

Photophysical studies of 7-hydroxy-4-methyl-8-(4'-methylpiperazin-1'-yl) methylcoumarin: A new fluorescent chemosensor for zinc and nickel ions in water

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Abstract

The title compound, a new coumarin based fluorophore having a piperazine moiety as the photoinduced electron transfer (PET) switch was prepared and its photophysical properties studied in various solvents and under different pH. Solvatochromic shift in the fluorescence spectrum revealed an increase in the dipole moment in the lowest excited singlet state compared to that in the ground state. The compound also showed an interesting intramolecular photoinduced proton transfer phenomenon in the excited state under neutral pH. It was effectively utilized as a new Chelation-enhanced fluorescence (CHEF) based chemosensor for zinc and nickel ions in water.

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1. Introduction

The development of fluorescent chemosensors for the sensing of metal ions is an important goal in chemistry and biology [1–6]. Such chemosensors should have high sensitivity and selectivity, and ideally should be able to operate in aqueous medium. Chelation-enhanced fluorescence (CHEF) is an attractive design principle for developing new fluorescent chemosensors. These chemosensors are made up of a signaling part, usually a strong fluorophore and a recognition part, usually a metal-coordinating Lewis basic site, such as amines, in close proximity. In the absence of metal ions, the fluorescence intensity of the fluorophore is greatly reduced due to photoinduced electron transfer (PET) from the donor amines to the fluorophore (“turn-off state”). In the presence of metal ions that can bind to the amine centres via chelation, the oxidation potentials of the amines are raised. This, in turn,

inhibits the PET process leading to a large enhancement in the fluorescence intensity of the fluorophore (“turn-on state”).

Coumarins are a group of strongly fluorescent dyes whose photophysical properties have widely been studied [7]. However, they are sparsely used as the signaling part in CHEF based metal chemosensors. Only recently, a few 4-aminomethylcoumarins have been developed as fluorescent chemosensors for zinc ions [8]. 7-Hydroxy-4-methylcoumarin (HMC, **1**) is a readily available, strongly fluorescent laser dye, whose ground state and excited state photophysical properties have been the subject of many studies [9–16]. We reasoned that the Mannich bases of **1**, i.e. its 8-aminomethyl derivatives, by virtue of (a) their bidentate (N, O) nature that can potentially bind to various metals and (b) the presence of the 8-aminomethyl substituent, which as a strong electron donor, can operate as a PET “on-off” switch, would constitute novel CHEF based fluorescence chemosensors. We were especially interested in developing efficient chemosensors for zinc ions that can operate in aqueous medium. Many hydrolytic enzymes contain zinc at their active sites and utilize the zinc-bound water or hydroxide as the nucleophile [17]. Moreover, metabolic

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disorders of zinc has now been closely associated with a number of neurological diseases, such as Alzheimer's disease, Parkinson's disease, epilepsy and hypoxia-ischemia. [18]. Hence, much current attention has been focused on developing new chemosensors for detecting free zinc ions in biological systems [19]. In this paper, we describe the synthesis and photophysical properties of 7-hydroxy-4-methyl-8-[(4'-methylpiperazin-1-yl)methyl]coumarin, **2**, and its use as a novel fluorescent chemosensor for zinc and nickel ions in aqueous medium.

2. Experimental

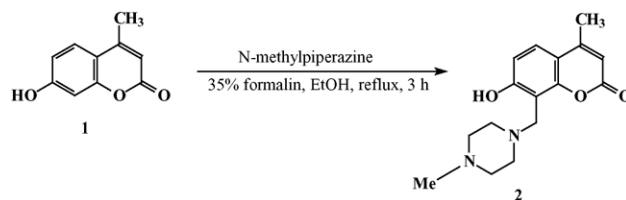
IR spectra were taken on a Perkin-Elmer 297 spectrometer as KBr pellets. NMR spectra were recorded on a Bruker Avance 300 instrument. The absorption and steady state fluorescence measurements were recorded on a Shimadzu MPS 2000 spectrophotometer and a Spex Fluorolog-2 spectrofluorimeter, respectively. The optical density of the solution for fluorescence measurement was less than 0.15 at the excitation wavelength. The fluorescence quantum yields were determined with respect to quinine sulphate in 0.1N H₂SO₄ solution ($\phi = 0.54$) [20]. The pHs of the solutions was measured on a Systronics μ pH System 361. The solvents used were of UV spectroscopic grade (Spectrochem India). Triply distilled water was used wherever required.

