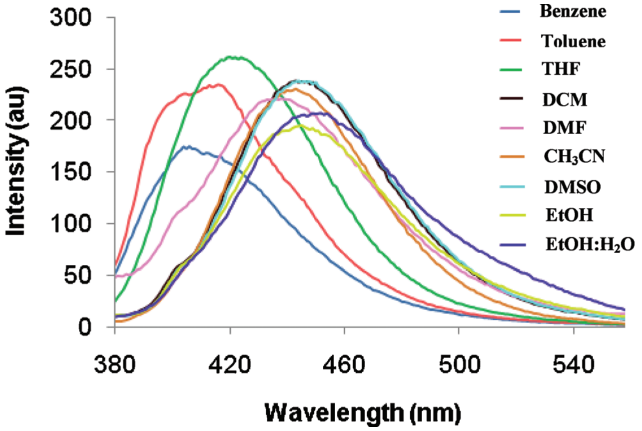

Fig. 3 Fluorescence spectra of **3** (1.0 μM) in the various polar and non-polar solvents; λ_{ex} = 360 nm.

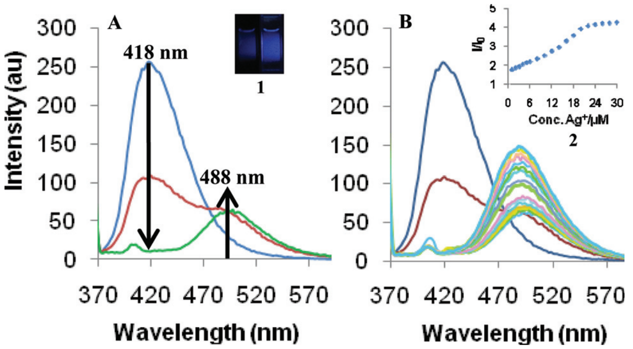

Fig. 4 Fluorescence spectra of **3** (1.0 μM) with Ag^+ ions in THF; λ_{ex} = 360 nm; (A) in the presence of 0–2 equiv of Ag^+ ions; (B) in the presence of 0–30 equiv of Ag^+ ions; inset (1) the fluorescence change: (a) before; (b) after the addition of Ag^+ ions and (2) the fluorescence intensity I/I_o (I_o = initial fluorescence intensity at 488 nm; I = fluorescence intensity after the addition of Ag^+ ions at 488 nm) as a function of Ag^+ ions concentration.

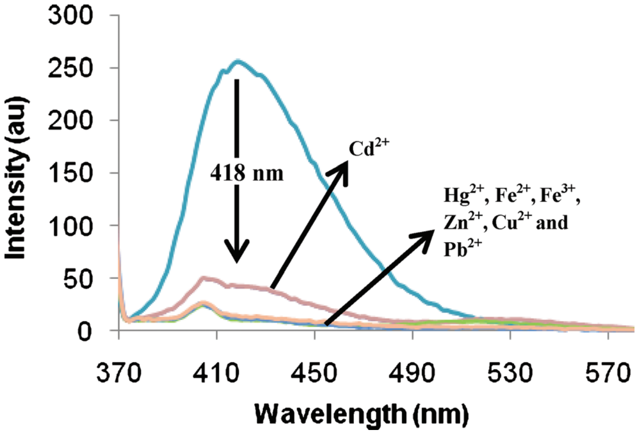

Fig. 5 Fluorescence spectra of **3** (1.0 μM) with Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} ions (30 equiv each) showing the linear decrease of the emission at 418 nm in THF; λ_{ex} = 360 nm.

binding constants (Table 1). From these results it is clear that the binding of silver with compound **3** is relatively strong in comparison to the binding of metal ions like Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Ba^{2+} and Mg^{2+} with compound **3**.

The fluorescence spectrum of compound **3** (1.0 μM) in THF exhibits a strong emission at 418 nm when excited at 360 nm (Fig. 3). The intense fluorescence emission of receptor **3** at 418 nm is due to the extended conjugated system which involves redistribution of charge in the excited state and makes a twisted intramolecular charge transfer (TICT) state. To confirm that the emission observed for receptor **3** in THF is based on this twisted intramolecular charge transfer, we studied the fluorescence behaviour of receptor **3** in various polar and non-polar solvents (Fig. 3, see ESI S2†). In non-polar solvents (benzene and toluene) receptor **3** shows unresolved emission corresponding to both a delocalized excited (DE) state at short wavelength (402 nm) and a twisted intramolecular charge transfer (TICT) state at longer wavelength (414 nm). Any increase in polarity of the solvents did not affect the position of the delocalized excited band. In comparison to the delocalized excited band, the TICT band shows a large red shift when moving from non-polar to polar solvents. For example, in THF a red shift of the TICT band (4 nm) was observed in comparison to non-polar solvents, while the presence of the delocalized excited band is hardly observed as in this case the delocalized excited band goes underneath the envelope of the TICT emission band. Thus, the appearance of the red shifted emission band in polar solvents clearly indicates that the emission of receptor **3** in THF is due to the twisted intramolecular charge transfer state.[16]

