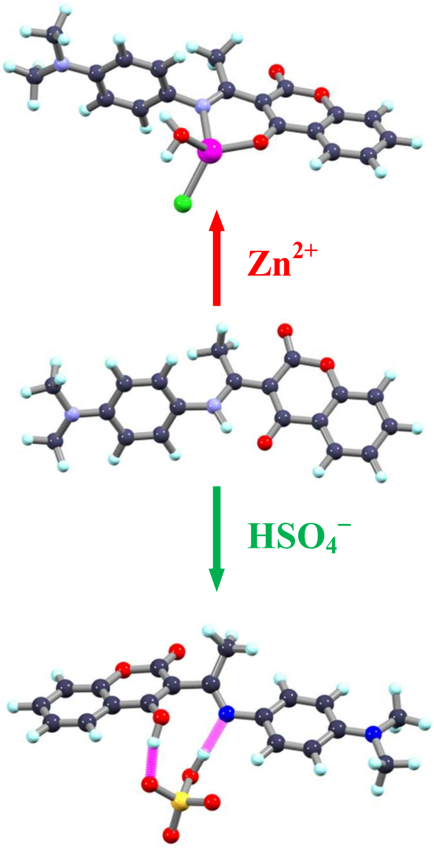
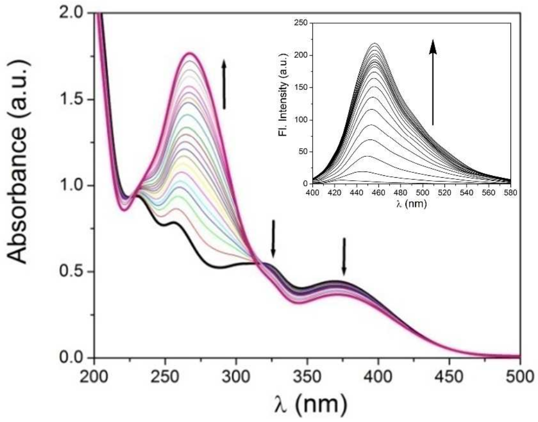
RSC Advances

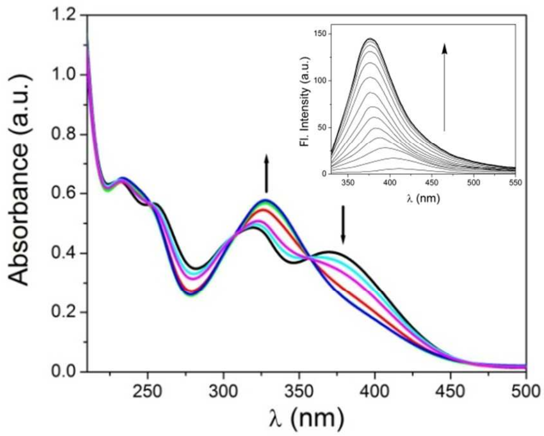
ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Abstract: A highly sensitive and selective coumarin based fluorescence ‘turn-on’ chemosensor (HL) for the efficient detection of Zn^{2+} and HSO_4^- over other ions has been developed. The emission intensity of chemosensor (HL) enhanced by 27 fold in presence of Zn^{2+} and the maxima has been red shifted by 35 nm. Upon gradual addition of HSO_4^- to the receptor solution, emission intensity increases by 17 fold and the emission maxima shows a blue shift of 46 nm. Theoretical study interprets the electronic structure and sensing property of the developed HL.







Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Coumarin based dual switching fluorescent ‘turn-on’ chemosensor for selective detection of Zn^{2+} and HSO_4^-: An experimental and theoretical study

Deblina Sarkar, Ajoy Kumar Pramanik and Tapan Kumar Mondal[*]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Abstract: A highly sensitive and selective coumarin based fluorescence ‘turn-on’ chemosensor (HL) for the efficient detection of Zn^{2+} and HSO_4^- over other ions has been developed. Theoretical study interprets the electronic structure and sensing property of the developed HL.

Introduction

Development of artificial optical chemosensor for recognizing biologically and environmentally important analytes has become an active field of research[1] with outstanding potential application in the field of analytical chemistry,[2] clinical biology including environmental studies.[3] These molecules with photoinduced switching property have great deal of application in the field of molecular electronics and sensor device application.[4] However most of the reported chemosensors are effective only in selective recognition of a particular analyte.[5] Thus development of multifunctional chemosensors for the detection of more than one analyte still remains a challenging field of research.[6]

Zinc is the second most abundant and essential element in human body with active participation in various biologically essential processes like oxygen transport,[7] gene expression,[8] energy generation[9] and cellular metabolism.[10] But unregulated level of Zn^{2+} in human body may lead to several life threatening diseases such as β-thalassemia, Friedreich’s ataxia, and several neurodegenerative diseases including Alzheimer’s disease, Parkinson’s disease and epilepsy.[11] Again Zn^{2+} is also a harmful pollutant for our environment.[12] Thus it is highly important to develop artificial chemosensors for the efficient detection of Zn^{2+} both ‘in vivo’ as well as ‘in vitro’ cases. Due to this immense demand in the field of development of artificial chemosensors for Zn^{2+}, several sensing devices comprising of Schiff base skeleton, polythiacrown ethers, have been developed in the recent few years.[13] However most of the artificial fluorescent probes used for detection of Zn^{2+} suffer the problem of insufficient selectivity due to special interference from Cd^{2+}.[14] FluoZin-3, a commonly used Zn^{2+} sensor suffers the problem of interference from Ca^{2+} at higher concentratiom.[15]