2.1. 7-Hydroxy-4-methyl-8-(4'-methylpiperazin-1'-yl)methylcoumarin, **2**

To a solution of 7-hydroxy-4-methylcoumarin **1** (0.40 g, 2.27 mmol) and *N*-methylpiperazine (0.25 g, 2.50 mmol) in EtOH (5 cm³) was added 35% formalin (0.21 g, 2.50 mmol) and the solution heated under reflux for 3 h. It was then cooled in ice and the precipitate formed was filtered and washed with cold ethanol to give **2** (0.57 g, 88%); mp 128–130 °C (from EtOH); (Anal. Calcd. for C₁₆H₂₀N₂O₃: C, 66.64; H, 6.99; N, 9.71. Found: C, 66.29; H, 6.76; N, 9.82); IR (KBr) 3500 (br), 3070, 2950, 2810, 1720, 1600, 1575, 1375, 1305 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 2.32 (3 H, s), 2.38 (3 H, s), 2.36–2.98 (8 H, br m), 4.07 (2 H, s), 6.07 (1 H, s), 6.76 (1 H, d, *J* 8.4), 7.41 (1 H, d, *J* 8.4), 8.09 (1 H, br s); ¹³C NMR (75 MHz, CDCl₃) 18.7, 45.7, 52.4, 53.7, 54.6, 107.4, 110.5, 112.2, 113.3, 124.6, 152.4, 153.3, 161.2, 162.3.

3. Results and discussion

The choice of a piperazine group in **2** as the recognition site stems from its strongly electron donating character and its ability to bind several metal ions including zinc [21]. However, despite these advantages, CHEF based chemosensors having a piperazine ring as their recognition site are few and far between [22]. Mannich reaction of 7-hydroxy-4-methylcoumarin (HMC, **1**) with aqueous formaldehyde and



Scheme 1.

N-methylpiperazine in refluxing ethanol gave **2** as a pale yellow solid in 88% yield (Scheme 1).

The photophysical properties of HMC (**1**) have been widely studied and shown to be both solvent and pH dependent [9–16]. The excited state properties of **1** are somewhat complex, especially in protic solvents, due to photoinduced proton transfer from the phenolic OH group giving rise to different emitting forms: neutral (N), cation (C) anion (A) and tautomer (T). The relative proportions of these emitting forms depend on the solvent polarity, protic character of the solvent and the pH of the medium. These complications that arise due to the polar excited state of HMC and its tendency to undergo facile photoinduced proton transfer from the phenolic OH group are the main deterrents towards its use in fluorescent chemosensors. Since the signaling part of **2** is essentially a HMC unit, given the above complications in the excited state photophysics of HMC, we decided to first investigate the absorption and emission behavior of **2** in some detail before embarking on its metal ion sensing ability. Since we intended to use **2** as a chemosensor for zinc in aqueous media and given that the fluorescent properties of HMC are solvent and pH dependent, especially in protic media, it was necessary to first establish the appropriate pH conditions under which **2** would best function as a CHEF based sensor. The absorption spectra of **2** in different solvents are shown in Fig. 1 and the data collected in Table 1.

In non-aqueous solvents (heptane, dioxan, dichloromethane and acetonitrile), **2** showed an absorption maximum at 320 nm irrespective of the solvent polarity. The high

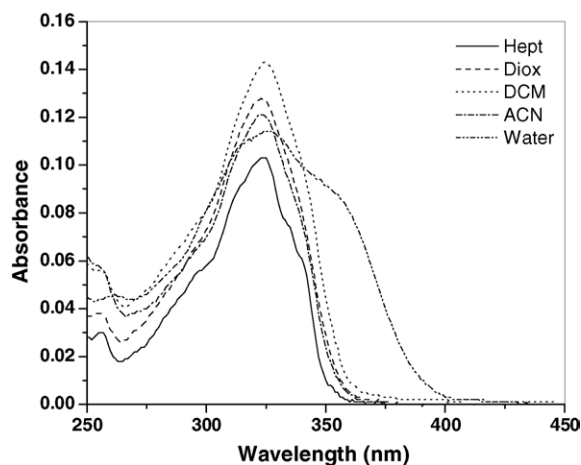


Fig. 1. Absorption spectra of **2** in different solvents.

