Synthesis and characterization of chromone-based ligand and its fluorescence property towards Zn$^{2+}$

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Abstract. Zinc (Zn) is a type of element that are commonly found in the Earth’s environment and may be originated either naturally from the environment or produced by human activities. Zn has been identified as a hazardous metal which can give harmful effects to human health and Earth’s environment. Therefore, it is very important to develop a simplest method which does not require laborious work in order to detect Zn metal ions. Ligand of AFCMSH was synthesized by the mean of reflux reaction between 2-amino-3-formylchromone (AFC) and 4methylbenzenesulfonylhydrazide (MSH). The molecular structure of the ligand in the ground state was optimized using density functional theory (DFT/B3LYP) method with 6-311G(d,p) basis set. Characterization of ligand was conducted using spectroscopic techniques such as Fourier Transform Infra-Red spectroscopy (FT-IR), Gas Chromatography Mass Spectrometry (GC-MS), Nuclear Magnetic Resonance spectroscopy (NMR) and Ultraviolet-visible spectroscopy (UV-VIS). Meanwhile the fluorescence property of ligand in the presence of metal cations was recorded using Fluorescence Spectrophotometer. Ligand shows almost no fluorescence property in the presence of various metal ions except for Zn$^{2+}$ ion when observed under UV light. Interestingly, ligand exhibits a remarkable fluorescence response by giving yellow-green fluorescence with strong fluorescence intensity in the emission spectrum at 501 nm at excitation of 375 nm upon addition of one equivalent of Zn$^{2+}$.

1. Introduction
Zinc (Zn), the twenty fourth most abundant elements that exists in both natural and anthropogenic sources. The main sources of Zn from human activities can be related to metal production, waste incineration, burning of fossil fuel, phosphate fertilizer and cement production [1]. Excessive concentration of Zn in the environment especially in river might cause toxic response to aquatic animals such as reproductive and behavioral problem [2-4]. Zn exposure towards human may cause bad responses such as skin irritation, immunological effects, abdominal pain, nausea, vomiting, and even cancer if exposed at high dosage and long term [5]. In water, the maximum concentration of Zn have
been set at 120μg/L by Water Quality Criteria (WQC) [6], whereas the recommended dietary allowance (RDA) on daily intake of Zn for men and women were set at 11mg/day and 8mg/day respectively [7].

Due to uncontrollable Zn exposure in the environment and their danger towards the ecosystem, a new tool of molecular sensors for detecting Zn$^{2+}$ ions should be designed. The great effort of researchers in this field is directed towards the development of new selective chemosensors based on fluorescence property because they are easy to perform, inexpensive and usually very sensitive (parts per billion/trillion). Although a number of fluorescent chemosensors for zinc ion have been studied, it is still desirable to develop a new potential fluorescent chemosensor with extremely high affinity and good selectivity over other relevant metal ions. In addition, the designing of chemosensor for Zn$^{2+}$ via chelation enhanced fluorescence (CHEF) is still challenging. Reported probes for Zn$^{2+}$ detection includes quinoline-based, rhodamine6G, Tris(3-(2-hydroxyacetophenone)propyl)amine and pyrazoline-based compounds [8-11]. Our developed chemosensor from chromone-based ligand namely as 2-amino-3-formylchromone-toluenesulfonhydrazide (AFCMSH) is thus an important addition to the list of other turn-on fluorescence chemosensors which can recognize Zn$^{2+}$ effectively.

In this study, we report a chromone-based ligand as a turn-on fluorescent chemosensor for the detection of Zn$^{2+}$ (Figure 1). The chemosensor performs remarkably with the addition of Zn$^{2+}$ compared to other metal ions with enhanced fluorescence intensity. The free probe of AFCMSH shows no fluorescence emission, the addition of Zn$^{2+}$ ions causes a significant fluorescence emission with over 15-fold. The molecular structure of AFCMSH in the ground state was optimized using density functional theory (DFT) calculation to give an initial assumption where the most probable sites during chelation.

2. Experimental

2.1. Materials and measurements

All materials and solvents for the synthesis were purchased from Acros and Aldrich and were used without further purification. The ligand AFCMSH was synthesized by method in previous literature [9]. The ligand was characterized by different spectroscopic method. Infrared spectra were obtained from Thermo Nicolet Nexus using KBr pellets. UV-vis spectra were recorded on Agilent, Cary 60 spectrophotometer. Melting point of ligand was obtained from Stuart Scientific Melting Point Apparatus SMP3. The $^1$H-NMR and $^{13}$C-NMR spectra were obtained from Jeol, JNM-ECX-500. Fluorescence spectra were recorded using Agilent, Cary Eclipse. The mass spectra for ligand were collected from Central Laboratory, Universiti Malaysia Terengganu using Gas Chromatograph Mass Spectrometer GCMS-QP2010.

