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Selective recognition of Zn^{2+} by salicylaldimine appended triazole-linked di-derivatives of calix[4]arene by enhanced fluorescence emission in aqueous-organic solutions: role of terminal $-CH_2OH$ moieties in conjunction with the imine in recognition ☆

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ABSTRACT

A series of lower rim 1,3-di-derivatives possessing Schiff's base cores were synthesized using triazole unit as linker moiety by further introducing butyl (L_2), one $-CH_2OH$ (L_3) and two $-CH_2OH$ (L_4)-containing moieties, respectively, in order to bring additional support for ion binding. Based on fluorescence and absorption spectroscopies it has been shown that Zn^{2+} could be selectively recognized by the Schiff's base core and not by the triazole core among the ten metal ions studied both in methanol and in aqueous solutions of methanol and acetonitrile, wherein the $-CH_2OH$ moieties augment the fluorescence response by providing additional coordinations to the Zn^{2+}. Thus L_4 exhibited a fluorescence enhancement of ~65, ~48 and ~25-fold in methanol, aqueous solutions of methanol and acetonitrile, with minimum detection limits of 174, 313 and 320 ppb, respectively. Both the excitation and emission wavelengths fall in visible region.

Zn^{2+} is one of the most abundant transition metal ions present in living cells, including those from human, by exhibiting functional as well as structural roles.[1] Cellular studies[2a] showed that many mammalian organs including brain[2b,c], pancreas[2d,e] and prostate[2f] accumulate pools of labile Zn^{2+} which has been shown by imaging. A Zn^{2+} metabolic disorder is closely associated with several neurological diseases.[3] To expound the biological role of Zn^{2+} which is spectroscopically and magnetically silent, it is necessary to have a direct recognition method. Different families of fluorescent Zn^{2+} probes have been reported in the literature on the basis of small as well as large supramolecular systems.[4–6] Supramolecular systems containing calixarenes have received much attention as basic molecular scaffolds for building appropriate binding core suitable for ion recognition as well as for host guest chemistry.[7] There are a number of reports available for selective recognition of Zn^{2+} by other systems[5,6], but calix[4]arene-based examples are rather limited.[8] Recently, we reported calix[4]arene based Zn^{2+} and Hg^{2+} chemosensors.[9] In the present Letter, we report the synthesis, characterization and fluorescence recognition properties of a triazole-linked calix[4]arene derivatives of salicylaldimines towards Zn^{2+}. Such Schiff's base conjugates have been developed owing to their good binding capacity towards metal ions by exhibiting appropriate changes in their absorption and emission properties. A series of related derivatives, namely, L_1, L_2, L_3 and L_4, have been synthesized in order to demonstrate the binding ability of the terminal $-CH_2OH$ groups in conjunction with the imine moiety towards metal ions in general and Zn^{2+} in particular. L_1, not possessing Schiff's base core, has been used as a control molecule in these studies.

In order to demonstrate the selective recognition of Zn^{2+}, a series of salicylaldimine appended triazole-linked calix[4]arene di-derivatives (namely, L_2, L_3 and L_4) have been synthesized (SI 01) by going through a number of steps[10] as shown in Scheme 1 and the binding cores of the conjugates have been marked in Figure 1. A control molecule that possesses only triazole moiety (L_1) has also been synthesized (SI 01). All the molecules were characterized by various spectral techniques such as ^1H and ^{13}C NMR, ESI MS and elemental analysis (SI 01, SI 02) and were found to be in cone conformation based on NMR spectral data. These conjugates have two different metal ion binding cores, namely, one with the preorganized Schiff base N_2O_4 and the other with the lower rim phenolic–OH plus triazole nitrogens. Thus L_2, L_3 and L_4 exhibit two binding cores, whereas L_1 exhibits only one (Fig. 1) as expected.

Recognition of metal ions, namely, Mg^{2+}, Ca^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}, by these conjugates has been studied by fluorescence and absorption spectroscopies (SI 03) besides addressing the role of the solvent. In methanol, L_4 exhibited a weak

☆ We wish to dedicate this paper to Professor C.N.R. Rao on his 75th birthday.

