

# Fluorescent Studies of Salicylaldehyde and Other Related Carbonyl Compounds for the Selective and Sensitive Detection of Zinc(II) Ions in Aqueous Solution

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**Abstract** Salicylaldehyde was found to have a high selectivity for zinc ions with simultaneous enhancement of fluorescence in aqueous buffer solution at optimum pH 8.5. The stoichiometry of the complex was determined to be 1:1 with a  $K_a$  value of  $3.4 \times 10^4 \text{ M}^{-1}$  at 298 K. The fluorescence of the complex is not affected by common anions and  $\text{Zn}^{2+}$  binds preferentially to salicylaldehyde in the presence of alkali, alkaline earth and heavy metal cations ( $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$ ). This property is not observed with related phenolic compounds bearing a carbonyl group such as esters, amides, carboxylic acids and ketones.

**Keywords** Salicylaldehyde · Zinc · Fluorescence · Selectivity · Metal ions

## Introduction

Zinc is an essential trace element which is critical in many biological systems. It acts as a cofactor for many enzymes and it is closely associated to regulatory proteins involved in DNA repair, gene control and apoptosis [1–3]. Zinc is also essential for growth and development. Zinc deficiency in children has been linked to growth retardation, delayed sexual maturation, diarrhea and a lowered immunity against infection [4]. An imbalance of zinc could be an indication of cancer, diabetes, or Alzheimer's disease [5]. The serum concentration of zinc

can be used as a diagnostic tool to assess the health condition of a person. In the environment, an excess of zinc is regarded as a pollutant that may lead to the death of plants and is detrimental to the growth of useful soil bacteria [6]. Therefore, detection and monitoring of zinc ion concentration in living systems and in the environment are important activities. The literature abounds of analytical methods for the determination of zinc level in biological and environmental samples. Common techniques such as atomic absorption spectrometry (AAS), ion selective electrodes (ISE), and flame photometry have been employed for the quantitative analysis of zinc [7]. Fluorometry is another method which has attracted much attention in recent years because of the substantial advantages it offers in terms of low cost, simplicity, selectivity, sensitivity and good response time. Many fluorometric sensors have been developed based on the photo-physical changes that can occur when zinc forms a complex with a ligand [8]. These include photo-induced electron transfer (PET) [9], photo-induced charge transfer (PCT), intramolecular charge transfer (ICT) [10], excimer-excimer formation and extinction and fluorescence resonance energy transfer (FRET) [11]. Imines and hydrazones of salicylaldehyde occupy a prominent place among the various ligands that have been employed for the determination of zinc [12, 13]. These ligands have high binding affinity to zinc and their complexes show strong fluorescence. Moreover many of these zinc complexes exhibit a shift in either their excitation or emission energies which makes the ligands suitable for accurate and quantitative determination of zinc ion concentration [11]. Fluorescence in these complexes has been explained by the prevention of isomerization across the C=N bond when complexed to zinc, decreasing the probability of non-radiative decay [13, 14].

During the course of our investigation of salicylaldimines as potential  $\text{Zn}^{2+}$  specific sensors, we observed that when

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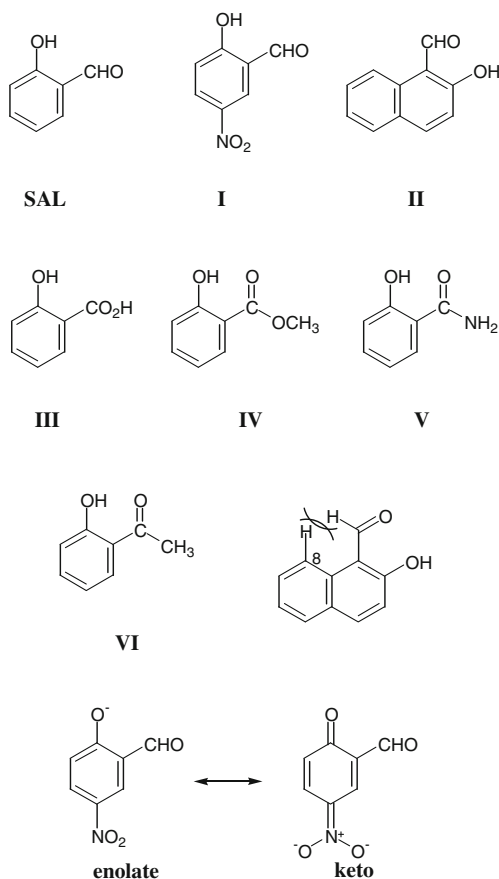
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$\text{Zn}^{2+}$  was added to a buffered aqueous solution of salicylaldehyde (SAL) (Scheme 1) a pronounced change in the UV profile of the mixture occurs along with an enhancement in fluorescence (Fig. 1). To the best of our knowledge this observation has not been described. Herein we report the study of nature of the complex between SAL and  $\text{Zn}^{2+}$  and the parameters that affect its photophysical properties. As an extension we also studied other carbonyl-containing compounds and their  $\text{Zn}^{2+}$  complexes. Salicylaldehyde can potentially be used as a cheap and environmentally friendly  $\text{Zn}^{2+}$  fluorescent sensor.