2.2. Synthesis of ligand, AFCMSH

The proposed structure of AFCMSH was given in Figure 1. Mass of 0.189 g (1 mmol) of 2-amino-3formylchromone was dissolved in 15 mL ethanol, and was added gradually to 0.186g (1 mmol) of 4-methylbenzenesulfonhydrazide, dissolved in 15 mL ethanol. The reaction mixture was refluxed for 24 h. The resulting yellow precipitate was filtered-off, washed with cold ethanol, and dried in desiccator. Yield, 70%, m.p: 260 °C. FT-IR (KBr, cm$^{-1}$): ν = 3196 (N-H), 1644 (C=O), 1605 (C=N), 1310 (S=O$_2$), 1158 (S=O$_3$). UV-vis: (DMSO): $\lambda_{\text{max}}$/nm ($\varepsilon$/mol$^{-1}$Lcm$^{-1}$) 282, 207. MS (m/z): 357. $^1$H NMR (DMSO-d$_6$, 400 MHz): $\delta$ 11.04 (1H, s, N-H$_2$), $\delta$ 8.25 (3H, s, CH$_2$=N-N-H$_3$), $\delta$ 7.90 (1H, d, H$_6$), $\delta$ 7.90 (1H, d, H$_8$), $\delta$ 7.36 (1H, m, H$_7$), $\delta$ 7.36 (1H, m, H$_9$), $\delta$ 7.32 (1H, m, H$_{10}$), $\delta$ 7.22 (3H, s, C-H$_{25, 26, 27}$). $^{13}$C NMR (DMSO-d$_6$, 400 MHz): δ 173.8 (C$_{12}$), 163.0 (C$_{14}$), 153.1 (C$_{13}$), 145.5 (C$_{23}$), 144.2 (C$_{16}$), 136.0 (C$_{18}$), 133.9 (C$_7$), 130.3 (C$_{29}$), 127.6 (C$_{21}$), 125.6 (C$_{31}$), 125.5 (C$_{33}$, C$_{35}$), 121.8 (C$_{28}$), 117.2(C$_{19}$), 92.6 (C$_{15}$), 31.2 (C$_{17}$), 21.5 (C$_{24}$).
2.3. Computational method
The molecular structure of AFCMSH in the ground state was optimized using density functional theory (DFT) by a hybrid functional B3LYP (Becke’s three parameter hybrid functional using the Lee, Yang, and Parr correlation functional) methods at 6-311G(d,p) basis set. The calculation was performed on a personal computer using Gauss View 5.0 molecular visualization program [12] and Gaussian 09W program package [13] without specifying any symmetry for the title molecule. In addition, the NBO analysis of the compound was also calculated at the B3LYP/6-311G(d,p) level.

2.4. Analysis of fluorescence property
Stock solutions of metal acetate salts of Zn\textsuperscript{2+}, Cu\textsuperscript{2+}, Co\textsuperscript{2+}, Hg\textsuperscript{2+}, Mn\textsuperscript{2+}, Ni\textsuperscript{2+} and Pb\textsuperscript{2+} (1 mM) in DMSO were prepared. Stock solution of AFCMSH (1 mM) was prepared in DMSO. Test solution for selectivity study was prepared by adding 15 µL of the probe solution into cuvette, later, appropriate aliquot of each metal ions stock solution were added into the cuvette and let to rest for 5 min. The solution was diluted to 3 ml with DMSO solution. Both excitation and emission slit widths for the analysis was set to 5 nm. The excitation wavelength was set to 375 nm.

3. Results and Discussion
3.1. General characterization
The structure of the ligand was explained by IR, UV-Vis spectra, 'H NMR, \textsuperscript{13}C NMR and mass spectra. The IR spectral of the ligand showed characteristic absorption bands at 3368 and 3196 cm\textsuperscript{-1} assigned to \(\nu(\text{NH}_2)\) and \(\nu(\text{NH})\). The absorption bands at 1644, 1605, 1307 and 1158 cm\textsuperscript{-1} were attributed to \(\nu(C=O\text{ketone})\), \(\nu(C=N)\), \(\nu(S=O\text{as})\) and \(\nu(S=O\text{s})\) respectively. The electronic spectral data of AFCMSH in DMSO were observed for having two bands at 282, and 207 nm. Addition of Zn\textsuperscript{2+} showed a new emission peak at 375 nm. The structure of ligand was further supported by \textsuperscript{1}H NMR spectral data (\(\delta\) ppm) dissolved in DMSO-\textsuperscript{d6}. \textsuperscript{1}H NMR spectra showed that the ligand was completely synthesized with \(\delta\) 11.04 signal was assigned for N-H and \(\delta\) 8.25 signal was assigned for C=O. \textsuperscript{13}C NMR spectra obtained showed there are seventeen signals which have the same amount of C in AFCMSH. The mass spectra give out 357 m/z similar to the molecular weight of AFCMSH 357 g/mol.