Table 1
Photophysical properties of **2** in different solvents

Solvent	$E_T(30)$ (kcal M ⁻¹)	ϵ (cm ⁻¹ M ⁻¹)	$\lambda_{\text{max(abs)}}$ (nm)	$\lambda_{\text{max(emiss)}}$ (nm)	Quantum yield (ϕ)
Heptane	31.1	9915	322	414	0.02
Dioxan	36.0	10216	320	422	0.56
CH ₂ Cl ₂	40.7	11237	320	424	0.71
CH ₃ CN	45.6	10216	318	440	0.68
Pr ⁱ OH	48.4	12019	320	440	0.59
EtOH	51.9	10637	320	440	0.59
MeOH	55.4	11418	320	440	0.56
Water	63.1	–	320, 360	440	0.50

molar absorption co-efficient ($\epsilon > 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) indicated that the absorption band is due to π – π^* transitions in all the solvents studied. However, when measured in water, an additional shoulder appeared at 360 nm. All these features are quite similar to those observed for the parent dye HMC (**1**) [10] and led us to assign the 320 nm band to the neutral form (N) of **2** and the shoulder at 360 nm, to its anionic form (A). The emission spectra of **2** (λ_{exc} 320 nm) were recorded in various aprotic and protic solvents (Table 1). In aprotic solvents, the emission maximum underwent a gradual red shift from 420 to 440 nm on increasing the solvent polarity (heptane \rightarrow dioxan \rightarrow dichloromethane \rightarrow acetonitrile).

Plots of Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) and the energy corresponding to the fluorescence maximum (E_f) as a function of solvent polarity parameter $E_T(30)$ reflects linear relationships between Stokes' shift as well as fluorescence energy against $E_T(30)$ of the solvent [23,24]. The good correlation of Stokes shift and fluorescence energy with $E_T(30)$ is indicative of the fact that the dielectric solute–solvent interaction is responsible for the observed solvatochromic shift for the present molecule [24]. The solvatochromic shift of the spectral position allowed us to determine the excited state dipole moment of **2**, relative to its ground state value. The difference in the dipole moment of the excited state and ground state ($\Delta\mu$) was calculated by plotting the Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) of the fluorescence maximum against the E_T^N values of the different polar aprotic solvents (Fig. 2). The $\Delta\mu$ was then determined

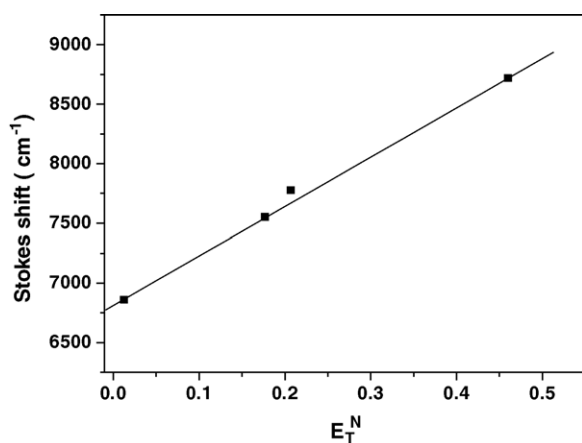
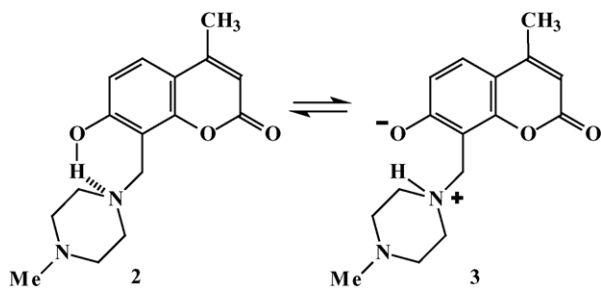


Fig. 2. Plot of the Stokes shift of **2** in pure solvents against E_T^N

from the slope of the above plot and Onsager's radius (' a ') for **2**, taking the literature values of $\Delta\mu$ and ' a ' for some reference dyes as described by Ravi et al. [25,26]. The excited state dipole moment was estimated to be 9.37 D, compared to the ground state dipole moment of 3.82 D (corresponding to the optimized geometry of **2** through AM1 calculation). The large dipole moment value of **2** in the excited state indicated a more polar nature of the excited state than the ground state and aptly explained the solvatochromic shift observed in its emission spectra.