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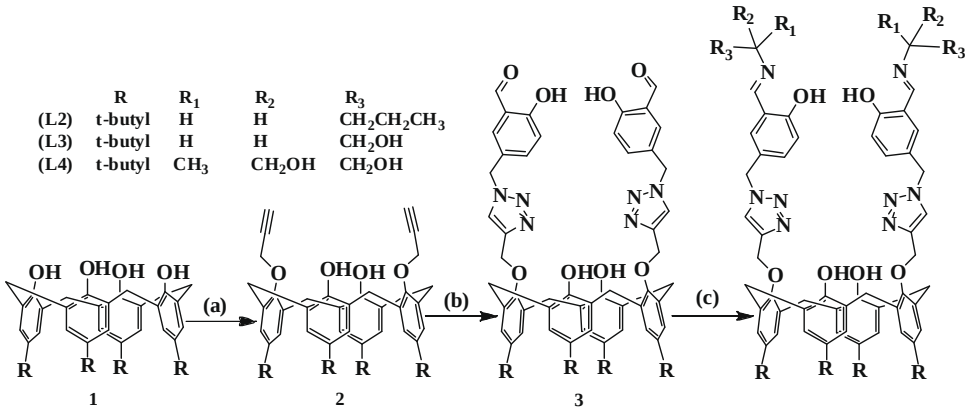

Scheme 1. Synthesis of lower rim calix[4]arene-1,3-di-derivatives through triazole link: (a) propargyl bromide, K_2CO_3, acetone, reflux; (b) 4-azidomethyl salicylaldehyde; $CuSO_4{\cdot}5H_2O$ and sodium ascorbate in dichloromethane/water (1:1), rt, 12 h; (c) appropriate amine, methanol or ethanol, rt, 4 h. R = *tert*-butyl.

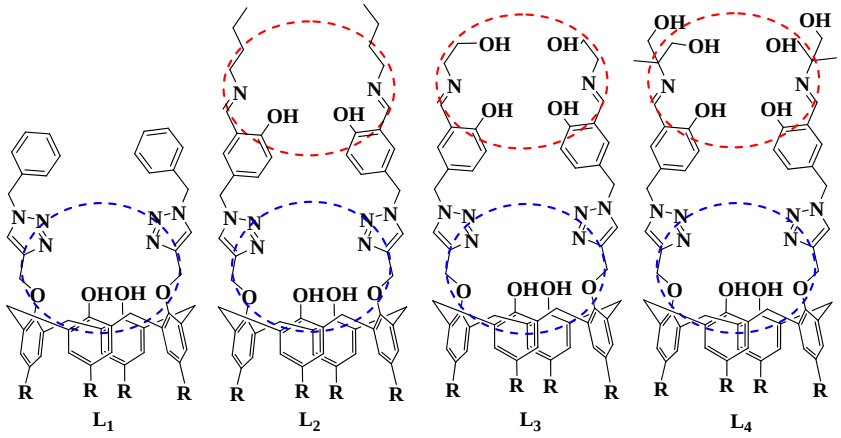

Figure 1. Schematic representation of the structures of L_1, L_2, L_3 and L_4. Binding cores are shown by encircling.

emission at ~440 nm when excited at 320 nm or at 390 nm. When L_4 is titrated with M^{2+} in CH_3OH, a progressive fluorescence enhancement was observed with Zn^{2+} and the enhancement reaches 65 ± 5-fold at saturation that occurs at ~5 equiv (Fig. 2) owing to the chelation followed by prevention of the photoelectron transfer. Zn^{2+} titrations have been repeated by exciting the solutions at 390 nm and measuring the fluorescence spectra, and found an enhancement of >50 fold (SI 04). The number of fold of fluorescence enhancement observed in the present case is much higher than that observed with a calixarene-based naphthalidene Schiff's base.[9a] Based on the fluorescence data, the association constant for L_4 with Zn^{2+} was found to be 37700 ± 500 using Benesi–Hilderand equation. The minimum concentration of Zn^{2+} that can be detected by L_4 was found to be 174 ppb in methanol (SI 05). On the other hand, L_4 exhibited almost no change or little quenching in fluorescence intensity in the presence of other metal ions (Fig. 2b). To further explore the selectivity of L_4 towards Zn^{2+} over Cd^{2+}, two types of competitive metal ion titrations were carried out in methanol solution. While in one, it is the Zn^{2+} bound L_4 that was titrated with Cd^{2+},namely, {L+10 equiv Zn^{2+}} versus Cd^{2+}, in the second case it