Further, upon addition of just two equivalents (0–2 μM) of Ag^+ ions to the receptor **3** in THF, the emission band centered at 418 nm quenches completely, and a new emission band appears at 488 nm with a bathochromic shift of about 70 nm (Fig. 4). With further additions of Ag^+ ions (2–30 μM) the emission band at 488 nm shows significant fluorescence enhancement. The fluorescence behaviour of compound **3** in the presence of Ag^+ ions is attributed to the alteration in the electronic properties of **3** *i.e.* increased intramolecular charge transfer (ICT) on metal ion complexation.[19] The nitrogen atoms of the imino moieties get involved in coordination with the silver ions, which enhances the electron withdrawing ability of imino nitrogen atoms leading to an enhanced intramolecular charge transfer process and consequently results in a large red shift. This type of emission shift is not observed with the addition of any other metal ions (Fig. 6A). The addition of metal ions like Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} shows a linear decrease in the emission at 418 nm (Fig. 5). Fluorescence quenching in the case of Hg^{2+} and Pb^{2+} may be attributed to spin–orbit coupling.[20] For Cu^{2+} and Fe^{3+} it may be due to the paramagnetic nature of these ions[21] and for Fe^{2+}, Zn^{2+} and Cd^{2+}, it may be due to

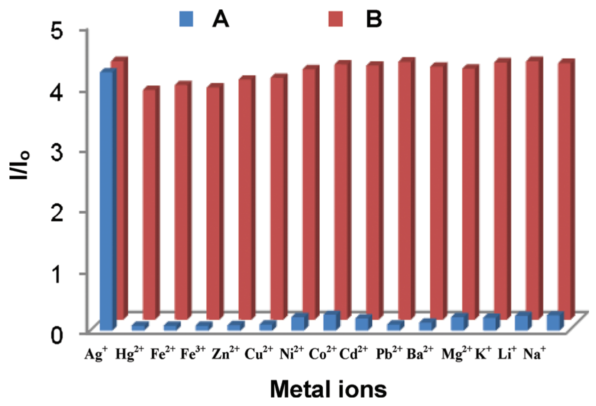

Fig. 6 Fluorescence response of **3** (1.0 μM) to various cations (30 μM each) in THF; λ_{ex} = 360 nm. Bars represent the emission intensity ratio (I/I_o) (I_o = initial fluorescence intensity at 488 nm; I = final fluorescence intensity at 488 nm after the addition of metal ions). Blue bars represent selectivity (I/I_o) of **3** upon addition of different metal ions; red bars represent competitive selectivity of receptor **3** towards Ag^+ ions (30 μM) in the presence of other metal ions (30 μM).

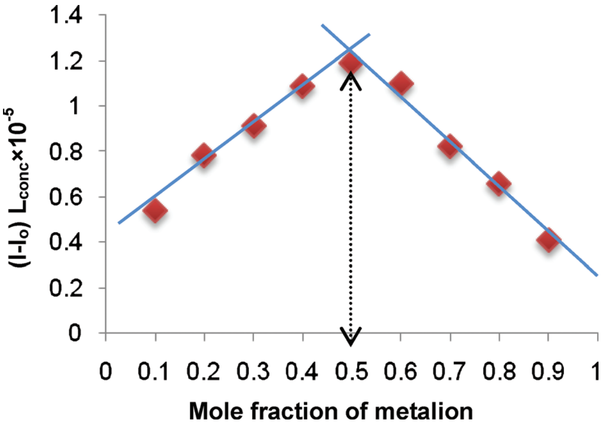

Fig. 7 Job's plot of **3** with Ag^+ ions in THF representing 1 : 1 stoichiometry.