3.2. Optimized structure of AFCMSH
Quantum chemical calculations were carried out using density functional theory (DFT) at the B3LYP/6-311G(d,p) level to obtain the optimized structural parameters and determine the properties of the frontier molecular orbitals. Molecular Electrostatic Potential (MEP) is studied to determine the probability of coordination properties of AFCMSH ligand. The optimized structure of ligand was shown in Figure 2 with atoms numbering. The selected structural parameters of ligand (bond lengths and bond angles) computed from the DFT-B3LYP/6-311G(d,p) basis set level calculation are listed in Table 1.
Figure 2. The optimized structure of AFCMSH.

Table 1. Selected bond lengths (Å) and angles (°) determined by B3LYP/6-311G(d,p) theoretical calculations.

| Bond length | Value (Å) | Bond Angle | Value (°) |
|-------------|-----------|------------|-----------|
| S1-O4       | 1.4239    | O4-S1-O5   | 120.1708  |
| S1-O5       | 1.4208    | O4-S1-N7   | 109.1767  |
| S1-N7       | 1.6193    | O4-S1-C18  | 107.8171  |
| S1-C18      | 1.7525    | O5-S1-N7   | 103.4074  |
| O2-C13      | 1.3721    | N7-S1-C18  | 106.5971  |
| O2-C14      | 1.3330    | C13-O2-C14 | 118.7329  |
| O3-C32      | 1.2318    | N7-N6-C16  | 113.6930  |
| N6-N7       | 1.3791    | C9-C11-C13 | 118.7535  |
| N6-C16      | 1.2705    | C9-N7-N6   | 119.7689  |
| N7-H8       | 0.8594    | C11-C9-C31 | 121.8083  |
| C9-H10      | 0.9302    | C9-C11     | 116.9712  |
| C9-C11      | 1.3718    | O2-C13-C11 | 116.9712  |
| C9-C31      | 1.3923    | O2-C13-C28 | 121.5257  |
| C14-N37     | 1.4700    | O2-C14-C15 | 125.0063  |
| C15-C16     | 1.4484    | O2-C14-N37 | 117.5023  |
| C16-H17     | 0.9301    | C15-C14-N37| 117.4914  |
| C18-C19     | 1.3699    | C14-C15-C16| 123.0689  |
| C21-C23     | 1.3810    | N6-C16-C15 | 124.0056  |
| C23-C24     | 1.5004    | N6-C16-H17 | 118.0472  |
| C24-C25     | 0.9604    | S1-C18-C19 | 119.0016  |
| C28-C29     | 1.4048    | C14-N37-H38| 109.4712  |

Most of the calculated bond lengths and bond angles were slightly different from experimentally reported in related ligands. For example the reported experimental bond lengths of S=O, S-N, C=N, NN, C=O and C-O are 1.4240(15)-1.436(15) Å, 1.6336(17)-1.6448(17) Å, 1.274(2)-1.282(3) Å, 1.3969(19)-1.433(2) Å, 1.223(2)-1.233(2) Å, 1.344(2)-1.348(2) Å respectively [14-17]. Meanwhile the reported experimental bond angles of O=S=O, N-S=O, N-N-S, C=N-N were 119.23(10)119.94(9)°, 103.87(9)-104.12(9)°, 113.01(13)-113.54(12)°, 111.66(16)-115.26(15)° respectively [14, 15]. The differences due to the theoretical calculations were carried out for the gas phase and the experimental results were for the solid phase. Furthermore it could be affected by the existence of a crystal field along with the intermolecular interactions of hydrogen bonds that connect the molecules together in solid phase [18].
3.3. Frontier molecular orbitals analysis

Frontier molecular orbitals analysis provides important information on the electrical and optical properties, as well as in electronic absorption and chemical reactions. The ability of molecule to donate an electron can be explained by the highest occupied molecular orbital (HOMO), while the view of ability to gain an electron can be described from the lowest unoccupied molecular orbital (LUMO) [18, 19]. The HOMO and LUMO for the title compound were calculated at B3LYP/6311G (d,p). Figure 3a showed the view of electron excitation from the ground state HOMO to the excited state LUMO.