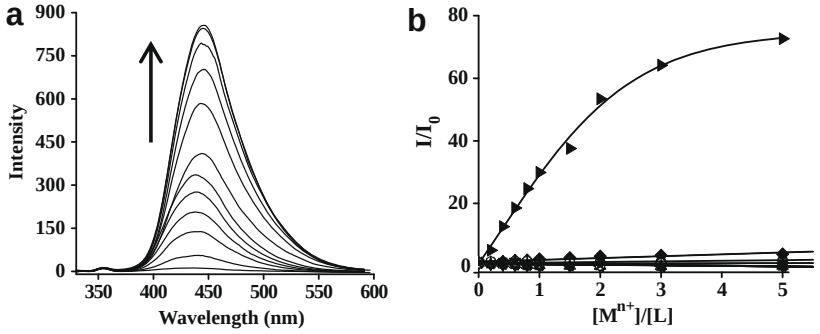

Figure 2. Fluorescence titration data for L_4 with metal ions in methanol (λ_{ex} = 320 nm) (a) spectral traces obtained during the titration of L_4 with Zn^{2+}; (b) relative fluorescence intensity ratio (I/I_0) as a function of $[M^{2+}]/[L_4]$ mole ratio for different metal ions; symbols correspond to ■ = Fe^{2+}; ▲ = Co^{2+}; ▼ = Ni^{2+}; ◄ = Cu^{2+}, ► = Zn^{2+}; ♦ = Cd^{2+}; ○ = Hg^{2+}; □ = Ca^{2+}; ● = Mg^{2+} and ★ = Pb^{2+}.

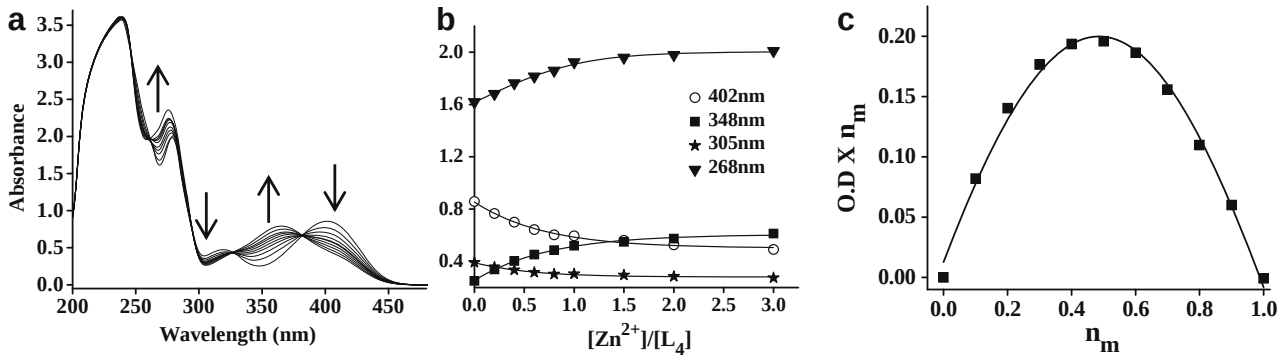

Figure 3. Absorption titration data for L_4 with Zn^{2+} in methanol: (a) spectral traces obtained during the titration; (b) absorbance versus $[Zn^{2+}]/[L_4]$; (c) Job's plot of n_m verses $A \quad n_m$ where n_m is mole fraction of the metal ion added and A is absorbance.

was the reverse type of titration, namely, {L+20 equiv Cd^{2+}} by Zn^{2+}. Based on the two titrations, it was noticed that Cd^{2+} has negligible affect on Zn^{2+} sensing by L_4 as can be seen from the fluorescence intensity ratio plots (SI 06).

Binding of Zn^{2+} with L_4 in methanol has been further shown by the changes observed in the bands, namely, 269, 305, 348 and 405 nm, in their absorption spectra (Fig. 3a and b) that arise from the imine in conjugation with the phenolic moieties. The isosbestic points observed at 261, 295, 326 and 382 nm were indicative of the transition between the unbound and Zn^{2+} complexed species. These results are clearly suggestive of the binding of Zn^{2+} at the Schiff's base core. Stoichiometry of the complex formed between L_4 and Zn^{2+} was found to be 1:1 based on Job's plot obtained using the absorption data (Fig. 3c). The 1:1 complexation has also been further confirmed by carrying out ^1H NMR titration of L_4 with Zn^{2+} which found that the intensity of the Schiff's base sal–OH and the $-CH_2OH$ protons decrease by 50% and 25%, respectively, indicating the disappearance of one proton each from sal–OH and $-CH_2OH$ moieties which in turn involve in binding to Zn^{2+}.

