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ARTICLE

A New Highly Zn²⁺-Selective and “Off-On” Fluorescent Chemosensor Based on Pyrene Group

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In this work, an “Off-On” type zinc ion fluorescent chemosensor H₂L with pyrene as fluorophore was investigated. The chemosensor H₂L demonstrates a Zn²⁺-specific emission enhancement linearly with a 1:1 binding ratio even in the presence of a wide range of competing metal ions. This may be correlated to the efficient Zn²⁺ binding of H₂L, which promotes a good chelation-enhanced fluorescence (CHEF) effect and prevents the photoinduced electron transfer (PET) effect, and C=N isomerization is inhibited. Importantly, the fabricated chemosensor can selectively distinguish Zn²⁺ from Cd²⁺. And the recognition behaviour has been proved experimentally and computationally.

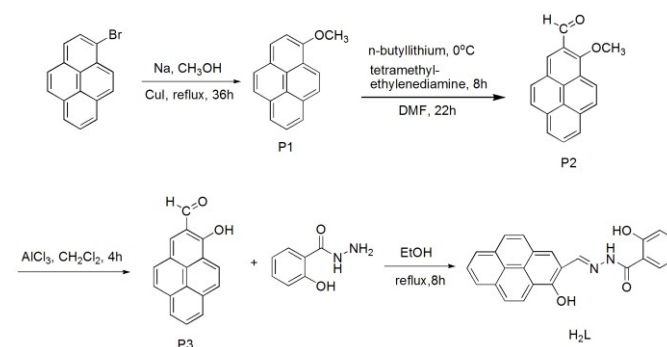
1. Introduction

Zn²⁺ is an essential element for normal growth and development of human body^{1,2}. It plays a key role in cellular processes such as DNA repair³ and apoptosis⁴ as well as in the synthesis of insulin and the pathological state of diabetes.⁵ Failing to maintain zinc homeostasis has been implicated in a number of severe neurological diseases.⁶ As a consequence, the development of novel fluorescent chemosensors for detecting Zn²⁺ accurately has received considerable attention.⁷ Although, a number of fluorescent chemosensors for Zn²⁺ based on quinoline⁸, fluorescein⁹, coumarin¹⁰, and peptides¹¹ have been reported to date, there is still a challenge to develop chemosensors that can selectively detect Zn²⁺ from Cd²⁺ as these two cations setting in the same group of the periodic table, have similar chemical properties, thus causing similar spectral changes after interacting with chemosensors.

Recently, particular attention has been paid to the synthesis and study of metal complexes of Schiff bases.¹² Some of the Schiff base metal complexes possess antitumor properties,¹³ antioxidative activities,¹⁴ and attractive electronic and photophysical properties¹⁵. In addition, Schiff base derivatives incorporating a fluorescent moiety are appealing tools for fluorescent sensing of metal ions. Schiff base is very easy to synthesize by reaction of aldehyde and amine, what is more, the nitrogen atom of amine could coordinate with metal ion. Consequently, organic molecule possessing Schiff

base structure has potential application in sensors.

In this work, we designed chemosensor H₂L using pyrene as fluorophore, and 2-hydroxybenzohydrazide as ionophore to construct a small organic molecule containing Schiff base motif. Schiff base structure was obtained by the reaction of 1-hydroxypyrene-2-carbaldehyde and 2-hydroxybenzohydrazide in boiling ethanol with satisfactory yield. In this compound, the Zn²⁺ chelator 2-hydroxybenzohydrazide was incorporated with 1-hydroxypyrene-2-carbaldehyde at its formyl group position as the synergic Zn²⁺ coordination motif. Then, both 1:1 binding mode between Zn²⁺ and H₂L and higher Zn²⁺ binding affinity were expected. The synthetic route of H₂L is depicted in Scheme 1.



Scheme 1. Synthetic route of the fluorescent chemosensor H₂L.