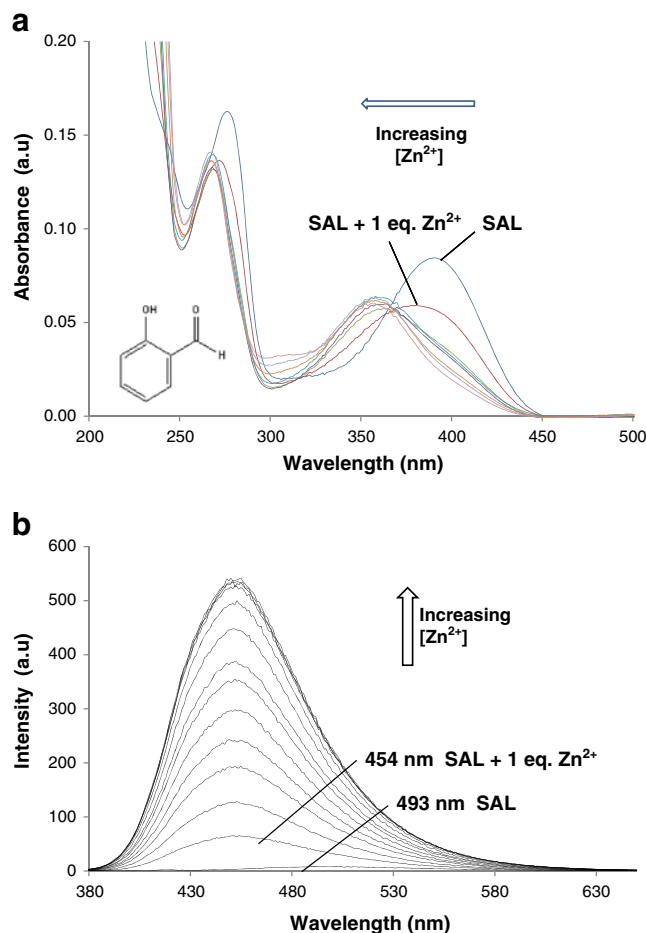
## Experimental

### Reagents

Doubly deionized water DDI (MilliQ) was used in all experiments. Dimethyl sulfoxide (DMSO), obtained from Merck, was used without any further purification. 3.00 mM stock solution of salicylaldehyde (SAL) was prepared by dissolving the compound in 1 mL DMSO and then diluting the solution to 100 mL with water. 3.00 mM of metal ions



**Scheme 1** Structures of SAL and other carbonyl compounds (I–VI); keto-enolate tautomerism of I and the restricted rotation of II



**Fig. 1** Titration of 30  $\mu\text{M}$  SAL in 10 mM Tris buffer 8.5 with increasing  $[\text{Zn}^{2+}]$  A: absorbance spectra and B: fluorescence spectra

were prepared from either their nitrates or chlorides (analytical grade) in water and 3.00 mM anions were obtained from their sodium or potassium salts. 10 mM Tris-HCl buffer solutions at different pH were prepared from 50 mM Tris-HCl stock solution and the pH was adjusted either with analytical grade HCl or NaOH. Salicylamide, salicylic acid, methyl salicylate, 5-nitrosalicylaldehyde, 2-hydroxyacetophenone were purchased from Aldrich and used as received.

### Apparatus

Absorption spectra were measured on a CARY 50 Conc. UV Visible spectrophotometer and fluorescence spectra were obtained from CARY Eclipse Fluorescence spectrophotometer using a xenon lamp and 10 mm quartz cuvettes. All measurements were performed at room temperature.

### Absorption and Fluorescence Measurements

A fluorimetric cell was filled with 3.0 mL SAL (30  $\mu\text{M}$ ) in 10 mM Tris buffer pH 8.5 solution and its emission