Recognition and sensing of HSO_4^- is specially an active field of research as this anion can be found in agricultural fertilizers and industrial raw materials which can affect the environment adversely.[16] HSO_4^- dissociates at higher pH producing sulphate ion which causes skin problems, irritation to eyes and also creates respiratory problems. HSO_4^- ion can also be used for preventing environmental damage caused due to radioactive waste.[17] HSO_4^- also plays an important role in biological systems[18] but till date only a few chemosensors for the detection of this anion have been reported so far.[19]

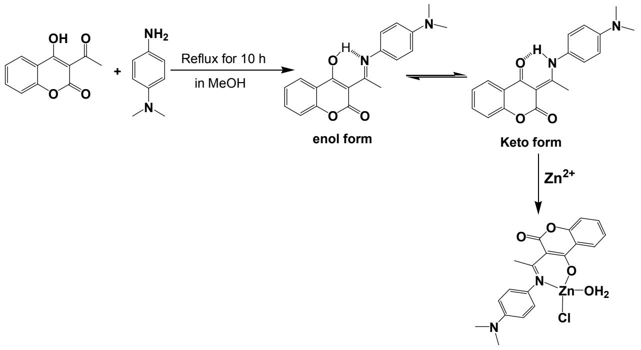
Thus herein we report a coumarin based chemosensor showing dual switching ‘turn-on’ property for both Zn^{2+} and HSO_4^- . Coumarin framework has been used as the basic fluorophore due to its various interesting photophysical properties such as Strokes shift and visible excitation and emission wavelengths.[20] Moreover coumarin moiety has high importance as fluorescent dyes.[21] Gradual addition of Zn^{2+} to HL in CH_3CN / H_2O, 1:1, v/v (at 25°C) shows an excellent fluorescence emission intensity enhancement of 27 fold. Whereas in presence of HSO_4^-, HL shows an emission intensity increase of 17 fold. The synthesized chemosensor HL is highly selective towards Zn^{2+}

even in presence of other metal ions and is also highly selective for HSO_4^- over other anions. Moreover the receptor HL can also act as a water soluble fluorescent sensor for HSO_4^-. Only a few water soluble chemosensors have been reported so far for HSO_4^-.[22]

Results and discussion

Synthesis and spectral characterization

Synthetic route towards receptor HL involves a very facile and economically cheap route involving the Schiff base condensation of 3-Acetyl-4-hydroxycoumarin and N,N′-Dimethyl-p-phenylenediamine in 1:1 molar ratio in methanolic medium under reflux condition. Excellent yield of 77% has been obtained (Scheme 1). The receptor HL has been characterized by elemental and mass spectral analysis along with several other spectroscopic techniques (IR, UV–Vis, NMR etc.).



Scheme 1. Synthesis of chemosensor HL and its Zn^{2+} complex

In the IR spectrum, the lactone C=O stretching frequency appears at 1709 cm^{-1} and the keto C=O appears at 1616 cm^{-1} and C=C appears at 1568 cm^{-1}. In ^1H NMR spectrum of the sensor HL in $CDCl_3$, hydrogen bonded NH proton appears at δ 15.58[23] which disappears in the HL-Zn^{2+} complex due to coordination of HL to the metal in the enol form. The aromatic protons in HL appear as expected in the region δ 8.08-6.73. The $-COCH_3$ protons appear at δ 2.68 as singlet (Fig. S1) and the $-NCH_3$ appear at δ 3.01 as singlet as expected. In the HL-Zn^{2+} complex all aromatic protons appear at a bit downfield position compared to that of HL, which can be clearly explained due to the coordination of Zn^{2+} with HL. ^{13}C NMR spectrum of HL shows a peak at δ 181.5 corresponding to the keto C=O carbon while at δ 175.6 the peak corresponds to the C-N carbon, and at δ 162.6 corresponds to lactone carbon in the coumarin ring. The $-NCH_3$ carbon appears at δ 40.4 while the acetyl carbon appears at δ 20.8 (Fig S2). Mass spectra show m/z peak corresponding to $[M+H]^+$ at 323.2 for HL (Fig. S3) and at 461.2 corresponding to $[M+Na]^+$ for the HL-Zn^{2+} complex (Fig. S4) thus supporting 1:1 complex formation.

Cation sensing studies of HL

UV-Vis study

Receptor HL (10 μM) shows absorbance bands at 230 nm, 256 nm, 321 nm and 369 nm in 1:1, v/v $CH_3CN:H_2O$ using HEPES buffered solution at pH=7.2. Upon gradual addition of $ZnCl_2$ (100 μM) solution the band at 256 nm shifts and a new strong absorption band appears at 267 nm. The absorption band at 321 nm and 369 nm gradually decreases on addition of Zn^{2+} and a distinct isosbestic point appears at 314 nm. This red shift and gradual decrease in absorption intensity is due to the coordination of HL to Zn^{2+} (Fig. 1). UV-Vis spectrum of HL is also studied in presence of other metal ions i,e, Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Hg^{2+} but there is hardly any change in the spectral pattern (Fig. S5).