2. Experimental section

2.1. Materials, methods and instrumentation

All chemicals were purchased from commercial suppliers and used without further disposal. ¹H NMR spectra were obtained at 400 MHz and ¹³C NMR spectra at 100 MHz with JEOL RESONANCE spectrometer in *d*₆-DMSO solution with DMSO as an internal standard and in CDCl₃ solution with tetramethylsilane (TMS) as an internal standard. Elemental analysis were conducted using an

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Elementar Vario EL. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 360 FT-IR spectrometer using KBr pellets in the range of 4000–400 cm^{-1} . UV-vis absorption spectra were determined on a Varian UV-Cary100 spectrophotometer. Hitachi F-4500 fluorescence spectrophotometer was used to record on steady state luminescence spectra. ESI-MS spectra were determined on a Bruker Daltonics Esquire 6000 spectrometer.

All of the detections of metal ions were operated in tris(hydroxymethyl)aminomethane (Tris)-HCl (20 mM, pH 7.36), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v). The stock solution of **H₂L** (1, 10 mM) was prepared in DMSO solution. Stock solutions of the perchlorate salts of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+} , Al^{3+} , Pb^{2+} , Cr^{3+} , Cd^{2+} , Ag^+ , Fe^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} and Hg^{2+} (10 mM) were prepared in doubly distilled water, respectively. The volume of cationic stock solution added was less than 100 μL to maintain the concentration of **H₂L** unchanged. All fluorescence spectra were recorded at 25 $^\circ\text{C}$ with the excitation wavelength of 490 nm.

2.2. Calculation methods

To investigate the interaction mode, we carried out density functional theory (DFT) calculations with B3LYP/6-31G(d) method. The geometry of the molecules was optimized with Gaussian 09¹⁶ package at the B3LYP/6-31G(d) levels for C, H, O, N atoms and LANL2DZ¹⁷ levels for Zn.

2.3. Synthesis of chemosensor **H₂L**

The synthesis was performed according to literature¹⁸ as follows: 1-Hydroxypyrene-2-carbaldehyde (160 mg, 0.65 mmol) and 2-hydroxybenzohydrazide (98 mg, 0.65 mmol) were mixed in boiling ethanol with stirring for 6 hours under Ar, then yellow precipitates was filtered, washed with ethanol and dried at 50 $^\circ\text{C}$ under vacuum to give **H₂L** (173 mg, 0.46 mmol, 70%) as a yellow solid. FT-IR (KBr disc, cm^{-1}): 3442, 3039, 16131 (C=O), 1608, 1561, 1542, 1492, 1459, 1348, 1305, 1236, 1218, 1160, 1096, 841, 751. Anal. Calcd for $\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_3$: C, 75.71; H, 4.21; N, 7.36. Found: C, 75.52; H, 4.29; N, 7.47. ^1H NMR (400 MHz, DMSO): δ 12.38 (1H, s), 11.70 (1H, s), 8.45 (1H, d), 8.37 (1H, s), 8.16 (3H, t), 8.05 (2H, m), 7.92 (2H, d), 7.50 (1H, t), 7.03 (2H, m). (Figure S1). ^{13}C NMR (100 MHz, DMSO): δ 162.9, 160.4, 150.6, 141.6, 141.1, 136.2, 132.5, 132.1, 128.8, 127.5, 127.4, 126.7, 125.9, 124.3, 124.1, 123.9, 122.2, 121.7, 117.6. (Figure S2). MS (ESI+): m/z 381.1 (M+H)⁺ (Figure S3).