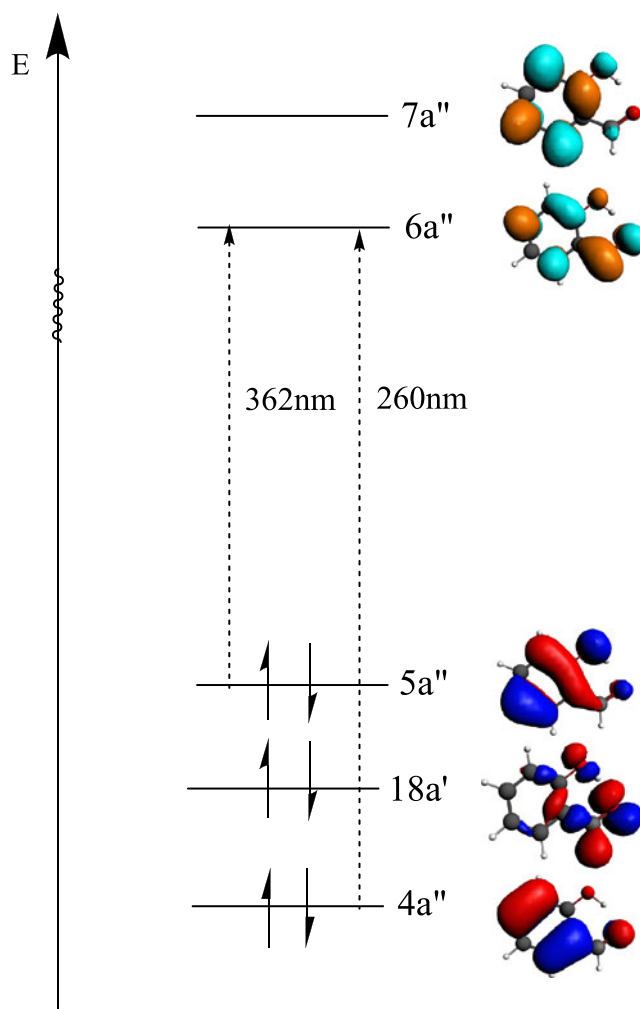
spectrum was measured. For  $\text{Zn}^{2+}$  binding studies this solution was titrated with 3.00 mM  $\text{Zn}^{2+}$  solution. Fluorescence studies were performed by exciting the sample at 360 nm with 5 nm spectral bandwidth monochromators for excitation and emission. All the experiments were run at least three times and the average was used for the different plots with error bars showing the standard deviations.

### Computational Details

All electronic structure calculations were performed using the Amsterdam Density Functional (ADF 2010.01) program [15]. The structures of salicylaldehyde, 1-hydroxy-2-naphthaldehyde and 2-hydroxy-1-naphthaldehyde were optimized under  $C_s$  symmetry and verified to be energy minima through vibrational frequency calculations. The structures of the  $\text{Zn}^{2+}$  complexes were optimized without symmetry constraints. Exchange and correlation effects were included in the optimization calculations through the BP (Becke-Perdew) functional [16, 17]. Triple- $\zeta$  basis sets with polarization functions were used for all atoms. Time dependent DFT calculations were used to predict the absorption spectrum of salicylaldehyde and assign the observed absorption bands to specific transitions [18, 19].

### Results and Discussions

Salicylaldehyde, (SAL), is a naturally occurring compound found in buck wheat and it shows two absorption maxima at 277 and 389 nm [20]. The absorption spectrum is reproduced well using gas-phase TDDFT calculations, which predict two absorption maxima in the region 250 nm–600 nm. The absorption maxima are calculated to occur at 260 nm (oscillator strength 0.175) and 362 nm (oscillator strength=0.044). Both absorptions correspond to  $\pi$ - $\pi^*$  transitions. The higher energy absorption arises from a transition between the HOMO-2 ( $4a''$ ) and LUMO ( $6a''$ ) of salicylaldehyde, and the lower energy absorption corresponds to the HOMO ( $5a''$ )→LUMO ( $6a''$ ) transition. An energy level diagram with isosurfaces of the orbitals involved is given in Fig. 2. When excited at either of these wavelengths, a very weak to negligible emission occurs at 302 and 493 nm respectively. This observation is likely due to the free rotation of the carbonyl group in SAL which induces fast fluorescence decay. In contrast, the related salicylic acid (**III**, Scheme 1) is strongly fluorescent as the presence of intramolecular H-bonding confers rigidity to the system. However, when  $\text{Zn}^{2+}$  is added to SAL an enhancement of fluorescence is seen with a concomitant blue shift in the emission ( $\lambda_{\text{em}}$  SAL=493 nm,  $\lambda_{\text{em}}$  SAL/ $\text{Zn}^{2+}$ =453 nm). The interaction of SAL with  $\text{Zn}^{2+}$  is also reflected in its UV spectrum as a titration of SAL with  $\text{Zn}^{2+}$

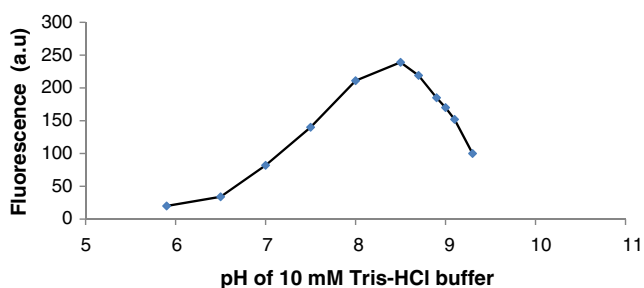


**Fig. 2** Energy level diagram showing the calculated transitions and orbital isosurfaces of salicylaldehyde

shows a gradual blue shift of the native ligand (389 nm→361 nm) (Fig. 1a). The maximum shift is only reached after the addition of 40 equivalents of  $\text{Zn}^{2+}$ . This suggests that the binding affinity of  $\text{Zn}^{2+}$  for SAL is relatively low. We therefore looked at the effect of various parameters on the photophysical properties of the SAL- $\text{Zn}^{2+}$  complex.