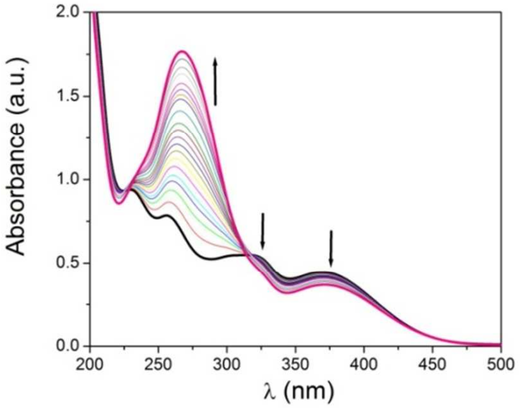


Fig. 1. Changes in UV-Vis spectrum of HL (10 μM) upon gradual addition of Zn^{2+} (100 μM) in 1:1, v/v $CH_3CN:H_2O$ using HEPES buffered solution at pH=7.2

Fluorescence study

In the absence of metal ions the emission spectrum of the synthesized chemosensor HL shows a very weak emission band with maxima (F_0) at 422 nm ($\lambda_{excitation}$, 370 nm). The fluorescence quantum yield (ϕ = 0.006) is very poor. Gradual addition of Zn^{2+} to the above solution shows an excellent fluorescence enhancement by 27 fold (ϕ = 0.128) and the maxima has been red shifted by 35 nm due to coordination of Zn^{2+} with HL (Fig. 2). The life time decays of HL and HL-Zn^{2+} complex fit well with bi-exponential decay profile with life time 0.69 and 2.03 ns respectively (Fig. S6). This fluorescence enhancement reflects a strong selective OFF-ON fluorescent signalling property of HL for Zn^{2+}.

Jobs plot of emission intensity shows a maxima in the plot corresponds to ~0.5 mole fraction indicating 1:1 complex formation of HL with Zn^{2+} (Fig. S7). From emission spectral change, limit of detection of the chemosensor for Zn^{2+} is determined using the equation LOD= K × SD/S where SD is the standard deviation of the blank solution and S in the slope of the calibration curve (Fig. S8). The limit of detection for Zn^{2+} is found to be 6.541×10^{-5} M from fluorescent spectral titration. This result clearly demonstrates that the chemosensor is highly efficient in sensing Zn^{2+} even in very minute level. From fluorescent spectral titration the association constant of HL with Zn^{2+} is found to be 4.8×10^{5} and stoichiometry of the reaction n = 1.113 indicating 1:1 complex formation (Fig. S9).

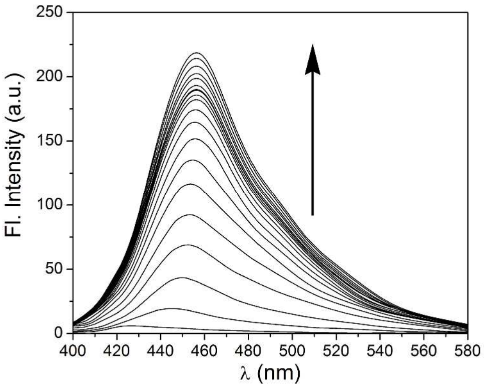


Fig. 2. Changes in emission spectrum of HL (10 μM) upon gradual addition of Zn^{2+} (100 μM) ($\lambda_{excittion}$ = 370 nm) in 1:1, v/v CH_3CN:H_2O using HEPES buffered solution at pH=7.2

Fluorescence emission intensity of HL (10 μM) is studied in presence of other metals i,e, Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Hg^{2+} (100 μM) in CH_3CN : H_2O (1:1, v/v, pH=7.2) but there is hardly any increase in emission intensity of HL (Fig. 3). Then to these solutions Zn^{2+} is added which then shows an instant fluorescent enhancement (Fig. S10). Thus the synthesized receptor HL is highly efficient in detection of Zn^{2+} in presence of other metals and thus it can detect Zn^{2+} in biological or environmental samples where other metals usually co-exist with Zn^{2+}.

Anion sensing study

UV-Vis study

Upon gradual addition of HSO_4^- (100 μM) to HL (10 μM) in 50% aqueous acetonitrile medium, that absorption band at 321 nm shows a gradual red shift and a new band appears at 330 nm, while the band at 369 nm is gradually vanished resulting in two distinct isosbestic points at 307 nm and 357 nm. Thus a distinct change in absorption pattern is observed due to complexation of HL with HSO_4^- (Fig. 4). The UV-Vis of HL (10 μM) is studied in presence of other anions i,e, F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_2^-, NO_3^-, OAc^-, S^{2-}, $H_2PO_4^-$ and ClO_4^- (100 μM) but no significant changes have been observed (Fig. S11).