In the ground state of HOMO, the charge density are mainly located on the sulfonyl (SO$_2$), azomethine (C=N), amino group and carbonyl (C=O) functional groups of the ligand. The charge density spread over to the other chromone ring in the case of LUMO. Thus, the HOMO→LUMO electron transition potentially occurs from sulfonohydrazone to chromone moieties with 5.493 eV. The highly charge density of HOMO gives a hypothesis that the oxygen and nitrogen atoms are the potential atoms for intra- or intermolecular interaction and metallic bonding [19].

3.4. Molecular electrostatic potential

Molecular electrostatic potential (MEP) study was carried out to visual more the most probable coordination sites. In the present study, MEP was calculated at the B3LYP/6-311G(d,p) optimized geometry produced 3D plots as illustrated in Figure 3b. The negative region with maximum electron charge value of -0.503 e and -0.481 e is indicated as red colour located at O4 and O5 which belong to sulfonyl oxygen atoms. The other negative region also occurred at O3 that belong to carbonyl oxygen atom in chromone moiety with high electron charge value of -0.0352 e. Both negative regions provide information where the probability of preferred site for electrophilic attack [20]. Meanwhile the probability of preferred site for nucleophilic attack is observed as deep blue colour or maximum positive region occurred around H-N37 (0.278 e) and H-N7 (0.261 e) surface [20]. The probabilities of coordination sites information given by MEP calculation is in good agreement with HOMO-LUMO.

3.5. Fluorescence study

The emission changes were investigated in order to obtain information on the fluorescent behavior of AFCMSH. For this purpose, 1.0 eq. ligand was reacted with 1.0 eq. metal ions such as Co$^{2+}$, Cu$^{2+}$, Hg$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ in DMSO and diluted to 3 ml. The addition of metal ions such Co$^{2+}$, Cu$^{2+}$, Hg$^{2+}$, Mn$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ showed colour change from colourless to light yellow except of Pb$^{2+}$ when observed with naked eye (Figure 4a). However, under UV light, the reaction between AFCMSH and Zn$^{2+}$ give out an intense yellow-green fluorescence compared to other ions (Figure 4b). When viewed
under UV light, AFCMSH showed no or slight fluorescence property when treated with other metal ions. Fluorescence spectra were obtained by exciting AFCMSH at 375 nm. Ligand showed an interesting behavior towards Zn$^{2+}$ compared to other metal ions. New emission peak was observed at 501 nm upon addition of Zn$^{2+}$ (Figure 5a). The addition of other ions showed such as Co$^{2+}$, Cu$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ showed no changes in the fluorescence property of AFCMSH except a slight increase in fluorescence spectra of Mn$^{2+}$ and Ni$^{2+}$.

![Figure 4](image4.png)

**Figure 4.** Colour changes of AFCMSH when treated with 1.0 eq. metal ions when observed with naked-eye (a) and under UV light (b).

![Figure 5](image5.png)

**Figure 5.** (a) Fluorescence emission spectra of AFCMSH when treated with 1.0 eq. different metal ions and (b) Fluorescence emission spectra when treated with 0-1.0 eq. of Zn$^{2+}$.

Further study of the fluorescence property of AFCMSH was conducted via fluorescence titration experiment by adding 0-1.0 eq. Zn$^{2+}$ solution to the AFCMSH solution of 25 µl and diluted to 3 ml using DMSO. The addition of Zn$^{2+}$ showed shifting in the emission peak of the ligand from 441 nm to 501 nm (Figure 5b). The fluorescence intensity of the mixed solution also increased by 15-fold which prove the intense yellow-green fluorescence property of AFCMSH-Zn. From the results, AFCMSH can be used as a sensitive chemosensor to detect Zn$^{2+}$.