In all the protic solvents examined (PrⁱOH, EtOH, MeOH and water), the emission band was found at 440 nm, virtually unchanged by the solvent polarity. Interestingly, addition of as low as 0.5% water to dioxan led to a shift of the emission maximum from 422 (in pure dioxan) to 440 nm. Since the $E_T(30)$ value of 0.5% water in dioxan is less than that of CH₃CN, the red shift observed in the emission maximum of **2** in different solvents cannot be attributed to an increase in solvent polarity alone. It appears that protic factor also contributes substantially to the observed red shift. The most unexpected excited state feature that we encountered for **2** was the position of its emission band (λ_{max} 420–440 nm) which was much red shifted in all the solvents studied. Since all excitations were made at 320 nm, i.e. at the N form of **2** and because **1** and **2** have similar absorption maxima for their N forms, it was expected that the emission band of **2** would be close to the neutral emission band of **1**, i.e. \sim 370 nm. However, the emission λ_{max} of **2** at 420–440 nm actually matched with the anionic emission band of **1** (\sim 450 nm) suggesting that emission in **2** was taking place from the anionic state (A*). Since in case of **1** there was no possibility of formation of zwitterionic state so only anionic state was considered. On the other hand, in case of **2** the possibility of the formation of the latter one is very much reasonable. This was utterly surprising, since all the above spectral measurements with **2** were carried out under neutral pH conditions. Since the excitation spectra of **2** were similar to its neutral absorption spectra in all the solvents, showing that the ground state is indeed the N form, emission from the anionic form or zwitterionic form in **2** could only be explained by a transition from the N* to the A* or Z* form in the excited state. We believe that the N* state of **2** undergoes a facile, geometry assisted intramolecular proton transfer from its phenolic group to the N-1' nitrogen of the piperazine ring leading to the internal ion-pair **3** (Scheme 2). Emission then takes place from this ion-pair, i.e. the zwitterionic form of the coumarin fluorophore **2**.

In order to determine the feasibility of such photoinduced proton transfer, the ground state and the excited state acidity constants of **2** were calculated, the former by Weller's titrimetric method in which the absorbance intensities of the neutral and the anionic species were plotted against the solution pH (Fig. 3) [27–29] and the latter, using the Förster–Weller equation as given below (Eq. (1)) [30]. Using these methods, the ground state pK_a and the excited state pK_a^* of **2** were determined to be 9.75 and 4.40, respectively. The corresponding

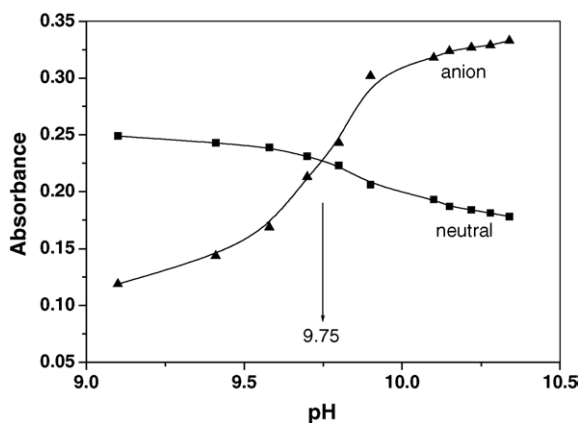
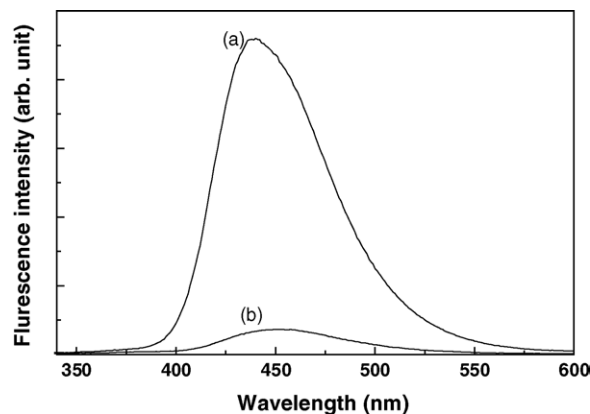


Scheme 2.

values for HMC (**1**) are reported to be 7.75 (pK_a) and 0.74 (pK_a^*) [16].

$$pK_a^* = \frac{pK_a + 0.625}{T} (\bar{\nu}_{\text{neu}} - \bar{\nu}_{\text{anion}}) \quad (1)$$