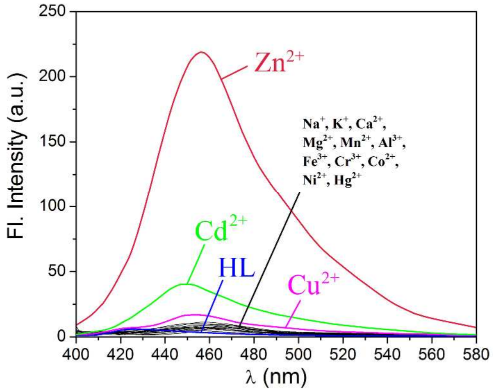


Fig. 3. Emission spectrum of HL upon addition of Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+} and Zn^{2+} in CH_3CN : H_2O (1:1, v/v, pH=7.2)

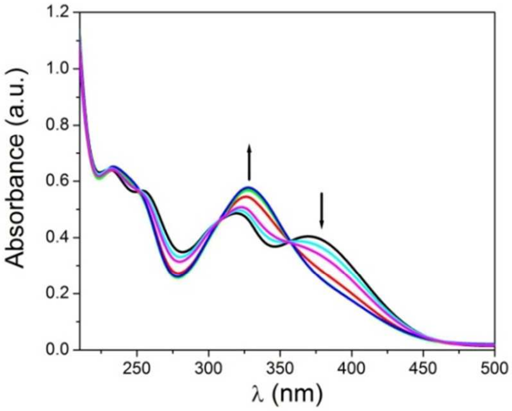


Fig. 4. Changes in UV-Vis spectrum of HL (7 μM) upon gradual addition of HSO_4^- (70 μM) in 1:1, v/v CH_3CN:H_2O

Fluorescence study

Upon gradual addition of HSO_4^- to the receptor solution, emission intensity increases by 17 fold and the emission maxima shows a blue shift of 46 nm and the new maxima centred around 376 nm (Fig. 5). This clearly indicates a 'Turn-On' response of the synthesized chemosensor for HL. The detection limit of HL for HSO_4^- is found to 0.274×10^{-6} M from emission spectral titration (Fig. S12). The association constant is found to be 1.17×10^{6} with an order of n = 1.11 (Fig. S13). Job's plot based on emission spectral titration clearly indicates that the maxima corresponds to mole fraction ~0.5 suggesting 1:1 complex formation of HL with HSO_4^- (Fig. S14). The emission intensity of HL with HSO_4^- in presence of several other anions has been studied and in every case there is no significant interference due to the presence of other anions (Fig. S15).

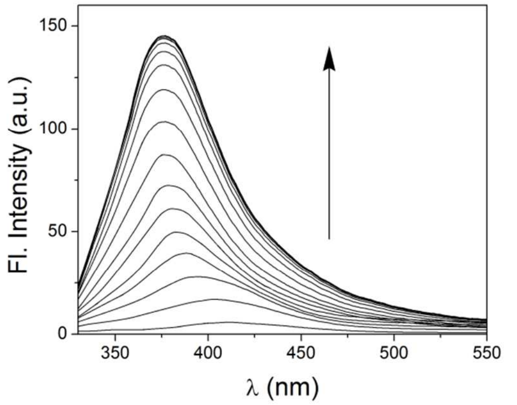


Fig. 5. Changes in emission spectrum of HL (10 μM) upon gradual addition of HSO_4^- (100 μM) in 1:1, v/v $CH_3CN:H_2O$

Electronic structure and DFT calculation

To interpret the electronic structure of HL, geometry optimization has been performed by DFT/B3LYP method in singlet ground state (S_0) (Fig. 6). The potential energy scan (Fig. 7) in S_0 state reveals that the keto form is more stable by an amount of energy of 7.15 kcal/mol than the corresponding enol form which is consistent with the X-ray structure of this type of molecules.[23] The geometry of HL-Zn^{2+} and HL-HSO_4^- have been optimized and the energy minimized structures are shown in Fig.8 and Fig. 9 respectively. Contour plot of selected molecular orbitals of HL and its complexes with Zn^{2+} and HSO_4^- are given in Fig. S16, Fig. S17 and Fig. S18 respectively. HL acts as a N,O bidentate ligand and gets coordinated to Zn^{2+} in a tetrahedral fashion with the other to sites occupied by a water molecule and chloride ion. In HL-HSO_4^-, hydrogen atom of HSO_4^- gets hydrogen bonded with the imine-N of HL with a distance of 1.78 Å. The O atom of HSO_4^- gets H bonded with OH of coumarin ring with a distance of 1.58 Å.

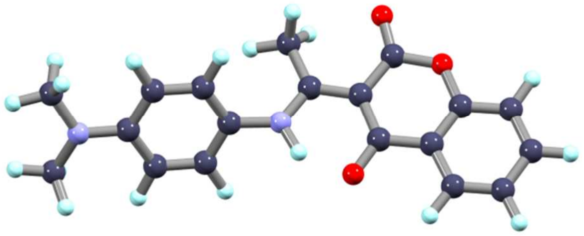


Fig. 6. Optimized structure of HL by DFT/B3LYP/6-31+G(d) method.

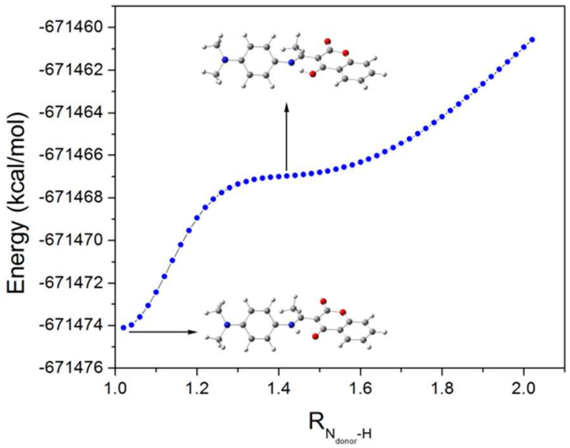


Fig. 7. Potential energy scan in singlet ground (S_0) state of HL by DFT/B3LYP/6-31+G(d) method