3.6. Binding study
From IR spectra, the assigned stretching of carbonyl of chromone 1644 cm$^{-1}$ reduced to lower frequency of 1630 cm$^{-1}$ after addition of Zn$^{2+}$. The vibration of C=N also shifted from 1605 cm$^{-1}$ to 1600 cm$^{-1}$. The changes in vibrational stretching suggest that Zn$^{2+}$ coordinated with carbonyl group of chromone and nitrogen from azomethine. The absence of v(N-H) vibrations after addition of Zn$^{2+}$ suggesting the proton on the amine nitrogen atom is lost upon the complexation [21]. The weaker intensity of v(S=O) at 1340 cm$^{-1}$ together with the appearance of new band at 1086 cm$^{-1}$ assigned to the binding v(SO$_2$) group might give out the possibilities of coordination between oxygen from S=O with Zn$^{2+}$. The band at 508 cm$^{-1}$ was assigned to v(Zn-O), which demonstrated formation of a coordinative bond between zinc and oxygen while for v(Zn-N) was assigned at 421 cm$^{-1}$ for coordination between zinc and nitrogen. The result was in a good agreement with the information given by the Frontier molecular orbitals analysis.
and Molecular electrostatic potential that the probabilities coordination are via oxygen and nitrogen atoms.

The absorption titration experiment was also conducted to determine the binding of AFCMSH with Zn$^{2+}$. Using 0.1-1.0 eq. volume of Zn$^{2+}$, the solution of metal ion was reacted with 1.0 eq. volume of AFCMSH. The electronic spectrum observed for free ligand AFCMSH exhibited two peaks at 282 and 207 nm at room temperature (Figure 6). The highest energy bands are assigned to π–π$^*$ transitions within the aromatic rings while the moderate energy bands can be assigned to n–π$^*$ transitions within C=O and C=N groups [22]. Upon treatment with Zn$^{2+}$, the absorption band at 282 and 207 nm gradually decreased, while a new peak was observed at 375 nm and gradually increased absorption intensity with the addition of Zn$^{2+}$. The new peak at 375 nm was assigned as charge transfer transition band indicating that the coordination between AFCMSH and Zn$^{2+}$ lead to the fluorescence emission of the ligand [9]. The appearance of isosbestic point at 343 nm and the shifting of absorption bands after addition of Zn$^{2+}$ implies that ligand AFCMSH bonded with Zn$^{2+}$ to form AFCMSH-Zn$^{2+}$ [23].

The $^1$H-NMR data of AFCMSH and its treatment with Zn$^{2+}$ were recorded in Table 2. The signal of H8(N-H) and H-17(CH=N) were δ 11.04 and δ 8.25 respectively. Upon addition of Zn$^{2+}$, the signal of H-8 disappeared completely while the signal for H-17 remains but shifted to higher field by δ 0.05. The remaining signals for protons in the benzene rings remain unchanged even after the addition of Zn$^{2+}$. This indicates the involvement of carbonyl of chromone moiety and the nitrogen atom of the –C=N group coordinated with Zn$^{2+}$.

|                  | -NH(H-8) | -N=CH(H-17) |
|------------------|----------|-------------|
| AFCMSH           | 11.04    | 8.25        |
| AFCMSH + Zn$^{2+}$ | -        | 8.30        |
| Change in δ      | -        | 0.05 (up-field) |

Theoretically the very low emission intensity of the ligand was due to quenching by the carbonyl group through a photoinduced electron transfer (PET), induced by the lone pair electrons from the ligand. The coordination AFCMSH to Zn$^{2+}$ through M-N (imine nitrogen atom) and M-O (carbonyl and sulfonyl oxygen atoms) was believed to enhance the fluorescence output via chelation-enhanced fluorescence (CHEF) effect by interrupting the PET process, thus give the “OFF-ON” fluorescence signal in the presence of Zn$^{2+}$ [21].

To the best of our knowledge, there is no report regarding the potential turn-on fluorescence selective towards Zn$^{2+}$ using AFCMSH ligand and our present findings show that it is worth exploring more in the future. Thus, studies of sensitivity against other competing metal ions and the limit of detection should be investigated to confirm the ability of ligand to serve as a practical chemosensor in detecting Zn$^{2+}$.
4. Conclusion
In summary, we have successfully synthesized chromone-based ligand (AFCMSH) which has potential to be used in detecting Zn$^{2+}$. The compound exhibited high selectivity for Zn$^{2+}$ over other metal ions with over 15-fold fluorescence enhancement. The finding also showed the compound has a good fluorescence behavior which emits yellow-green fluorescence when viewed under UV light compared to other metal ions. Thus, we believed AFCMSH had the ability to be used as a potential fluorescent chemosensor for detecting Zn$^{2+}$ in environment. In addition, we believed that the oxygen atom of sulfonyl moiety and azomethine nitrogen donor atoms play important role in coordination with Zn$^{2+}$ ion. This study might provide a general insight for designing and producing new sensors useful to detect zinc contaminant in the environments.

5. References
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