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Thiacalix[4]crown based optical chemosensor for Fe^{3+}, Li^+ and cysteine: a Fe^{3+}/Li^+ ion synchronized allosteric regulation†

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A heteroditopic chemosensor **2** based on a thiacalix[4]crown with a 1,3-*alternate* conformation has been synthesized and shows a selective fluorescence turn-off response with Fe^{3+} ions in mixed aqueous media. Furthermore, the **2**–Fe^{3+} complex can be used as a chemosensing system for the detection of Li^+ and cysteine based on two different approaches. Moreover, the sequence addition of Fe^{3+} and Li^+ triggers an Fe^{3+}/Li^+ switchable on-off-on fluorescence chemosensor with negative allosteric regulations.

Introduction

Iron is a vital element for the activities of numerous physiological processes involving electron transfer and oxidation reactions[1] because of its redox-active nature and it is an essential trace metal ion that plays a crucial role in chemical, biological as well as in environmental systems.[2] The deficiency of iron throughout the developmental phases is linked with the permanent loss of motor skills.[3] On the other hand, an excess quantity of iron in the central nervous system is responsible for a number of diseases such as Parkinson's, Huntington's and Alzheimer's disease.[4] Keeping in mind the roles played by iron in day to day life, the development of techniques for simple and rapid sensing of iron in biological and environmental systems is very important. In this respect, fluorescence signalling,[5] owing to its sensitivity, is widely employed to quantify trace amounts of iron.[6]

Furthermore, the need for miniaturization is encouraging the design of single molecule based molecular devices as they can perform switching operations analogous to those executed by their macroscopic analogues.[7] These signalling devices consist of molecular systems which change their optical or electrical properties upon interaction with external chemical inputs, and the design of such molecular switches is of great significance as such organic molecules are expected to open new perceptions for the realization of artificial functions at the molecular level.[8]

Our research work involves the design and synthesis of fluorescent chemosensors for the selective sensing of soft metal ions and anions as well as to further evaluate their switching behaviour.[9] Recently, we have reported a ditopic chemosensor, based on the 1,3-*alternate* conformation of a thiacalix[4]arene bearing amine groups appended with pyrene moieties and a crown-4 ring, exhibiting selectivity towards Cu^{2+} ions and which can act as a Cu^{2+}/Li^+ ion switchable fluorescent chemosensor.[10] As a continuation of this work, now we have synthesized a new heteroditopic chemosensor **2** based on the 1,3-*alternate* conformation of thiacalix[4]crown-4 bearing two imino moieties appended with 2-hydroxy-5-nitrophenyl groups. The presence of the crown ring for metal ion complexation as an additional binding site in 1,3 *alternate* (thia)calix[4]arene system provides a platform to achieve heteroditopic complexation with allosteric regulation.[11] Such systems can also be used for mimicking allosteric regulation which plays a major role in biological systems and further opens the possibility of controlling molecular functions by external stimuli. Receptor **2** exhibits selective fluorescence quenching with Fe^{3+} ions in mixed aqueous media, ascribed to the inhibition of the ESIPT phenomenon, whereas Li^+ coordinates with the crown ether ring which is accountable for the small fluorescence enhancement in receptor **2**. Furthermore, we used the **2**–Fe^{3+} complex as a system for the turn-on detection of Li^+ ions and cysteine based on two different mechanisms. The addition of cysteine followed the displacement approach while Li^+ exerts a negative allosteric behaviour which is responsible for the turn-on fluorescence changes. In addition, the metal ion exchange triggers an Fe^{3+}/Li^+ switchable on-off-on fluorescent chemosensor with negative allosteric regulations between the Fe^{3+} and Li^+ ions.