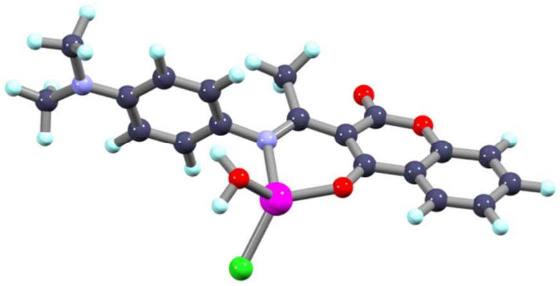


Fig. 8. Optimized structure of HL-Zn^{2+} by DFT/B3LYP/6-31+G(d) method.

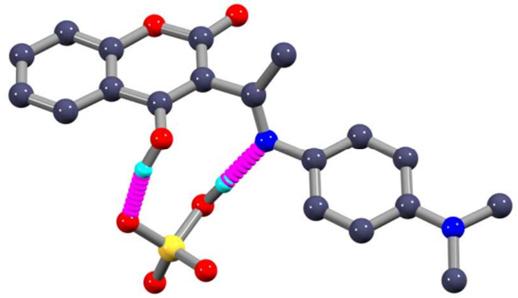


Fig. 9. Optimized structure of HL-HSO_4^- by DFT/B3LYP/6-31+G(d) method.

Sensing mechanism

In the absence of Zn^{2+}, HL shows a weak emmision band centered around 422 nm. Upon gradual addition of Zn^{2+}, the receptor HL shows an excellent fluorescence intensity enhancement of 27 fold. The developed chemosensor HL can exist in 'keto' and 'enol' tautermeric forms due to excited state intramolecular proton transfer (ESIPT) process[24] but in the ground state (S_0) the equilibrium predominantly shifts towards the keto form which has low emmision intensity.[19a] The ground state of HL in the keto form is actually in the fluorescence-OFF mode. Upon addition of the analyte the sensor HL shifts its equilibrium to the enol form to bind with Zn^{2+}. Thus fluorescense intensity enhancement is observed in presence of Zn^{2+}. In case of HSO_4^- hydrogen bonded interaction with the receptor HL, in the enolic form, shows an increase in emmision intensity.

Experimental Section

Material and methods

4-Hydroxycoumarin and *N,N*-Dimethylbenzene-1,4-diamine were purchased from Aldrich. All other organic chemicals and inorganic salts were available from commercial suppliers and used without further purification.

Elemental analysis was carried out in a 2400 Series-II CHN analyzer, Perkin Elmer, USA. ESI mass spectra were recorded on a micromass Q-TOF mass spectrometer. Infrared spectra were taken on a RX-1 Perkin Elmer spectrophotometer with samples prepared as KBr pellets. Electronic spectral studies were performed on a Perkin Elmer Lambda 25 spectrophotometer. Luminescence property was measured using Perkin Elmer LS 55 fluorescence spectrophotometer at room temperature (298 K). NMR spectra were recorded using a Bruker (AC) 300 MHz FTNMR spectrometer in $CDCl_3$. Fluorescence lifetimes were measured using a time-resolved spectrofluorometer from IBH, UK. The instrument uses a picoseconds diode laser (NanoLed-03, 370 nm) as the excitation source and works on the principle of time-correlated single photon counting.[25] The goodness of fit was evaluated by χ^2 criterion and visual inspection of the residuals of the fitted function to the data.

The luminescence quantum yield was determined using carbazole as reference with a known ϕ_R of 0.42 in MeCN. The complex and the reference dye were excited at the same wavelength, maintaining nearly equal absorbance (~0.1), and the emission spectra were recorded. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield is calculated according to the following equation:

$$\phi_S/\phi_R = [A_S / A_R] \times [(Abs)_R / (Abs)_S] \times [\eta_S^2/\eta_R^2].$$

Here, ϕ_S and ϕ_R are the luminescence quantum yield of the sample and reference, respectively. A_S and A_R are the area under the emission spectra of the sample and the reference respectively, $(Abs)_S$ and $(Abs)_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and η_S and η_R are the values of refractive index for the respective solvent used for the sample and reference.

Synthesis of 3-[1-(4-dimethylamino)phenylimino]ethyl-4-hydroxy-2H-chromen-2-one (HL)

3-Acetyl-4-hydroxy-2H-chromen-2-one (L)[26] (0.306 g, 1.5 mmol) and *N,N′*-Dimethylbenzene-1,4-diamine (0.204 g, 1.5 mmol) were refluxed for 10 hours in methanolic medium. Excess solvent was evaporated under reduced pressure and then dissolved in dichoromethane which is further subjected to silica gel (60-120 mesh) column chromatographic separation. The desired light yellow solid product was obtained by elution with 20% ethylacetate:petether (v/v) mixture. Yield : 0.371 g, 77%.