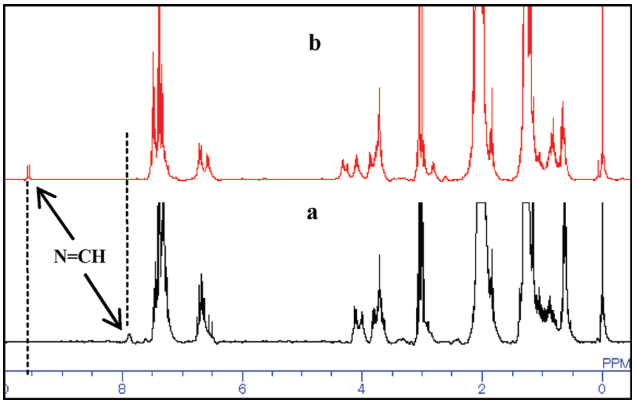

Fig. 8 ^1H NMR (300 MHz) spectra of **3** in $CDCl_3/CD_3CN$ (8 : 2); (a) Free ligand; (b) Free ligand + 1.0 equiv. of silver perchlorate.

photoinduced electron transfer from the photoexcited dimethyliminocinnamaldehyde moiety to the metal ions.[22] However, the preferred ICT process from the nitrogen atom of the dimethylamino moiety (donor) to the metal bound imino nitrogen atom (acceptor) may also contribute to the observed fluorescence quenching. The addition of other metal ions such as Ba^{2+}, Mg^{2+}, K^+, Li^+, Na^+, Ni^{2+}, Co^{2+} did not alter the fluorescence emission of compound **3** (see ESI S3†).

Further, by considering the ratio of the fluorescence intensity at 488 nm (I_{488}) to that of 418 nm (I_{418}), we observed 13-fold fluorescence enhancement in the case of **3**-Ag^+ complex in comparison to the free receptor (0.11). The fluorescence quantum yield[23] (see ESI S5†) of **3**-Ag^+ complex is 0.32 (at λ_{em} = 488 nm) as compared to that of free **3** (0.47, at λ_{em} = 418 nm) which shows good agreement with fluorescence spectra obtained for receptor **3** in the presence of Ag^+ ions. To check the practical ability of compound **3** as a Ag^+ selective fluorescent sensor, we carried out competitive experiments in the presence of Ag^+ at 30 μM mixed with Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Ba^{2+}, Mg^{2+}, K^+, Li^+ and Na^+ at 30 μM. As shown in Fig. 6B no significant variation in emission was observed by comparison with or without the other metal ions. It was found that **3** has a detection limit of 70×10^{-9} mol L^{-1} for Ag^+ ions which is sufficiently low for the detection of a nanomolar concentration range of Ag^+ ions (see ESI S6†) found in many chemical systems.[24] Fitting the changes in the fluorescence spectra of compound **3** with Ag^+ ions using the nonlinear regression analysis program SPECFIT[18] gave a good fit and demonstrated that 1 : 1 stoichiometry (host : guest) was the most stable species in solution with a binding constant (log β) = 6.73 with ± 0.17 error which is comparable with that determined by the absorbance method. The method of continuous variation (Job's plot) was also used to prove the 1 : 1 stoichiometry (Fig. 7).[25] The binding mode of receptor **3** with Ag^+ ions is proved by ^1H and ^{13}C NMR spectroscopy. The imino protons of receptor **3** undergo a downfield shift of $\Delta\delta$ = 1.69 ppm on addition of 1.0 equiv of Ag^+ ions proving interaction of receptor **3** with Ag^+ ions through the nitrogen atoms of the imino moiety (Fig. 8, see ESI S13†). The participation of sulphur atoms in the thiacalix[4]arene ring towards Ag^+ ions coordination is proved by ^{13}C NMR studies of compounds **1** and **3** in the presence of Ag^+ ions. In the presence of 1.0 equiv of Ag^+ ions compounds **1** and **3** undergo a downfield shift of signals corresponding to the carbons of the aromatic ring of the thiacalixarene moiety from 126.16–128.68 ppm to 126.23–131.32 ppm (see ESI S16–17†) and 123.23–130.67 ppm to 126.30–131.40 ppm (see ESI S14–15†), respectively. The downfield shifts of signals corresponding to the carbons of the aromatic ring of the thiacalixarene moiety in both cases elucidate the role of the sulphur atoms in the thiacalix[4]arene ring in the coordination with Ag^+ ions. The binding of Ag^+ ions with receptor **3** is also proved by mass spectroscopy (see ESI S11†). The mass spectrum showed a peak at m/z 1412.7 corresponding to the **3**-$AgClO_4$ complex, which not only confirms the binding of Ag^+ ions with receptor **3** but also proves the 1 : 1 stoichiometry of the host and guest species. In addition to this, we also carried out a reversibility experiment, which proves that the binding of Ag^+ ions to receptor **3** is reversible (Fig. 9). Addition of tetrabutylammonium chloride to the solution of the **3**-Ag^+ complex restored the fluorescence signal of **3** to its original level. Further, addition of Ag^+ ions to the same solution gives a **3**-Ag^+ complex indicating the reversible