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Experimental

General information

All reagents were purchased from Aldrich and were used without further purification. The experiments were carried out in a mixture of AR grade THF and HEPES buffer (9 : 1, v/v; pH 7.0). UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer with a quartz cuvette (path length 1 cm). The cell holder was thermostated at 25 °C. The fluorescence spectra were recorded with a SHIMADZU 5301 PC spectrofluorimeter. ^{1}H and ^{13}C spectra were recorded on a JEOL-FT NMR-AL 300 MHz spectrophotometer using $CDCl_3$ as a solvent and tetramethylsilane as the 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 a 5.0 μM solution of the ligand in THF–H_2O (9 : 1, v/v). Typically, aliquots of freshly prepared $M(ClO_4)_n$ (M = Pb^{2+}, Hg^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Ba^{2+}, Mg^{2+}, Ni^{2+}, Ca^{2+}, K^+, Na^+, Li^+, Fe^{2+}, Ag^+, Zn^{2+} and Cd^{2+}; n = 1 or 2 or 3) standard solutions (10^{-1} M to 10^{-3} M) were added to record the UV-vis and fluorescence spectra.

Quantum yield calculations

Fluorescence quantum yields[12] were determined using an optically matching solution of naphthalene (Φ_{fr} = 0.23 in ethanol) as the standard at an excitation wavelength of 300 nm and the quantum yield could then be calculated using the equation:

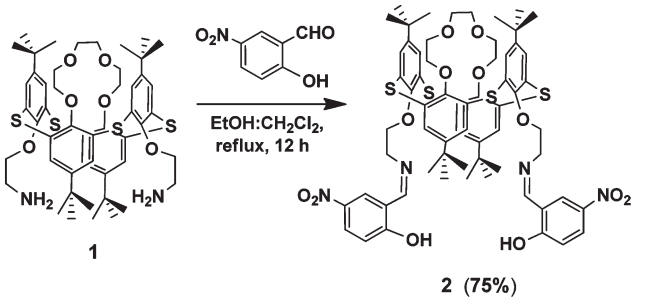
$$\Phi_{fs} = \Phi_{fr} \times \frac{1 - 10^{-A_r L_r}}{1 - 10^{-A_r L_s}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

where Φ_{fs} and Φ_{fr} are the radiative quantum yields of the sample and reference respectively, A_s and A_r are the absorbance of the sample and reference respectively, D_s and D_r are the respective areas of emission for the sample and reference. L_s and L_r are the lengths of the absorption cells of the sample and reference respectively. N_s and N_r are the refractive indices of the sample and reference solutions (pure solvents were assumed respectively).

Synthesis of 1,3-*alternate*-25,27-bis[2-(2-hydroxy-5-nitrophenyl)iminoethoxy]thiacalix[4]crown-4 (2). A mixture of compound **1** (0.1 g; 0.10 mmol) and 2-hydroxy-5-nitrobenzaldehyde (0.03 g; 0.21 mmol) in a mixture of ethanol–dichloromethane was refluxed for 12 h. After the completion of the reaction, the solvent was evaporated and the residue left behind was crystallized from $CHCl_3$–CH_3OH to give compound **2** in a 75% yield; m.p. 220 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.28 (s, 18 H, $C(CH_3)_3$), 1.29 (s, 18 H, $C(CH_3)_3$), 2.51 (br, 4 H, CH_2), 3.24 (t, J = 6 Hz, 4 H, OCH_2), 3.50 (br, 4 H, OCH_2), 4.03 (br, 4 H, OCH_2), 4.15 (t, J = 6 Hz, 4 H, OCH_2), 7.01 (d, J = 6 Hz, 2 H, Ar-H), 7.33 (s, 4 H, Ar-H), 7.48 (s, 4 H, Ar-H), 8.18–8.21 (m, 4H, Ar-H), 8.31 (s, 2 H, HC═N), 14.12 (br, OH) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 31.31, 31.49, 34.39, 34.44, 56.37, 66.03, 68.66, 69.95, 71.30, 117.22, 118.39, 127.22, 127.69, 12.13, 128.48, 139.52, 146.39, 147.02, 154.78, 158.26, 164.62, and 167.25 ppm. MS ES+, m/z: = 1219.5 $[M + H]^+$. $C_{64}H_{74}N_4O_{12}S_4$: calcd. C 63.03, H 6.12, N 4.59; Found C 63.14, H 6.32, N 4.86.