Anal. Calc. for $C_{19}H_{18}N_2O_3$ (HL): Calc. (%) C 70.79, H 5.63, N 8.69. Found (%), C 70.93, H 5.59, N 8.52. IR data (KBr, cm^{-1}): 1709 υ(lactone C=O); 1616 υ(keto C=O), 1568 υ(C=C). ^1H NMR data ($CDCl_3$, 300 MHz): δ 15.58 (1H, s), 8.08 (1H, d, J= 7.7 Hz), 7.53-7.55 (1H, m), 7.22-7.25(1H, m), 7.07 (1H, d, J = 8.8 Hz), 6.73 (1H, d, J= 8.9 Hz), 3.01 (6H, s), 2.68 (3H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 181.5, 175.6, 162.6, 153.8, 149.9, 133.8, 126.1, 126.0, 124.7, 123.5, 120.3, 116.6, 112.4, 97.8, 40.4, 20.8. Melting point: 205^0C

General method for UV-Vis and fluorescence titration

UV-Vis method

Stock solution of the receptor HL (10 μM) in [(CH_3CN/H_2O), 1:1, v/v] (at 25°C) using HEPES buffered solution (50 mM) at pH=7.2 was prepared. The solution of the guest cations and anions using their chloride salts and sodium salts respectively in the order of 10^{-4} M were prepared in deionised water. Solutions of various concentrations containing host and increasing concentrations of cations and anions were prepared separately. The spectra of these solutions were recorded by means of UV-Vis method.

Fluorescence method

For fluorescence titrations, stock solution of the sensor was prepared following the same procedure as used in case of UV-Vis titration. The solution of the guest cations and anions using their chloride salts and sodium salts respectively in the order of 10^{-4} M, were prepared in deionized water. Solutions of various concentrations containing sensor and increasing concentrations of cations and anions were prepared separately. The spectra of these solutions were recorded by means of fluorescence methods.

Job's plot by fluorescence method

A series of solutions containing HL (10 μM) and $ZnCl_2$ (10 μM) were prepared in such a manner that the sum of the total metal ion and HL volume remained constant (4 ml). $CH_3CN:H_2O$ (1:1, v/v) was used as solvent at pH 7.2 using HEPES buffer. Again a series of solutions containing HL (10 μM) and $NaHSO_4$ (10 μM) were prepared such that the sum of the total volume remained constant (4 ml). Here also $CH_3CN:H_2O$ (1:1, v/v) was used as solvent at pH 7.2 using HEPES buffer. Job's plots were drawn by plotting ΔF versus mole fraction of Zn^{2+} or HSO_4^- [ΔF = change of intensity of the emission spectrum at 457 nm (for Zn^{2+}) and at 376 nm (for HSO_4^-) during titration and X_g is the mole fraction of the guest in each case, respectively].

Computational method

All computations were performed using the Gaussian09 (G09) program.[27] Full geometry optimization of HL and its Zn complex were carried out using the DFT method at the B3LYP level of theory.[28] The 6-31+G(d) basis set was assigned for C, H, N and O atoms. The lanL2DZ basis set with effective core potential was employed for the Zn atom.[29] The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima of potential energy surface and there are only positive eigen-values.

Conclusion

Thus in brief we report herein a coumarin based organic moety which shows dual sensing fluorescent 'Turn-On' property in presence of both Zn^{2+} and HSO_4^- ions. The developed chemosensor is synthesized using a very simple and economically cheap synthetic route with excellent yield. The developed chemosensor shows high selectivity for Zn^{2+} and HSO_4^- even in presence of several other ions. We believe that in near future our developed chemosensor HL will be useful in designing more selective and efficient receptors for recognizing Zn^{2+} in biological systems.

Acknowledgement

The authors thank Department of Science and Technology India, New Delhi, India for their financial support. D.Sarkar and A. K. Pramanik thank CSIR, India for their fellowship. Jadavpur University is acknowledged for providing infrastructural facility.

Notes and references

Department of Chemistry, Jadavpur University, Kolkata-700032, India;
E-mail: tkmondal@chemistry.jdvu.ac.in

†Electronic Supplementary Information (ESI) available: [Association constant determination, detection limit determination, ^1H NMR, ^{13}C NMR, ESI MS spectroscopy, UV-Vis titration spectra of HL with different metal ions etc.]. See DOI: 10.1039/b000000x/

[1] (a) Z. Kösterel, K. Severin, *Chem. Commun*., 2012, **48**, 5841; (b) M. Zhang, B. C. Ye, *Chem. Commun.,* 2012, **48**, 3647; (c) J. F. Callan, A. P. de Silva, D. C. Magri, *Tetrahedron,* 2005, **61**, 8551; (d) R. Martinez-Manez, F. Sancenon, *Chem. Rev*., 2003, **103**, 4419; (e) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. R. Rademache, T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.

[2] (a) M. Vonlanthen, N.S. Finney, *J. Org. Chem.,* 2013, **78**, 3980; (b) V.A. Babain, A.V. Legin, D.O. Kirsanov, A.M. Rudnitskaya, Y.M. Tatuev, V.E. Baulin, *Radiochim. Acta.,* 2009, **98**, 479; (c) H. Hisamoto, H. Tohma, T. Yamada, K. Yamuchi, D. Siswanta, N. Yoshioka, K. Suzuki, *Anal. Chim. Acta.*, 1998, **373**, 271.

[3] (a) S. E. Martinez, C. L. Sayre, N. M. Davies, *Biomed. Chromatogr.*, 2013, **27**, 67; (b) Z. Wang, D. M. Han, W.P. Jia, Q.Z. Zhou, W.P. Deng, *Anal. Chem.,* 2012, **84**, 4915; (c) M. Alexy, M. Hanko, S. Rentmeister, J. Heinze, *Sens. Actuators B, Chem.*, 2006, **114**, 916.