In order to cross check whether the Zn^{2+} is going to the triazole core or not, fluorescence studies were carried out using a control molecule, namely, L_1, which possesses only the triazole core and not the Schiff's base core (Fig. 1) and found no change in the fluorescence intensity even at high equivalents of Zn^{2+}. Even the Zn^{2+} titration of L_1, by measuring absorption spectra, exhibited no isosbestic point suggesting a non-binding nature of L_1 towards Zn^{2+}. Thus, both the fluorescence and absorption spectral studies (SI 07) clearly indicated that triazole core is not congenial for Zn^{2+} binding, at least under the present conditions. When a benzyl moiety is present on a lower rim calix[4]arene of 1,3-di-derivative similar to L_1, the derivative seems to bind to Ca^{2+} at about 10 equiv.[6b]. On the other hand, the presence of pyrene groups in place of benzyl moieties resulted in binding and recognition of Zn^{2+} and Cd^{2+} with no selectivity to either, which is attributable to the orientation of the two pyrene moieties[8c] in presence of the metal ion. Comparison of these two cases with the present case, namely, L_1, suggests that the orientation of the triazole portions is not well suited for Zn^{2+} binding. Hence, the Zn^{2+} goes to the Schiff's base binding core rather than to the triazole core.

In order to further reconfirm the binding of Zn^{2+} at the Schiff's base core, fluorescence studies were carried out with L_3 and L_2 (Fig. 1). While L_3 has one $-CH_2OH$ function, L_2 does not, but both of these contain Schiff's base core. Similar studies carried out with these molecules exhibited a fluorescence enhancement of ~25 and ~10-fold, respectively, for L_3 and L_2 when titrated with Zn^{2+} in CH_3OH (SI, 08). Comparison of the fluorescence enhancement fold observed with L_4, L_3 and L_2 towards Zn^{2+} (Fig. 4a) clearly suggested the involvement of $-CH_2OH$ in binding Zn^{2+} at the Schiff's base core. Even the absorption titration indicated changes commensurate with the number of $-CH_2OH$ groups available, wherein such changes follow an order, namely, $L_4 > L_3 > L_2$ (Figs. 3a and 4b–d). Of course, no change was observed in the absorption spectra of L_1 when titrated with Zn^{2+} (SI 07). Thus the results of both the fluorescence and absorption studies not only indicated binding zone for Zn^{2+} to be the Schiff's base core but also highlighted the role of the presence of terminal $-CH_2OH$ moiety and the support of these groups in forming a six-coordinated Zn^{2+} (as in L_4 and L_3) species in place of a four-coordinated one otherwise expected with L_2. Five- and six-coordinated Zn^{2+} species have already been shown by crystal structures of simple derivatives possessing such moieties wherein the 5th and 6th coordinations indeed are supported by the presence of $-CH_2OH$ groups.[11] Thus, L_4 is highly selective towards Zn^{2+}, the sensitivity of these molecules towards Zn^{2+} follow an order, namely, $L_4 \gg L_3 > L_2$ based on both the fluorescence and