Results and discussion

The condensation reaction of diamine **1**[13] with 2-hydroxy-5-nitrobenzaldehyde furnished compound **2** in a 75% yield (Scheme 1). The structure of compound **2** was confirmed from its spectroscopic and analytical data (see Fig. S5–S8, ESI†). The binding behaviour of compound **2** towards different cations (Pb^{2+}, Hg^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Mg^{2+}, Ni^{2+}, Fe^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Ba^{2+}, Ca^{2+}, K^+, Na^+, and Li^+) as their perchlorate salt was studied by UV-vis and fluorescence spectroscopy. The absorption spectrum of receptor **2** (5 μM; Fig. 1) in THF–H_2O (9 : 1, v/v) is characterized by typical absorption bands at 238, 262 and 288 nm. The addition of only Fe^{3+} ions (0–16 equiv.) results in a significant absorption enhancement corresponding to these absorption bands, while titrations with other transition and alkali metal ions did not alter the absorption spectrum of receptor **2** (see Fig. S2, ESI†). The fluorescence spectrum of receptor **2** (5.0 μM; THF–H_2O; 9 : 1, v/v) exhibits an emission band at 356 nm (Fig. 2), attributed to the very fast enol–imine to keto–amine tautomerism (Scheme 2) involving the phenomenon of excited state intramolecular proton transfer (ESIPT).[14]



Scheme 1 Synthesis of compound **2**.

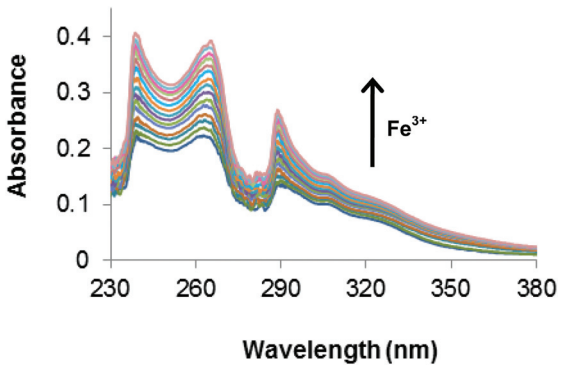


Fig. 1 UV-vis spectra of **2** (5.0 μM) with Fe^{3+} ions (16 equiv.) in THF–H_2O; (9 : 1, v/v) buffered with HEPES, pH = 7.0.

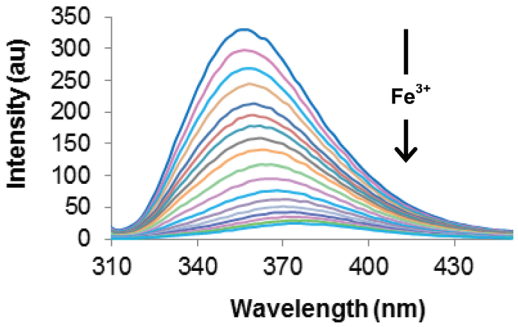
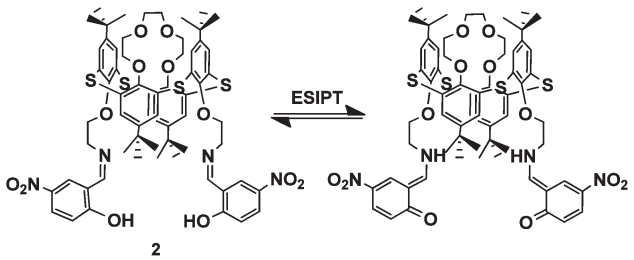


Fig. 2 Fluorescence spectra of **2** (5.0 μM) with Fe^{3+} ions (20 equiv.) in THF–H_2O; (9 : 1, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 300 nm.



2

Scheme 2 Fast enol–imine to keto–amine tautomerism in **2**.