### Effect of Buffer pH on Fluorescence of SAL- $\text{Zn}^{2+}$ Complex

The fluorescence intensity of SAL depends on its ability to bind  $\text{Zn}^{2+}$ . The extent of the binding is closely related to the degree of deprotonation of the phenolic group, which is in turn dependent on the pH of the medium. Samples of 30  $\mu\text{M}$  SAL and 10 equivalents of  $\text{Zn}^{2+}$  were taken in 10 mM Tris-HCl buffers with pH ranging from 5.8 to 10 and their fluorescence were measured. A plot of the results is provided (Fig. 3). It was found that SAL- $\text{Zn}^{2+}$  mixtures exhibited an optimum fluorescence at pH 8.7 although the complete deprotonation of SAL is expected to be around



**Fig. 3** Effect of pH on fluorescence of a mixture of 30  $\mu\text{M}$  SAL with 300  $\mu\text{M}$   $\text{Zn}^{2+}$

pH 10, which is two units above its  $\text{pK}_a$  (8.3) [21]. However, the maximum fluorescence was recorded at a much lower pH. The reason is that at higher pH, zinc metal ions start to precipitate: the literature value of the  $K_{sp}$  of  $\text{Zn}(\text{OH})_2$  is  $3 \times 10^{-17} \text{ M}^3$  [22]. We also looked at the effect of the concentration of the Tris-HCl buffer. Buffers within the range of 50  $\mu\text{M}$  to 50 mM did not have any effect on fluorescence. Therefore, all experiments were performed in the arbitrary buffer concentration of 10 mM tris-HCl buffer and at pH 8.5 for optimum fluorescence reading.

#### Binding of SAL with $\text{Zn}^{2+}$

The nature of the stoichiometry of the complex between SAL and zinc was also investigated. A titration of 30  $\mu\text{M}$  SAL in 10 mM tris-HCl buffer pH 8.5 was carried out by addition of incremental amounts of 3 mM aqueous zinc nitrate solution. The titration was monitored by UV-visible spectroscopy and it showed a gradual  $\lambda_{\text{max}}$  shift from 389 nm to 358 nm suggesting that there is an interaction between SAL and  $\text{Zn}^{2+}$  (Fig. 1a). At about 40 equivalents of  $\text{Zn}^{2+}$  no further change in the absorbance profile is observed. The UV-visible plots also show the presence of an isobestic point at 367 nm. The latter was used as excitation wavelength for subsequent fluorometric studies. When a large excess of  $\text{Zn}^{2+}$  ( $> 50$  equivalents) was added to the SAL solution, two new UV bands appear at 267 and 304 nm and their intensities grew until a 1000 fold excess of  $\text{Zn}^{2+}$  was added. Our initial thought was directed to the formation of a new SAL- $\text{Zn}^{2+}$  species. However, in a control experiment, we added 1000 equivalents of  $\text{Zn}^{2+}$  (achieved by addition of 3 M  $\text{Zn}^{2+}$  solution) to the 10 mM Tris buffer pH 8.5 in the absence of SAL and we were surprised to observe the new bands. We concluded that at pH 8.5, the buffering agent *tris*(hydroxymethyl)amino-methane,  $(\text{HOCH}_2)_3\text{CNH}_2$  is acting as a ligand for  $\text{Zn}^{2+}$ . This association predominates only at very high concentration of  $\text{Zn}^{2+}$ .

The titration was also followed by fluorescence spectroscopy in which SAL- $\text{Zn}^{2+}$  mixtures were excited at 367 nm and the  $\lambda_{\text{em}}$  and fluorescence units were recorded. Upon addition of 0.1 equivalent of  $\text{Zn}^{2+}$ ,  $\lambda_{\text{em}}$  shifted

abruptly from 493 to 454 nm (Fig. 1a) due to complex formation between  $\text{Zn}^{2+}$  and SAL. The fluorescence intensity gradually increased upon further addition of  $\text{Zn}^{2+}$  due to  $\text{Zn}^{2+}$ /SAL complex build-up and a plateau was reached at about 1:40 SAL: $\text{Zn}^{2+}$  ratio. The fluorescence data were used to investigate the stoichiometry of the complex between SAL and  $\text{Zn}^{2+}$ .