It thus became evident that the acidity of the phenolic OH group in **2** is greatly increased in the excited state (pK_a^* 4.4) thus facilitating a photoinduced proton transfer to produce the zwitterion **3** in the excited state, even in aprotic solvents. A favourable molecular geometry (the presence of intramolecular H-bonding between the phenolic OH and the N-1' of piperazine ring in **2** was evident from its ^1H NMR spectrum which showed broadening of peaks for the benzylic methylene protons due to restricted rotation caused by the intramolecular H-bonding) also helps in this intramolecular proton transfer in the excited state (cf. Scheme 2). The relatively high pK_a value of **2** (9.75) also explains the appearance of the shoulder at 360 nm due to the anionic form (A) in its absorption spectrum in water (cf. Fig. 1), presumably due to the presence of the zwitterionic form **3** in water (cf. Scheme 2). Further support for photoinduced proton transfer in **2** was derived from the literature. For example, Weller has shown that ion-pair formation between 2-naphthol and triethylamine is more favoured in the excited state than in the ground state leading to emission from the A^* state of 2-naphthol, even in a non-polar solvent such as methylcyclohexane [31]. More pertinent to the present study is the

Fig. 3. Plot of absorbance of neutral and anionic forms of **2** vs. pH.Fig. 4. Fluorescence spectra of **2** in water at pH (a) 7.0 and (b) 10.96.

report by Moriya who has shown that emission from the parent coumarin **1** in non-polar solvents, such as benzene or dioxan, in the presence of triethylamine occurs from the A^* state due to a strong intermolecular ion-pair formation in the excited state [11]. The A^* state of **1** was also shown to be the most stable among all the photoexcited states [10], a feature which should be equally valid for **2**.

In search of the “turn-off state” for the sensor purpose, the emission behavior of **2** in water was examined under different pH conditions. Since proton transfer from the phenolic OH group in **2** in the ground state was evident in its absorption spectrum and that a photoinduced proton transfer occurred in the excited state under a neutral pH, no dramatic change was expected in its emission behavior under acidic conditions. However, under alkaline conditions, increasing the alkali concentration led to a gradual decrease in the fluorescence intensity of **2** reaching a minimum (12 times reduction) at pH 10.96 (Fig. 4). A red shift of its emission λ_{max} from 440 to 453 nm was also observed. In comparison, the fluorescence intensity of **1** decreased by only 2.5 fold at pH 10.96. The large decrease in fluorescence intensity of **2** in an alkaline pH must be due to PET quenching of the fluorophore by the piperazine ring nitrogens (“turn-off” state). In a strongly alkaline medium, zwitterions such as **3** cannot exist so that the piperazine ring nitrogens could freely participate in the PET quenching of the coumarin fluorescence. This experiment also enabled us to identify the conditions (“turn-off state”) under which the metal sensing ability of **2** could be probed.

Addition of $\text{Zn}(\text{ClO}_4)_2$ to an aqueous solution of **2** at pH 10.96 led to a gradual increase in the fluorescence intensity reaching a maximum of 10-fold increase ($\phi = 0.41$) (Fig. 5). This large increase in intensity can be attributed to the inhibition of the PET quenching of the coumarin fluorophore caused by complexation of the zinc(II) ions to the piperazine ring nitrogens. The fluorescence increase in **2** was instantaneous upon addition of the zinc ions suggesting a fast binding kinetics. Several CHEF based Zn-chemosensors, especially those having the polyaza macrocycles as the “recognition

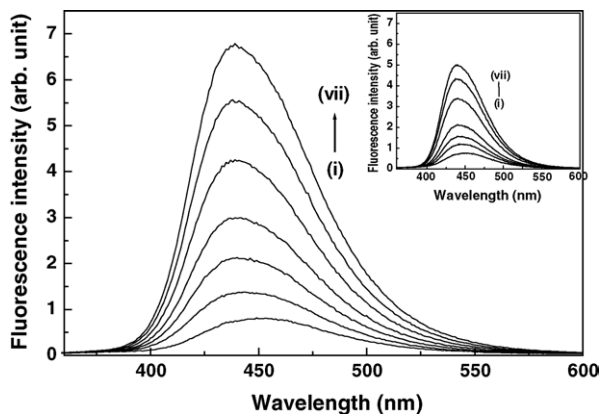


Fig. 5. Emission spectra of **2** (5×10^{-6} M) vs. Zn(II) ion. Curves (i) \rightarrow (vii) correspond to 0.0, 40, 46, 48, 50, 52 and 55 mM Zn(II) ion, respectively. [Inset: emission spectra of **2** vs. Ni(II) ion. Curves (i) \rightarrow (vii) correspond to 0.0, 55, 65, 71, 81, 88 and 94 mM Ni(II) ion, respectively.] $\lambda_{\text{exc}} = 320$ nm for both cases.

part”, reportedly show strong binding to the metal but suffer from slow binding kinetics ($\leq 50\%$ binding per hour) [8]. The sensor **2** is certainly superior in this respect. The 10-fold increase in intensity observed for **2** is comparable to the enhancements reported for other Zn-selective CHEF based chemosensors [19].