However, the gradual addition of Fe^{3+} ions (0–20 equiv.) to a solution of compound **2** results in a decrease in the fluorescence intensity at 356 nm. This decrease in the fluorescence intensity is ascribed to the participation of imino nitrogens towards the coordination of Fe^{3+} ions, which trammels the ESIPT phenomenon and hence quenched the fluorescence emission.

Furthermore, by considering the ratio of the fluorescence intensity of the free receptor at 356 nm (I_o) to that of receptor **2** with Fe^{3+} ions at 356 nm (I), we observed a 13-fold decrease in the fluorescence emission in the case of the **2**–Fe^{3+} complex. The fluorescence quantum yield of the **2**–Fe^{3+} complex is 0.02 compared to that of free **2** (0.32), which shows good agreement with the fluorescence spectra obtained for receptor **2** in the presence of Fe^{3+} ions. Fitting the changes in the fluorescence spectra of compound **2** with Fe^{3+} ions by using the nonlinear regression analysis program SPECFIT[15] gave a good fit and demonstrated that a 1 : 1 stoichiometry (host : guest) was the most stable species in the solution, with a binding constant (log β) = 4.78 ± 0.06. The method of continuous variation (Job's plot; Fig. 3) was also used to prove the 1 : 1 stoichiometry.[16] The detection limit[17] of **2** for Fe^{3+} ions was calculated to be of 30 × 10^{-9} mol L^{-1}, which is sufficiently low for the detection of nanomolar concentrations of Fe^{3+} ions (see Fig. S3, ESI†). This type of fluorescence behaviour is not observed upon the addition of any other transition and alkali metal ions (Fig. 4 and 5). Thus, receptor **2** acts as an efficient fluorescence 'turn-off' chemosensor for the selective detection of Fe^{3+} ions in mixed aqueous media. However, the addition of Li^+ ions to a solution of **2** results in a slight enhancement of the emission at 356 nm (Fig. 6). This enhancement in the

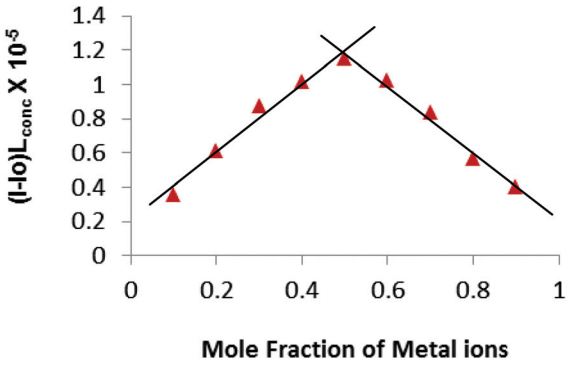


Fig. 3 Job's plot for determining the stoichiometry (1 : 1) of **2** and the Fe^{3+} ions.

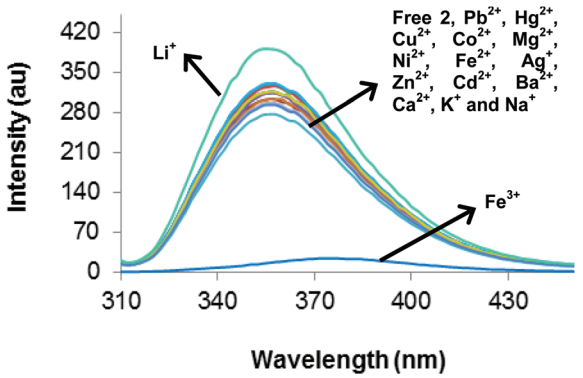


Fig. 4 Fluorescence spectra of **2** (1.0 μM) in the presence of various metal ions (20.0 μM) in THF–H_2O; (9 : 1, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 300 nm.