[4] (a) M. V. Alfimov, O. A. Fedorova, S. P. Gromov, *J. Photochem. Photobiol*., 2003, **183**, 2; (b) M. Irie, *Chem. Rev.*, 2000, **5**, 1683.

[5] (a) Q. Qu, A. Zhu, X. Shao, G. Shib, Y. Tian, *Chem. Commun.*, 2012, **48**, 5473; (b) K. Ghosh, T. Sarkara, A. Samadderb, *Org. Biomol. Chem.* 2012, **10**, 3236; (c) J. Zhang, C. Yu, G. Lu, Q. Fu, N. Li, Y. Ji, *New J. Chem*., 2012, **36**, 819; (d) C. Lodeiro, F. Pina, *Coord. Chem. Rev.,* 2009, **253**, 1353; (e) L. Basabe-Desmonts, D. N. Reinhoudt, M. Crego-Calama, *Chem. Soc. Rev.,* 2007, **36**, 993; (f) P. A. Gale, *Acc. Chem. Res.*, 2006, **39**, 465; (g) E. A. Katayev, Y. A. Ustynyuk, J. L. Sessler, *Coord. Chem. Rev.*, 2006, **250**, 3004.

[6] (a) Z. Guo, I. Shin, J. Yoon, *Chem. Commun.*, 2012, **48**, 5956; (b) H. Sharma, N. Kaur, N. Singh, *Inorg. Chim. Acta*., 2012, **391**, 83; (c) T. Konry, D. R. Walt, *J. Am. Chem. Soc.*, 2009, **131**, 13232; (d) N. Kaur, S. Kumar, *Tet. Lett.* 2008, **49**, 5067; (e) M. Schmittel, H. W. Lin, *Angew. Chem. Int. Ed.* 2007, **46**, 893; (f) H. Komatsu, T. Miki, D. Citterio, T. Kubota, Y. Shindo, Y. Kitamura, K. Oka, K. Suzuki, *J. Am. Chem. Soc.*, 2005, **127**, 10798; (g) H. Komatsu, D. Citterio, Y. Fujiwara, K. Minamihashi, Y. Araki, M. Hagiwara, K. Suziki, *Org. Lett.* 2005, **7**, 2857; (h) D. Jimenez, F. Martinez-Manez, F. Sancenon, J. Soto, *Tet. Lett.* 2004, **76**, 5726.

[7] E. Loisel, L. Jacquamet, L. Serre, C. Bauvois, J.L. Ferrer, T. Vernet, A.M.D. Guilmi, C. Duurmort, *J. Mol. Biol.,* 2008, **381**, 594.

[8] R.A. Sperotto, T. Boff, G.L. Duarte, L.S. Santos, M.A. Grusak, J.P. Fett, *J. Plant Physiol.*, 2010, **167**,1500.

[9] H. Yang, Y. Peng, L. Haung, H. Zhang, Y. Wang, S. Xie, *J. Lumin.*, 2013, **135**, 26.

[10] D.J. Bobilya, J.T. Reynolds, K.L. Faia, M.B. Anderson, P.G. Reeves, *J. Nutr. Biochem.,* 1999, **10**, 139.

[11] (a) J. Lai, A. Moxey, G. Nowak, K. Vashum, K. Bailey, M. McEvoy, *J. Affect. Disord.,* 1999, **56**, 189; (b) J.H. Weiss, S.L. Sensi, J.Y. Koh, *Phamacol. Sci.*, 2000, **21**, 395; (c) M. Maes, N.D. Vos, P. Demedts, A. Wauters, H. Neels, *J. Affect. Disord.,* 2012, 136, 31.

[12] (a) E. Zhang, E. Lui, J. Shen, Y. Cao, Y. Li, *J. Environ. Sci.*, 2012, **24**, 1189; (b) J. Cherif, C. Mediouni, W.B. Ammar, F. Jemal, *J. Environ. Sci.,* 2011, **23**, 837.

[13] (a) D.B. Kevin, V.B. Mykhailo, F. Andrew, R.M. Alma, D.K. Oleksiy, A.M. Ivan, E.M. Artem, V.P. Olga, *J. Phys. Chem. B*, 2010, **114**, 9313; (b) H.M. Chawla, S. Richa, P. Shubha, *Tetrahedron Lett.,* 2012, **53**, 2996; (c) T.B. Wei, P. Zhang, B.B. Shi, P. Chen, Q. Lin, J. Liu, Y.M. Zhang, *Dyes and Pigments* 2013, **97**, 297.

[14] (a) E. Kimura, T. Koike, *Chem. Soc. Rev.*, 1998, **27**, 179; (b) P. Jiang, Z. Guo, *Coord. Chem. Rev.*, 2004, **248**, 205; (c) N.C. Lim, H.C. Freake, C. Bruckner, *Chem. Eur.J* , 2005, **11**, 38; (d) Z.C. Liu, B.D. Wang, Z.Y. Yang, T.R. Li, Y. Li, *Inorg. Chem. Commun.* , 2010, **13**, 606.