On the other hand, the absorption maximum of **2** at pH 10.96 underwent a blue shift upon addition of zinc ions (Fig. 6). Although an apparent isosbestic point was observed (at ~ 350 nm) at lower concentration range, it was destroyed at higher concentrations. This rules out a 1:1 stoichiometry between the Zn(II):**2** complex [32]. It is already known from the literature that because the coordination of the metal ions by a monodentate or a bidentate ligand is a stepwise process with complexes of different stoichiometries expected to be present in the solution, the isosbestic point is lost over a large concentration range of the metal ions [33]. Furthermore, since the fluorophore concentration used in the measurements

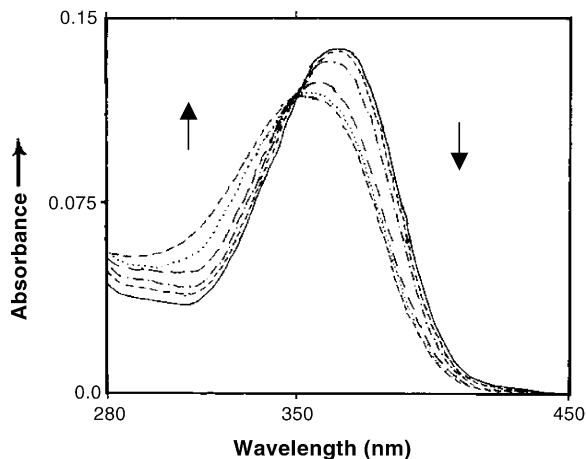


Fig. 6. Absorption spectra of **2** as a function of Zn(II) ion concentration.

is rather low compared to the concentration of the metal ions used for observation of effective fluorescence enhancement it is not always possible to determine the association constants spectrophotometrically under the present experimental conditions.

The molar absorption coefficient for the Zn(II):**2** complex at the excitation wavelength ($\lambda_{\text{exc}} 320$ nm) was found to be $1.5 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$. Such a large ϵ value at the excitation wavelength coupled with a large quantum yield of emission promised a high brightness for the sensor.

In a separate experiment, the sensor **2** was used for the detection of nickel ions. Addition of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ to a solution of **2** at pH 10.96 led to 7-fold increase in fluorescence intensity (inset Fig. 5). Thus, **2** can be qualitatively used as a chemosensor for both zinc and nickel ions. Notably, addition of $\text{Zn}(\text{ClO}_4)_2$ to an aqueous solution of the parent coumarin **1** at pH 10.96 did not lead to any significant change in the fluorescence intensity, attesting the importance of the piperazine ring as the “recognition part” in the chemosensor **2**. We believe that the piperazine ring in **2** performs a dual role: it acts as a ligand for Zn (in combination with the phenolic oxygen) and as a PET switch. To see the effect of interfering ions, a similar experiment was performed with Ca ion. No enhancement in the fluorescence was noticed reflecting that the interfering ions do not assist in prohibiting the PET process.

It is worth determining the binding constant between the fluorophore and the metal ions for an understanding of the relativistic interaction effect with different metals (like Zn and Ni). All our attempts to determine the same following Benesi–Hildebrand plot and Scatchard plot, unfortunately, did not show linearity, reflecting that there is no definite stoichiometry between the fluorophore and the metal ions. Thus, the above discussion reveals that using both absorption and fluorescence techniques it was not possible to determine the binding constants of the fluorophore with the metal ions. Consequently, a quantitative comparison between the effectively of the fluorescence enhancement by Zn and Ni ions could not be possible.

Although the majority of the literature represents the metal ion fluorescence enhancement in the neutral media [33,34 and the references therein] the present study is a report of the similar effect in alkaline medium. Reports of this sort are very limited in the literature [8].

In conclusion, a coumarin based fluorophore **2** having a piperazine moiety as the PET switch was prepared and its photophysical properties studied in various solvents and under different pH. The excited state dipole moment, in relation to that in the ground state, was determined from the solvatochromic shift in the fluorescence spectra in solvents of different polarity. The fluorophore showed an interesting photoinduced proton transfer phenomenon in the excited state under neutral pH leading to emission from its zwitterionic form. It was effectively utilized as a new sensitive CHEF based chemosensor for zinc and nickel ions in alkaline aqueous environment.

Acknowledgement

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