We used three modified Hildebrand-Benesi equations [23], which assume SAL: $\text{Zn}^{2+}$  ratios of 1:1 (Eq. 1), 1:2 (Eq. 2) and 2:1 (Eq. 3) respectively. In these equations  $F_0$  and  $F$  are the fluorescence intensities of the SAL in the absence and presence of  $\text{Zn}^{2+}$  and  $\alpha$  is a constant.

$$\frac{1}{F - F_0} = \frac{1}{[\text{Zn}^{2+}]K_a\alpha} + \frac{1}{\alpha} \quad (1)$$

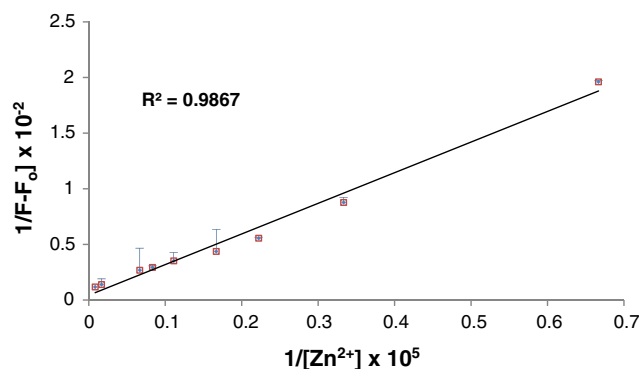
$$\frac{1}{F - F_0} = \frac{1}{[\text{Zn}^{2+}]^2K_{2a}\alpha} + \frac{1}{\alpha} \quad (2)$$

$$\frac{1}{F - F_0} = \frac{1}{[\text{Zn}^{2+}]^{1/2}K_{3a}\alpha} + \frac{1}{\alpha} \quad (3)$$

The fluorescence data fits well in Eq. 1 ( $R^2=0.9867$ ) suggesting that the SAL/ $\text{Zn}^{2+}$  complex is 1:1 (Fig. 4). The association constant,  $K_a$ , for the SAL/ $\text{Zn}^{2+}$  complex is calculated to be  $3.64 \times 10^4 \text{ M}^{-1}$  at 298 K. The  $K_a$  value is similar to those reported for other salicylaldehydes [13]. Plots constructed using Eqs. 2 and 3 resulted in curves rather than linear relationships.

#### Effect of Common Anions on Fluorescence of SAL- $\text{Zn}^{2+}$ Complex

The working solutions of SAL- $\text{Zn}^{2+}$  contain a relatively large amount of  $\text{Cl}^-$  which was introduced from the buffer, as aqueous HCl was used to adjust the pH of the solution. A small amount of  $\text{NO}_3^-$  is also present and is derived from



**Fig. 4** Hildebrand-Benesi plot for 1:1 SAL: $\text{Zn}^{2+}$  ratio showing linear relationship

the zinc nitrate used in this study. Nevertheless we introduced other anions to investigate their effects on the binding of SAL to Zn<sup>2+</sup> and subsequently on the fluorescence of the SAL-Zn<sup>2+</sup> complex. 10 equivalents of 3 mM aqueous anions were added to a 30 μM solution of SAL-Zn<sup>2+</sup> mixture in 10 mM Tris-HCl buffer pH 8.5. The anions that were chosen are Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, CH<sub>3</sub>COO<sup>-</sup>, in addition to those that possess the ability to hydrogen bond such as HCO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>. All anions were introduced as either potassium or sodium salts. Both UV-visible absorbance and fluorescence spectra were almost unchanged upon addition of the different anions at that particular concentration (Fig. 5). The results suggest that the anions tested have little influence on the photophysical properties of the complex and are mere spectators.

### Effect of Common Metal Ions on Fluorescence of SAL-Zn<sup>2+</sup> Complex

The specificity of the Zn<sup>2+</sup> response to SAL was investigated by screening other metals. Ten metal ions were used: the alkali metals Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, alkaline earth metals Mg<sup>2+</sup>, Ca<sup>2+</sup> for their relevance to biological systems, and the environmentally toxic metals Cd<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup> and Al<sup>3+</sup>. The cations cover a wide range of charges and sizes. The results are summarized in Fig. 6a. When SAL is mixed with 10 equiv. of the above metal ions, only Zn<sup>2+</sup> showed an enhancement in fluorescence. The other metals had absolutely no effect on fluorescence indicating that salicylaldehyde is showing specific response to zinc, at least based on the metals that have been tested. We also looked at the competition of Zn<sup>2+</sup> for SAL in the presence of other metals (Fig. 6b). The experiment was performed by adding 10 equivalents of both zinc and a second metal ion to a solution of SAL in tris-HCl buffer pH 8.5. The mixture was allowed to reach equilibrium for 15 min and fluorescence was measured. The results show that SAL would specifically bind to Zn<sup>2+</sup> in the presence of a variety of other