3. Results and discussion

The perchlorate salts of different metal ions were used to evaluate the binding property between the metal ions and chemosensor **H₂L**. The fluorescent spectroscopic properties of **H₂L** were studied in Tris-HCl (20 mM, pH 7.36), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v) solution after systematically looking for selective signalling towards various tested metal ions for potential applications. As shown in Fig. 1, the emission spectrum of **H₂L** exhibited the emission maximum at 556 nm with low fluorescence intensity when pyrene as fluorophore was excited at 490 nm ($\Phi = 0.033^{19}$). A significant fluorescence emission intensity enhancement was observed after addition of 1.0 equiv of Zn^{2+} to $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ buffer solution containing equivalent

molar of **H₂L** ($\Phi = 0.279$). The increase in emission intensity may be attributed to the formation of the **L-Zn** complex. When **H₂L** was coordinated with zinc ion, a large CHEF effect was observed because the stable complexation between **H₂L** and Zn^{2+} prohibited the PET process from the electron-donating group to the pyrene fluorophore ("On" state). In addition, the stable chelation of **H₂L** with zinc ion not only inhibited the C=N isomerization but also enhanced fluorescence intensity of **H₂L**²⁰. The emission intensity of **H₂L** was slightly quenched upon addition of Cu^{2+} , Co^{2+} and Ni^{2+} , which may be attributed to intrinsic paramagnetism of these metal ions^{12c}. Other metal ions such as Na^+ , K^+ , Mg^{2+} , Al^{3+} , Ca^{2+} , Cr^{3+} , Cd^{2+} , Mn^{2+} , Fe^{3+} , Hg^{2+} and Ag^+ had little effect on the fluorescence spectra of **H₂L**. These results showed the capability of chemosensor **H₂L** for distinguishing Zn^{2+} from other metals ions, in particular from Cd^{2+} . Moreover, the stability constant value of **H₂L** for Zn^{2+} was determined to be $7.01 \times 10^5 \text{ M}^{-1}$ (Figure S4). Therefore, chemosensor **H₂L** showed a significant fluorescence enhancement only with Zn^{2+} among the various metal ions examined including Cd^{2+} , indicating the higher selectivity of **H₂L** towards Zn^{2+} .

To further explore the selectivity of **H₂L** to Zn^{2+} , the intensity of **H₂L** in the presence of Zn^{2+} mixed with plentiful of various metal ions in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v) solution at pH 7.36 in Tris-HCl (Fig. 2) buffer was measured. A range of competing metal ions were mixed with the **H₂L** prior to addition of 1 equiv of Zn^{2+} . The test results of the above system showed that 5 equiv Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Hg^{2+} , Ag^+ , Cd^{2+} , Mn^{2+} , Cr^{3+} and Ni^{2+} had no or little effect on the chemosensor **H₂L** in detecting Zn^{2+} . However, Zn^{2+} -induced fluorescence enhancement of **H₂L** was prevented by the addition of 1 equiv Cu^{2+} and Co^{2+} . This may be ascribed to that these two metal ions would remain binding with the sensor **H₂L** and thus preventing the fluorescence enhancement²¹, even in the presence of 1 equiv of zinc ions.

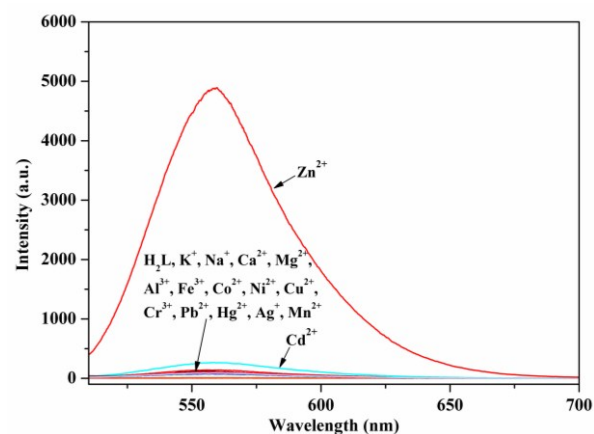


Fig. 1. Fluorescence spectra of **H₂L** in the presence of various metal ions such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+} , Al^{3+} , Pb^{2+} , Cr^{3+} , Cd^{2+} , Ag^+ , Fe^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} and Hg^{2+} in Tris-HCl (20 mM, pH 7.36), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v). Excitation wavelength was 490 nm. [**H₂L**] = 50 μM , [M^{n+}] = 50 μM .