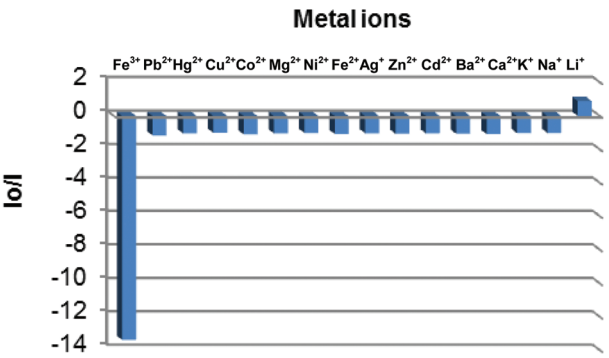


Fig. 5 Fluorescence response of **2** (5.0 μM) to various metal ions (20 equiv. each) in THF–H_2O; (9 : 1, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 300 nm. The bars represent the selectivity (I_o/I) of **2** upon the addition of different metal ions. I_o and I denote the fluorescence intensity at 356 nm before and after the addition of metal ions, respectively.

fluorescence intensity is attributed to the binding of Li^+ ions to the crown-4 ring,[11a] which suppresses the photoinduced electron transfer (PET) to the photoexcited 2-hydroxy-5-nitrophenyl groups. Furthermore, fitting the changes in the fluorescence spectra of receptor **2** with Li^+ ions by using the nonlinear regression analysis program SPECFIT gave a good fit and demonstrates that a 1 : 1 stoichiometry of the host and

guest was the most stable species in the solution, with a binding constant (log β) of 4.57 ± 0.3. To check the practical ability of compound **2** as a Fe^{3+} ion selective fluorescent sensor, we carried out competitive experiments in the presence of 20 equiv. of Fe^{3+} ions mixed with 20 equiv. of Pb^{2+}, Hg^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Mg^{2+}, Ni^{2+}, Fe^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Ba^{2+}, Ca^{2+}, K^{+}, Na^{+}, and Li^{+} ions. As shown in Fig. S4, ESI† no significant variation in the emission was observed with or without other metal ions.

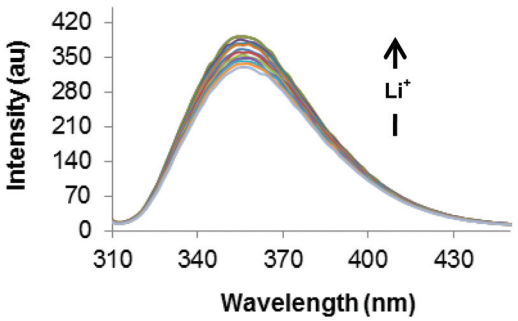


Fig. 6 Fluorescence spectra of **2** (5.0 μM) with Li^{+} ions (20 equiv.) in THF–H_2O; (9 : 1, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 300 nm.

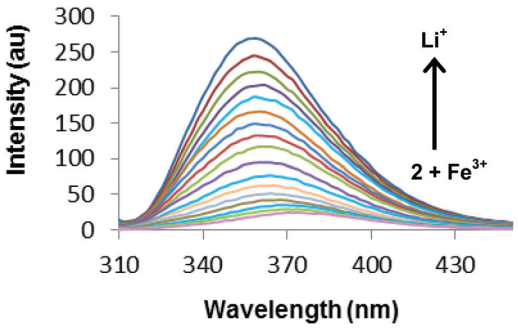


Fig. 7 Fluorescence spectra of **2** (5.0 μM) upon the addition of Li^{+} ions (70 equiv.) to the **2**–Fe^{3+} complex in THF–H_2O; (9 : 1, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 300 nm.