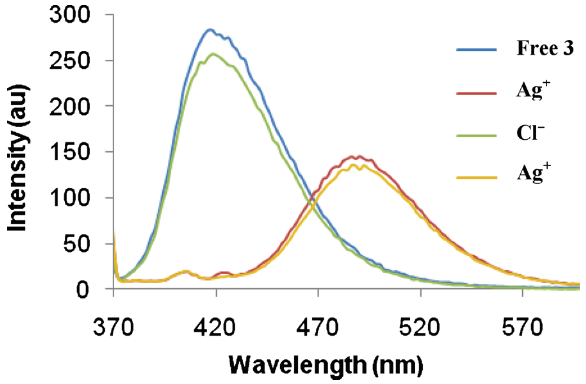

Fig. 9 Fluorescence spectra showing the reversibility of Ag^+ coordination to receptor **3** by Cl^- ions; blue line, free **3** (1 μM), red line, **3** + 30 μM Ag^+, green line, **3** + 30 μM Ag^+ + 30 μM Cl^-, orange line, **3** + 30 μM Ag^+ + 30 μM Cl^- + 80 μM Ag^+ in THF; λ_{ex} = 360 nm.

behaviour of chemosensor **3**. However, no precipitation was observed during the reversibility experiment.

Conclusions

In conclusion, we have designed and synthesized a receptor based on the 1,3-*alternate* conformation of thiacalix[4]arene possessing two dimethyliminocinnamaldehyde moieties. The Ag^+ ions bind with imino nitrogens of receptor **3** and thus, preferentially enhance the intramolecular charge transfer process from nitrogen atoms of the dimethylamino moiety to the imino moiety resulting in the significant spectral shift in fluorescence emission with a detection limit up to the nanomolar range. This type of emission shift is not observed in the case of any other transition or alkali metal ions.

Experimental

General information

All reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium and benzophenone and kept over molecular sieves overnight before use. UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length 1 cm). The cell holder was thermostatted at 25 °C. The fluorescence spectra were recorded with a VARIAN CARY ECLIPSE spectrofluorimeter. ^1H spectra were recorded on a JEOL-FT NMR-AL 300 MHz spectrophotometer using $CDCl_3/CD_3CN$ as solvent and tetramethylsilane as internal standards. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet), coupling constants J (Hz), integration and interpretation.

UV-vis and fluorescence titrations

UV-vis and fluorescence titrations were performed on 10.0 μM and 1.0 μM solutions of ligand in dry THF respectively. Typically, aliquots of freshly prepared metal perchlorates (Ag^+, Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Ba^{2+}, Mg^{2+}, K^+, Li^+ and Na^+) and standard solutions (10^{-1} M to 10^{-3} M) in dry THF were added to record the UV-vis and fluorescence spectra.

Synthesis of compound 3

A mixture of compound **1** (0.10 g, 0.08 mmol) and *N*,*N*-dimethylaminocinnamaldehyde (0.03 g, 0.17 mmol) in a 1 : 1 mixture of dry dichloromethane and dry methanol was refluxed for 24 h. After completion of the reaction, the solvent was evaporated and the residue left was crystallized from $CHCl_3/CH_3OH$ to give compound **3** in 78% yield; m.p. 212 °C; IR (KBr) ν_{max} = 1602 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.62 (t, J = 9 Hz, 6 H, CH_3), 1.02–1.09 (m, 4 H, CH_2), 1.26 (s, 18 H, $C(CH_3)_3$), 1.28 (s, 18 H, $C(CH_3)_3$), 2.99 (s, 12 H, CH_3), 3.05 (t, 4H, J = 9, NCH_2) 3.82 (t, 4 H, J = 9 Hz, OCH_2), 4.14 (t, J = 6 Hz, 4 H, OCH_2), 6.63–6.74 (m, 8 H, Ar-H, CH), 7.31–7.34 (m, 8 H, Ar-H), 7.41 (s, 4 H, Ar-H), 7.87 (d, J = 9 Hz, 2 H, HC=N) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 10.08, 22.10, 31.20, 31.50, 34.19, 40.02, 59.00, 67.25, 70.07, 112.06, 123.59, 123.80, 127.64, 127.80, 128.01, 128.68, 142.29, 145.50, 151.04, 156.45, 157.18, 164.29. MS ES+, *m*/*z*: = 1205.6; $C_{72}H_{92}N_4O_4S_4$: calcd. C 71.72, H 7.69, N 4.65; Found C 71.81, H 7.42, N 4.29.

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