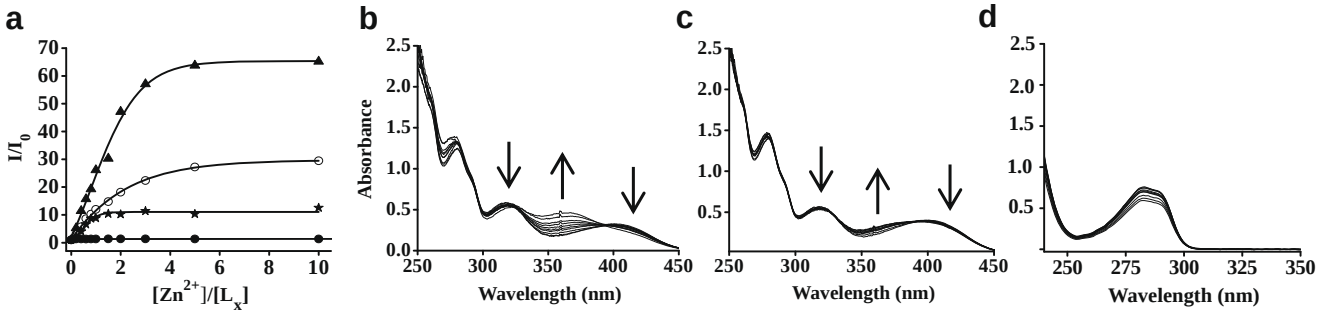

Figure 4. (a) Plot of I/I_0 as a function of $[Zn^{2+}]/[L]$ mole ratio with all four ligands L_1, L_2, L_3 and L_4 in methanol. The symbols correspond to ▲ = L_4; ○ = L_3; ★ = L_2 and ● = L_1. Absorption spectral traces during the titration with Zn^{2+}: (b) L_3; (c) L_2; (d) L_1.

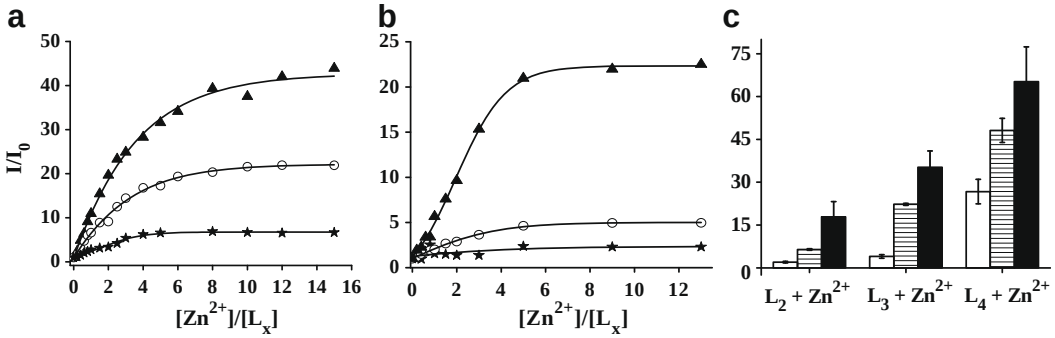

Figure 5. (a) Plot of I/I_0 versus $[Zn^{2+}]/[L_x]$ mole ratio with L_2, L_3 and L_4 in aqueous methanol. (b) Plot of I/I_0 versus $[Zn^{2+}]/[L]$ mole ratio with L_2, L_3 and L_4 in aqueous acetonitrile. The symbols carry same meaning as in Fig. 4a. (c) Histogram showing the fluorescence intensity enhancement fold in presence of Zn^{2+} in methanol (completely filled), in aqueous methanol (dashed) and in aqueous acetonitrile (unfilled). Error bars were calculated by repeating these experiments three to six times.

absorption studies. However, L_1 is not sensitive towards Zn^{2+} owing to the absence of any Schiff's base core. Even the L_2 and L_3 have also been subjected to the titration with other M^{2+} ions which was already studied with L_4 and found results similar to those observed with L_4, i.e., none other than Zn^{2+} shows any detectable fluorescence change (SI 09).

Since L_2, L_3 and L_4 have shown differential fluorescence enhancement for Zn^{2+} in methanol medium, titrations were carried out even in aqueous methanol (20:80) (SI 10) and in aqueous acetonitrile (1:1) (SI 11). Even the studies of aqueous solutions of methanol and acetonitrile resulted in a similar trend in the fluorescence enhancement for Zn^{2+} recognition, though the number of folds itself is less than that observed in methanol, owing to a higher solvation of the organic and inorganic components in water (Fig. 5). Thus, Zn^{2+} can be detected selectively among ten divalent metal ions studied even in both these aqueous solutions by L_4 with a fluorescence enhancement of about ~48-fold and ~25-fold, respectively, and with a minimum detection limit of 313 and 320 ppb, respectively, (SI 05). Hence L_4 can be a sensor for Zn^{2+}. The titration of L_4 with Zn^{2+} has been repeated at 390 nm excitation and similar results were found(SI 12). Absorption spectral changes observed in the titration of L_4, L_3 or L_2 with Zn^{2+} in aqueous methanol (SI 10) and aqueous acetonitrile (SI 11) were similar to those observed in methanol solution. In aqueous solutions, the sensitivity of these towards Zn^{2+} follows $L_4 >>> L_3 > L_2$, a trend that was also observed in methanol.