[15] (a) A. R. Kay and J. Neur, *Science*, 2003, **23**, 6847; (b) J. Zhao, B. A. Bertoglio, K. R. Gee and A. R. Kay, *Cell Calcium*, 2008, 44, 422; (c) G. K. Walkup, S. C. Burdette, S. J. Lippard and R. Y. Tsien, *J. Am. Chem. Soc.*, 2000, **122**, 5644; (d) S. C. Burdette, C. J. Frederickson, W. M. Bu and S. J. Lippard, *J. Am. Chem. Soc.*, 2003, **125**, 1778; (d) E. M. Nolan, S. C. Burdette, J. H. Harvey, S. A. Hilderbrand and S. J. Lippard, *Inorg. Chem.*, 2004, 43, 2624; (e) C. J. Chang, E. M. Nolan, J. Jaworski, S. C. Burdette, M. Sheng and S. J. Lippard, *Chem. Biol.*, 2004, **11**, 203.

[16] B.A. Moyer, L.H. Delmau, C.J. Fowler, A. Ruas, D.A. Bostick, J.L. Sessler, E. Katayeu, G.D. Pantos, J.M. Llinares, M.A. Hossain, S.O. Kang, K. Bowman-James, in: R.V. Eldik, K. Bowman-James (Eds.), *Advances in Inorganic Chemistry, Academic Press, New York*, 2006, pp. 175–204.

[17] B. A. Moyer, L. H. Delmau, C. J. Fowler, A. Ruas, D. A. Bostick, J. L. Sessler, E. Katayev, G. D. Pantos, J. M. Llinares, Md. A. Hossain, S. O. Kang, K. Bowman- James, *In Advances in Inorganic Chemistry: Template Effects and Molecular Organisation; R. Van Eldik, , K. Bowman-James, Eds.; Academia Press: London*, 2007, **59**, 175.

[18] J. W. Pflugrath, F. A. Quiocho, *Nature,* 1985, **314**, 257.

[19] (a) S. Goswami, S. Das, K. Aich, D. Sarkar, T. K. Mondal, *Tetrahedron Lett.,* 2013, **54**, 6892; (b) S. Goswami, A. K. Das, K. Aich, A. Manna, S. Maity, K. Khanrab, N. Bhattacharyya, *Analyst*, 2013, 138, 4593; (c) S. T. Yang, D. J. Liao, S. J. Chen, C. H. Hu, A. T. Wu, *Analyst* 2012, **137**, 1553; (d) W. J. Xue, L. Li, Q. Li, A. X. Wu, *Talanta* 2012, **88**, 734; (e) P. Li, Y. M. Zhang, Q. Lin, J. Q. Li, T. B. Wei, *Spectrochim. Acta Part A*, 2012, **90**, 152; (f) H. J. Kim, S. Bhuniya, R. K. Mahajan, R. Puri, H. G. Liu, K. C. Ko, J. Y. Lee, J. S. Kim, *Chem. Commun.*, 2009, 7128; (g) R. Shen, X. B. Pan, H. F. Wang, L. H. Yao, J. C. Wu, N. Tang, *Dalton Trans.*, 2008, 3574; (h) J. L. Sessler, E. Katayev, G. D. Pantosa, Y. A. Ustynyuk, *Chem. Commun.*, 2004, 1276; (i) A. Mallick, T. Katayama, Y. Ishibasi, M. Yasudab, H. Miyasaka, *Analyst*, 2011, **136**, 275; (j) M. Alfonso, A. Tarraga, P. Molina, *Org. Lett.,* 2011, **13**, 6432.

[20] D. Ray, P.K. Bharadwaj, *Inorg. Chem.*, 2008, 47, 2252.

[21] (a) N.C. Lim, J.V. Schuster, M.C. Porto, M.A. Tanudra, L.L. Yao, H.C. Freake, C. Bruckner, *Inorg. Chem.,* 2005, **44**, 2018; (b) H.E. Katerinopoulos, *Curr. Pharm. Des.,* 2004, **10**, 3835.

[22] (a) P. Li, Y.M. Zhang, Q. Lin, J. Q. Li, T. B. Wei, *Spectrochim. Acta Part A*, 2012, **90**, 152; (b) H.J. Kim, S. Bhuniya, R. K. Mahajan, R. Puri, H. G. Liu, K. C. Ko, J. Y. Lee, J. S. Kim, *Chem. Commun.* 2009, 7128; (c) M. Alfonso, A. Tarraga, P. Molina, *Org. Lett.* 2011, **13**, 6432.

[23] (a) A. Brahmia, T.B. Ayed, R.B. Hassen, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2013, **69**, o1296; (b) T. Shibahara, M. Takahashi, A. Maekawa and H. Takagi, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, **66**, o429.

[24] W.Rodriguez-Cordoba, C. Fregoso, E. Jugazagoitia, J. Peon, *J. Phys. Chem. A*, 2007, **111**, 6241.

[25] S. R. Stoyanov, J. M. Villegas, D. P. Rillema, *Inorg. Chem.,* 2002, **41**, 2941.

[26] N. Hamdi, C. Fischmeister, M.C. Puerta, P. Valerga, *Med. Chem. Res.*, 2011, **20**, 522.

[27] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[28] A.D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

[29] (a) P.J. Hay, W.R. Wadt, *J. Chem. Phys.,* 1985, 82, 270; (b) W.R. Wadt, P.J. Hay, *J. Chem. Phys.*, 1985, 82, 284; (c) P.J. Hay, W.R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.