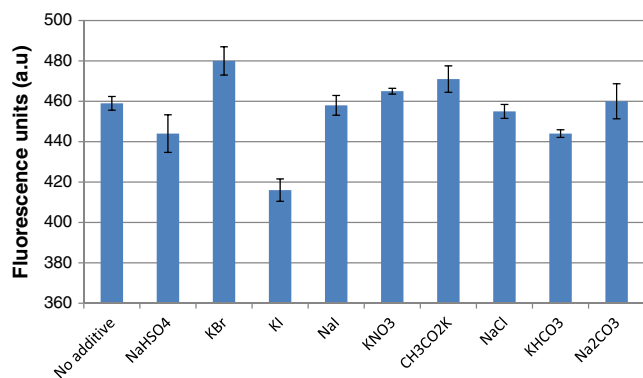


Fig. 5 Effect of anions on the fluorescence of SAL-Zn<sup>2+</sup> complex

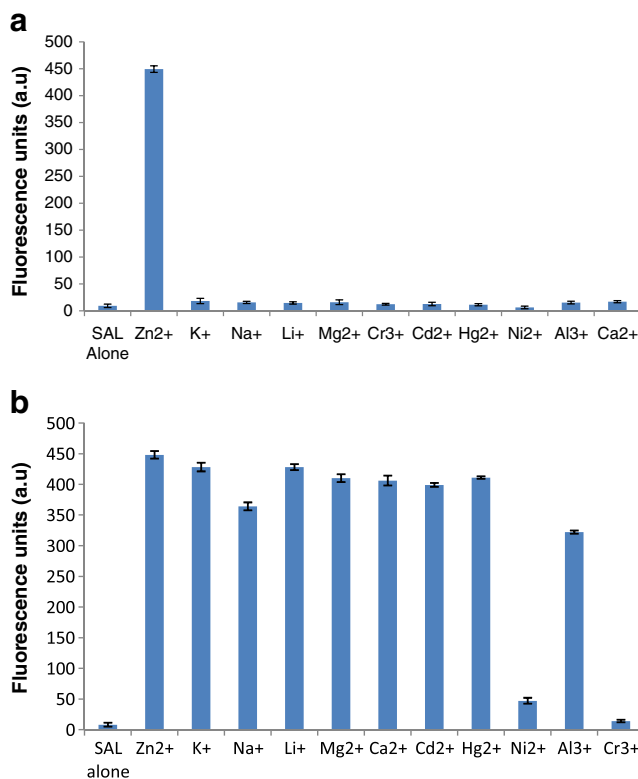


Fig. 6 Effect of metal ions on fluorescence of 30 μM SAL in 10 mM Tris-HCl buffer pH 8.5, A: SAL and 10 eq. of different metal ions and B: SAL, 10 eq. of Zn<sup>2+</sup> and other 10 eq. of another metal ion

metals including Hg<sup>2+</sup> and Cd<sup>2+</sup>. However, the presence of metals such as Al<sup>3+</sup>, Cr<sup>3+</sup> and Ni<sup>2+</sup> influenced both the fluorescence (Fig. 6b) and UV spectra of the mixture (Fig. 7). The higher charged Al<sup>3+</sup> ion competes favorably with Zn<sup>2+</sup> for SAL as indicated by the lower fluorescence value of the mixture. Ni<sup>2+</sup> and Cr<sup>3+</sup>, which are known fluorescence quenchers, completely suppress fluorescence [24]. The results also indicate that SAL binds preferentially

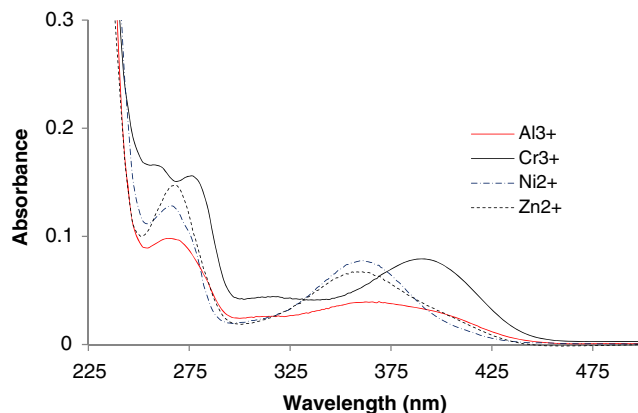


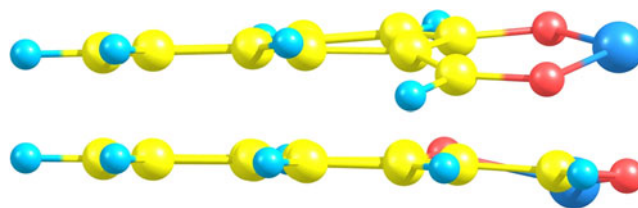
Fig. 7 Absorbance spectra of SAL in the presence of Zn<sup>2+</sup> and other metal ions

to  $\text{Ni}^{2+}$  and to greater extent to  $\text{Cr}^{3+}$ . A possible explanation is that the size of these transition metal ions is similar to  $\text{Zn}^{2+}$  and therefore fits well into the ligand cavity. The lack of a response to  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$  is attributed to the presence of non-radiative processes from the intraligand  $\text{I}t\text{-I}t^*$  singlet state to a d-d or a charge-transfer excited state. These processes occur only in transition metals with unfilled d-shells, as previously reported [24].