The Zn^{2+} recognition has been further supported by measuring the fluorescence life-times of the species formed by time-correlated single photon count (TCSPC) during the titration (Fig. 6). The TCSPC data obtained in case of simple receptor molecules, namely, L_2, L_3 and L_4, as well as their Zn^{2+} bound forms can be fitted to two species (τ_1 and τ_2) owing to their bi-exponential decay pattern. While the short-lived species (τ_1) of the free receptors have almost the same life-times (1.04 ns, 38% for L_2; 1.14 ns, 85% for L_3; 1.18 ns, 75% for L_4), their long lived counterparts (τ_2) exhibit increasing life times on going from L_2 (4.10 ns, 62%) to L_3 (4.32 ns, 15%) to L_4 (5.50 ns, 25%) indicating the involvement of the added –CH_2OH group(s) in the latter two cases. When Zn^{2+} is added to L_2, τ_1 increases by a factor of two (2.14 ns, 30%), whereas τ_2 (4.26 ns, 70%) does not change owing to the absence of any –CH_2OH moiety in L_2. However, when –CH_2OH groups are present, as in L_3 and L_4 (Fig. 1), the τ_2 exhibit substantial increase (6.57 ns, 47% in case of L_3; 7.17 ns, 60% in case of L_4) though the changes observed in the τ_1 were similar to those observed for L_2 (namely, 2.51 ns, 53% in case of L_3; 2.48 ns, 40% in case of L_4). Thus the fluorescence life time measurements of these receptors and their Zn^{2+} bound species have clearly shown the involvement of –CH_2OH moieties in the ion recognition.

Among the moieties present in the molecules reported in this Letter, it has been found that the triazole core is not effective for binding to metal ions, whereas the Schiff's base core exhibits high binding affinity towards the metal ions in general and Zn^{2+} in particular by exhibiting a large fluorescence enhancement. The sensitivity towards fluorescence response as well as selectivity of these molecules towards Zn^{2+} has been further augmented by the presence of the terminal –CH_2OH groups in a positive manner as supported by steady state as well as life-time fluorescence studies in addition to the absorption and ^1H NMR data. The number of folds of fluorescence enhancement was found to be dependent on the Zn^{2+} solvation ability of the medium. Maximum sensitivity and selectivity were observed with L_4. The sensitivity of L_4 towards Zn^{2+} has always been higher in methanol than in aqueous methanol followed by aqueous acetonitrile. Preferential binding of Zn^{2+} to these molecules, namely, $L_4 >>> L_3 > L_2$, has been clearly demon-

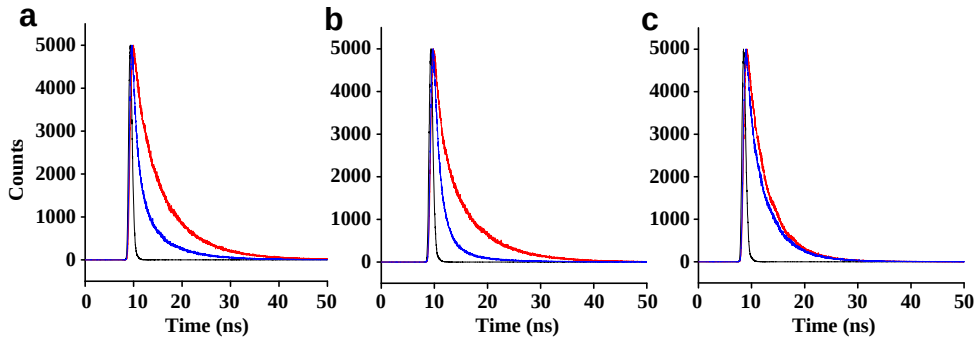

Figure 6. Fluorescence decay plots as a function of time using different molecules: (a) L_4; (b) L_3 and (c) L_2. In each plot: prompt (black); molecule (blue); molecule+Zn^{2+} (red).

strated. The ~48 and ~25-fold fluorescence enhancement observed for L_4 upon Zn^{2+} binding in aqueous solutions of methanol and acetonitrile, respectively, is considerably high and are indicative of the utility of L_4 for Zn^{2+} recognition even under the conditions of aqueous solutions. This is further augmented by the fact that the excitation and emission studies were both in the visible region. Therefore, L_4 is selective towards Zn^{2+} in organic as well as in aqueous organic solutions.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.126.

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