Furthermore, we utilized the **2**–Fe^{3+} complex system for the selective detection of Li^{+} and biothiols, such as cysteine, based on different approaches. The presence of the crown-4 moiety as an additional binding site other than the imino moiety in **2** raises the possibility of discrimination between the Fe^{3+} and Li^{+} ions. When Li^{+} ions (0–70 equiv.) were gradually added to a solution of the **2**–Fe^{3+} complex, the fluorescence intensity at 356 nm undergoes a regular increase in the fluorescence emission (Fig. 7). These results indicate that the decomplexation of Fe^{3+} ions taking place upon the addition of Li^{+} ions, ascribed to the binding of Li^{+} ions with the polyether ring (crown-4 moiety), is responsible for the conformational changes favouring the release of Fe^{3+} from the imino binding site and hence, the ESIPT phenomenon comes into operation and is answerable for the emission enhancement at 356 nm (Fig. 8). Thus, the addition of Li^{+} ions to the **2**–Fe^{3+} complex exerts a negative heterotropic allosteric effect which means the **2**–Fe^{3+} complex acts as a system for the selective detection of Li^{+} ions. The addition of other metal ions, even alkali metal ions such as Na^{+} and K^{+}, did not alter the fluorescence emission of the **2**–Fe^{3+} system (Fig. 9A), ascribed to the high selectivity of the crown-4 ring towards Li^{+} ions. For a system to be an efficient chemosensor, it must work in the presence of other analytes. Thus, we investigated the competitive selectivity of the **2**–Fe^{3+} system in the presence of 70 equiv. of Li^{+} ions mixed with 70 equiv. of other metal ions. As shown in Fig. 9B, no significant variation in the emission was observed on comparison with or without other metal ions.

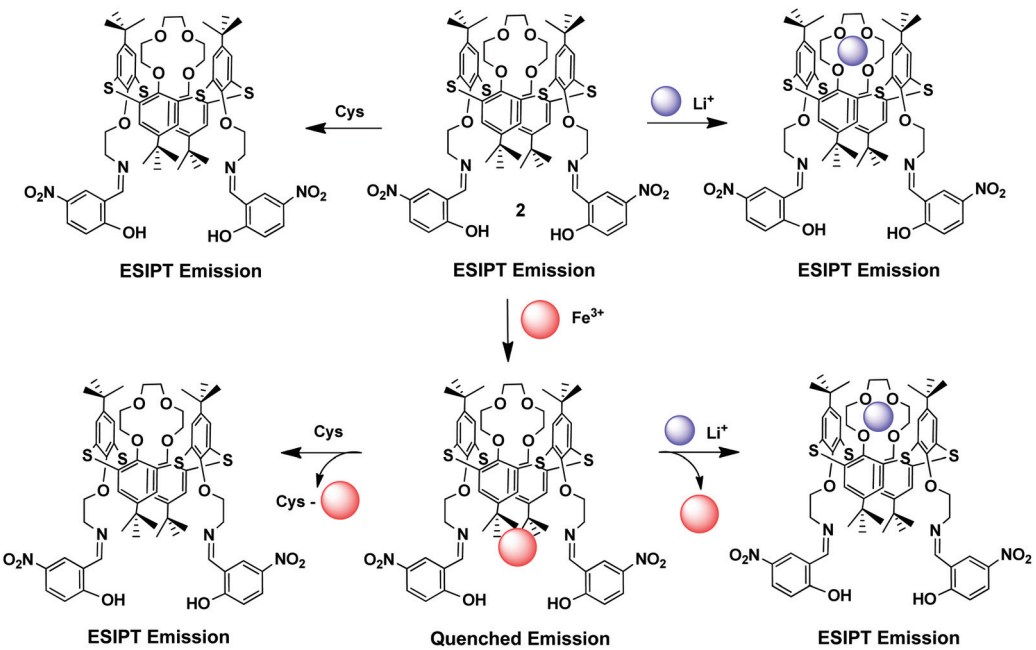


Fig. 8 Schematic representation of the Li^{+} and Cys induced fluorescence turn-on.