### Other Related Carbonyl Ligands

In order to improve the binding of salicylaldehyde with  $\text{Zn}^{2+}$  we considered derivatives which have electron-withdrawing groups. 5-Nitrosalicylaldehyde (**I**) has a higher acidity compared to the parent molecule ( $\text{pK}_a=5.5$ ) and is expected to be in the phenolate form at pH 8.5 (Scheme 1) [25]. 5-Nitrosalicylaldehyde has three UV absorption maxima at 246, 358 and 387 nm. Unfortunately upon addition of  $\text{Zn}^{2+}$  to **I** at pH 8.5 there was no significant change in the UV spectrum, even after addition of 25 equivalent of  $\text{Zn}^{2+}$  (Supporting Materials Fig. S1). When excited at its absorption maxima no enhancement of fluorescence was observed. A plausible explanation is that when **I** is deprotonated, it forms a quinoid-type structure (Scheme 1) in which the negative charge is delocalized onto the nitrogen. In this form its binding affinity is lowered. The existence of the keto form is partially supported by the presence of a UV band at 387 nm. A much milder electron-withdrawing group in **II**, 2-hydroxynaphthaldehyde, was also examined. This particular compound, which has a  $\text{pK}_a$  of 7.38 [13] ( $\lambda_{\text{max}}$  250, 308, 398 nm), is expected to be a better binder to  $\text{Zn}^{2+}$ . However **II**/ $\text{Zn}^{2+}$  mixtures did not show any fluorescence. DFT geometry optimization calculations on the structure of the complex between **II** and  $\text{Zn}^{2+}$  indicate that steric hindrance between the aldehyde hydrogen and C-8 hydrogen causes distortions away from planarity in the naphthyl group (Scheme 1). The corresponding 1-hydroxy-2-naphthaldehyde should not have this constraint but was not tested as it was not available. However, DFT calculations indicate that the naphthyl rings do remain co-planar upon binding  $\text{Zn}^{2+}$  for 1-hydroxy-2-naphthaldehyde, indicating it could be a good candidate for enhanced fluorescence. A side-on view, illustrating the calculated distortion in the  $\text{Zn}^{2+}$  complex of **II**, and the structure of the complex with 1-hydroxy-2-naphthaldehyde is given in Fig. 8.

As part of our investigation we also studied other carbonyl compounds that have similar backbone structures to salicylaldehyde, for their ability to fluoresce in the presence of  $\text{Zn}^{2+}$  (Scheme 1). These compounds differ only in carbonyl containing functional groups such as carboxylic acid **III**, ester **IV**, amide **V** and ketone **VI**



**Fig. 8** Side-on view of optimized structure for  $\text{Zn}(\text{II})$  complexes of 2-hydroxy-1-naphthaldehyde (**II** –top) and 1-hydroxy-2-naphthaldehyde (bottom)

with the following UV absorption maxima: **III** ( $\lambda_{\text{max}}$  300 nm), **IV** ( $\lambda_{\text{max}}$  292 nm), **V** ( $\lambda_{\text{max}}$  237, 300 nm), **VI** ( $\lambda_{\text{max}}$  237, 300 nm) (Supporting material Fig. S1 and S2). **III–VI** showed intrinsic fluorescence when excited at their  $\lambda_{\text{max}}$ . The magnitude of fluorescence of 30  $\mu\text{M}$  solutions of the compounds at pH 8.5 when excited at 300 nm increases in the following order: **III**, **IV**, **V**, **VI**, with fluorescence units of 40, 200, 390 and 790 units respectively. The addition of metal ions ( $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Al}^{3+}$ ) at varying equivalences to these ligands, in 10 mM tris buffer pH 8.5, had no effect on either the UV profile or fluorescence. The increasing intrinsic fluorescence of the compounds in the above order can be explained by the increasing degree of internal H-bonding between the phenol and the different carbonyl substituents, which confers rigidity to the molecules and thereby inhibits non-radiative decay. These findings suggest that salicylaldehyde is showing a unique fluorescence enhancement property when bound to  $\text{Zn}^{2+}$  and could be used for the selective detection of zinc ions in samples.

### Conclusion

The absorption bands of salicylaldehyde at 277 nm and 389 nm have been assigned to  $\pi\text{-}\pi^*$  transitions using TDDFT calculations. It has been shown that salicylaldehyde exhibits selective binding to  $\text{Zn}^{2+}$  with enhancement of fluorescence. This property is not observed in other related carbonyl containing compounds such as 2-hydroxysalicyl amides, ketones, esters and acids. The sensitivity for  $\text{Zn}^{2+}$  detection is not affected by the presence of common anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HCO}_3^-$ ,  $\text{HSO}_4^-$ , alkali and alkaline earth cations, or heavy metal pollutants such as  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$ . The maximum fluorescence was observed at tris buffer pH 8.5.

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## References

1. De Silva JJRF, Williams RJP (2001) Zinc: Lewis Acid Catalysis and Regulation. In the Biological Chemistry of Elements: The Inorganic Chemistry of Life (2nd ed.), Oxford UP, New York
2. Vallee BL, Falchuk KH (1993) The biological basis of zinc biology. *Physiol Rev* 73:79–111
3. Berg JM, Shi Y (1996) The galvanization of biology: a growing appreciation for the roles of zinc. *Science* 271:1081–1085
4. Salgueiro MJ, Zubillaga MB, Lysionek AE, Caro RA, Weill R, Boccio JR (2002) The role of zinc in the growth and development of children. *Nutrition* 18:510–519
5. Bush AI (2000) Metals and neuroscience. *Curr Opin Chem Biol* 4(2):184–191
6. Voegelin A, Jacquat O, Pfister S, Barmettler K, Scheinost AC, Kretzschmar R (2011) Time-dependent changes of zinc speciation in four soils contaminated with zincite or sphalerite. *Environ Part Sci Technol* 45(1):255–261
7. Soltyk K, Lozak A, Warowna-Grzeskiewicz M, Fijalek Z (2000) The AAS, ICP-MS and electrochemical determinations of zinc in selected pharmaceutical preparations. *Acta Pol Pharm* 57(4):261–266
8. Jiang P, Guo Z (2004) Fluorescent detection of zinc in biological systems: recent development on the design of chemosensors and biosensors. *Coord Chem Rev* 248(1–2):205–229
9. Xue L, Liu C, Jiang H (2009) Highly sensitive and selective fluorescent sensor for distinguishing cadmium from zinc ions in aqueous media. *Org Lett* 11(7):1655–1658
10. Fang Q, Zhang C, Zhang Y, He W, Gao X, Hu P, Guo Z (2009) Visible light excitable  $Zn^{2+}$  fluorescent sensor derived from an intramolecular charge transfer fluorophore and its in vitro and in vivo application. *J Am Chem Soc* 131:1460–1468
11. Nolan E, Lippard SJ (2009) Small-molecule fluorescent sensors for investigating zinc metalloneurochemistry. *Acc Chem Res* 42(1):193–203
12. Li HY, Gao S, Xi Z (2009) A colorimetric and “turn-on” fluorescent chemosensor for Zn(II) based on coumarin Schiff-base derivative. *Inorg Chem Commun* 12(4):300–303
13. Li L, Dang YQ, Li HW, Wang B, Wu Y (2010) Fluorescent chemosensor based on Schiff base for selective detection of zinc (II) in aqueous solution. *Tetrahedron Lett* 51(4):618–621
14. Yang GQ, Morlet-Savary F, Peng ZK, Wu SK, Fouassier JP (1996) Triplet-triplet absorption of 2-(2'-hydroxyphenyl)benzoxazole (HBO) in polar solvents. *Chem Phys Lett* 256:536–542
15. te Velde G, Bickelhaupt FM, Baerends EJ, van Gisbergen S, Guerra CF, Snijdersm JG, Ziegler T (2001) Chemistry with ADF. *J Comput Chem* 22:931
16. Becke A (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys Rev A* 38:3098
17. Perdew JP (1986) Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys Rev B* 34:7406
18. Kootstra F, de Boeij PL, Snijders JG (2000) Efficient real-space approach to time-dependent density functional theory for the dielectric response of nonmetallic crystals. *J Chem Phys* 112:6517
19. Romaniello P, de Boeij PL (2005) Time-dependent current-density-functional theory for the metallic response of solids. *Phys Rev B* 71:155108
20. Janes D, Kreft S (2008) Salicylaldehyde is a characteristic aroma component of buckwheat groats. *Food Chem* 109:293–298
21. Dean JA (1992) Lange's handbook of chemistry, 14th edn. New York, McGraw-Hill
22. Lide DR (1999) CRC Handbook of Chemistry and Physics
23. Benesi H, Hildebrand J (1949) A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons. *J Am Soc Chem* 71(8):2703–2707
24. Ohga K, Kurauchi Y (1987) Photochromic behavior of Pyridoxal- $\alpha$ -amino acid-Zn(II) complexes in methanol. *Bull Chem Soc Jpn* 60:3269–3275
25. Wohfeilt E, McMurray CH, Evans DR, Hudson RA (1985) Organomercurial reagents for the simultaneous introduction of mercury and a pH-sensitive reporter functional group into a protein containing no thiol group. *J Am Chem Soc* 107:3365–3366