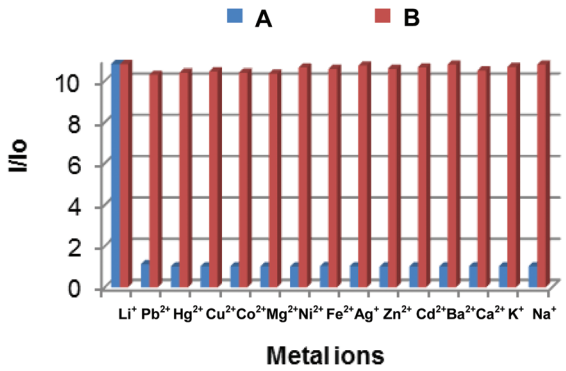


Fig. 9 Fluorescence response of the **2**–Fe^{3+} complex to various metal ions (70 equiv. each) in THF–H_2O; (9 : 1, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 300 nm. The bars represent the selectivity (I/I_o) of the **2**–Fe^{3+} complex upon the addition of different metal ions. (A) The blue bars represent the selectivity (I/I_o) of the **2**–Fe^{3+} complex upon addition of different metal ions; (B) the red bars represent the competitive selectivity of the receptor **2**–Fe^{3+} complex towards Li^+ ions (70 equiv.) in the presence of other metal ions (70 equiv.).

Moreover, we observed an 11-fold fluorescence enhancement in the case of the **2**–Fe^{3+} complex titration with Li^+ ions. The detection limit of the **2**–Fe^{3+} complex was found to be 55×10^{-8} mol L^{-1} for Li^+ ions. The substantial increase in the quantum yield from 0.2 to 0.26 also reveals the **2**–Fe^{3+} complex to be a fluorescence turn-on system for Li^+ ions. However, in the reverse of this cation exchange process, the addition of Fe^{3+} ions (50 equiv.) to a solution of the **2**–Li^+ complex results in fluorescence quenching corresponding to the emission band at 356 nm (Fig. 10b). This clearly indicates that Fe^{3+} moves in and Li^+ moves out of receptor **2**. Thus, negative allosteric switching is observed between the Fe^{3+} and Li^+ ions in mixed aqueous media. Therefore, the metal ion exchange between Fe^{3+} and Li^+ acts as a chemical input to trigger an on-off-on switchable fluorescent chemosensor (Fig. 11). However, the liberation of Fe^{3+} from the imino binding site of the **2**–Fe^{3+} complex requires excess addition of Li^+ which indicates the stronger binding of Fe^{3+} ions as compared to Li^+ binding by the polyether oxygen atoms, as supported by the binding constant data.

In addition to the use of the **2**–Fe^{3+} complex as a chemosensing system for Li^+ ions, we further employed this complex for the detection of cysteine based on the displacement approach. The addition of cysteine to a solution of the free receptor did not introduce any evident changes into the emission spectrum of **2**. However, the addition of cysteine to an aqueous solution of the **2**–Fe^{3+} complex results in the fluorescence enhancement corresponding to 356 nm (Fig. 12). This increase in the emission intensity is ascribed to the formation of a Cys–Fe^{3+} complex and thus, Fe^{3+} is no longer available to inhibit the excited state intramolecular proton transfer mechanism favouring the emission enhancement at 356 nm (Fig. 8). A 9.5-fold fluorescence enhancement is observed in the cysteine treatment with the **2**–Fe^{3+} complex. The considerable increase in the quantum yield (0.23) and detection limit of 12×10^{-8} mol L^{-1} of the **2**–Fe^{3+} complex for cysteine suggest this system is a proficient sensing platform for cysteine. Thus, the **2**–Fe^{3+} complex acts as a chemosensing system for the detection of Li^+ and cysteine based on two contrasting modes of action. The detection of Li^+ followed the negative allostery route while cysteine detection is associated with the displacement approach.

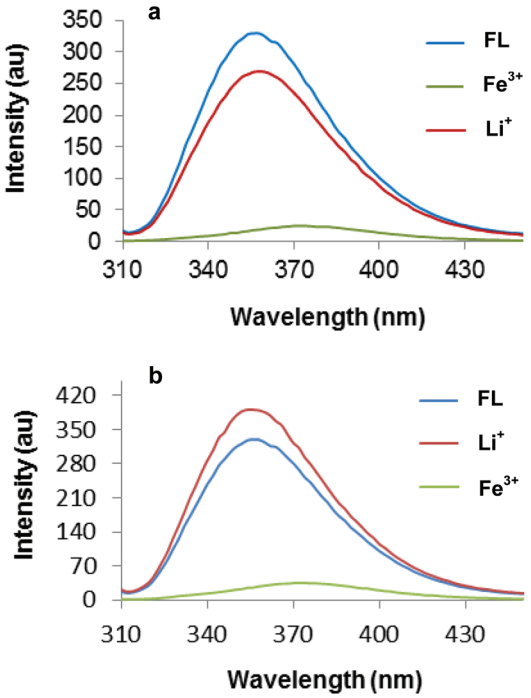


Fig. 10 (a) Change in the fluorescence emission spectra of the **2**–Fe^{3+} complex upon the addition of Li^+ ions. (b) Change in the fluorescence emission spectra of the **2**–Li^+ complex upon the addition of Fe^{3+} ions in THF–H_2O; (9 : 1, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 300 nm.

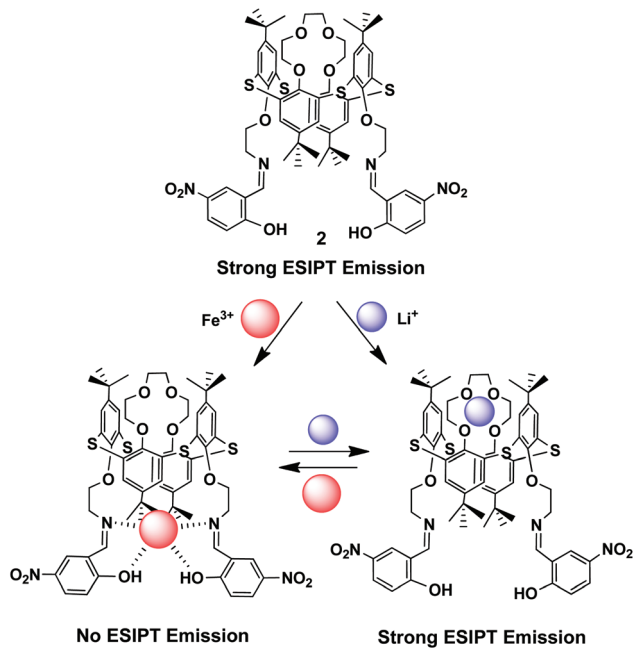


Fig. 11 Schematic representation of the ion exchange between metal ions.

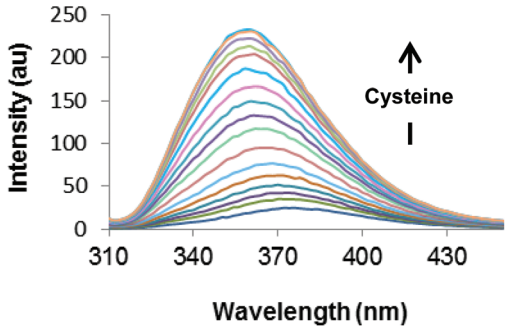


Fig. 12 Fluorescence spectra of **2** (5.0 μM) upon the addition of cysteine (50 equiv.) to the **2**–Fe^{3+} complex in THF–H_2O; (9 : 1, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 300 nm.

Conclusion

In conclusion, we synthesized a heteroditopic fluorescent chemosensor **2** based on a thiacalix[4]arene with the 1,3-*alternate* conformation which possesses a crown-4 moiety as an additional binding site other than the imino moieties. Receptor **2** shows a selective fluorescence turn-off response with Fe^{3+} ions in aqueous media with a detection limit on the nanomolar level, ascribed to the inhibition of the ESIPT mechanism. Furthermore, the **2**–Fe^{3+} complex behaves as a chemosensing system for the turn-on detection of Li^+ ions and cysteine based on the two different mechanisms. The addition of cysteine follows the displacement approach while Li^+ ions exert a negative allosteric behaviour responsible for the turn-on fluorescence changes attributed to the ESIPT process. Interestingly, the sequential addition of Fe^{3+} and Li^+ ions triggers a Fe^{3+}/Li^+ switchable on–off–on fluorescent chemosensor with negative allosteric regulations between these ions. The designs of such molecular based allosteric systems are better than simple host-guest systems as they open the possibility of controlling molecular function in biomimetic systems by chemical inputs.

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