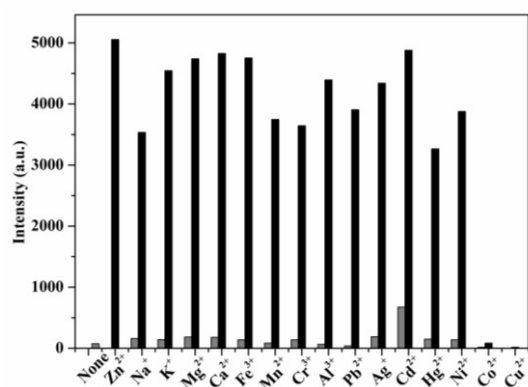


Fig. 2. Selectivity of **H₂L** for Zn^{2+} in the presence of other metal ions in Tris–HCl (20 mM, pH 7.36), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v), Excitation wavelength was 490 nm. Gray bars represent the addition of an excess of the appropriate metal ion (5.0 equiv Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cd^{2+} , Cr^{3+} , Al^{3+} , Mn^{2+} , Fe^{3+} , Hg^{2+} , Ag^+ , Pb^{2+} , Ni^{2+} , 1.0 equiv Cu^{2+} , Co^{2+}) to a 50 μM solution of **H₂L**. Black bars represent the subsequent addition of 1.0 equiv Zn^{2+} to the solution.

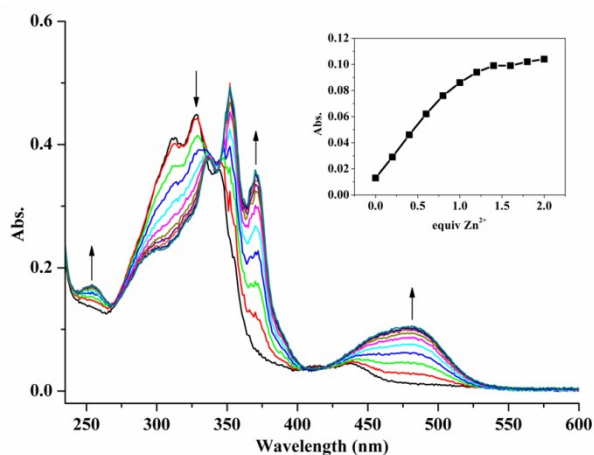


Fig. 3. UV–vis spectra of **H₂L** (10 μM) upon the titration of Zn^{2+} (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 equiv) in Tris–HCl (20 mM, pH 7.36), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v) at room temperature. The inset shows the plot of absorbance of **H₂L** at 478 nm versus Zn^{2+} concentration.

To investigate the binding property of chemosensor **H₂L** for Zn^{2+} , the UV–vis spectra of **H₂L** (10 μM) in the presence of a wide range of concentrations of Zn^{2+} (0–20 μM) was measured. Fig. 3 showed the absorbances at the 254, 370 and 480 nm bands increased while the band at 312 nm decreased. Two isosbestic points were observed at 269 and 342 nm, clearly indicating that the **H₂L** and the Zn^{2+} formed only one visible active zinc complex. The spectra change showed the binding mode between **H₂L** and Zn^{2+} was a 1:1 stoichiometry. Furthermore, the Job's plot suggested the stoichiometry of complex formed by **H₂L** and Zn^{2+} was also 1:1 (Fig. S5), this result further indicated that only a 1:1 complex was formed in the media. Free **H₂L** in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v) solution at pH 7.36 in Tris–HCl (Fig. 4) buffer showed weak fluorescence with the maximum emission band at 556 nm. Upon addition of

Zn^{2+} (0–1.0 equiv) to the above buffer, the emission intensity increased linearly. When the ratio reached to 1:1, however, higher $[\text{Zn}^{2+}]_{\text{total}}$ did not lead to any further fluorescence enhancement. The fluorescence addition result indicated the chemosensor **H₂L** can preferentially recognise Zn^{2+} , and exhibited a turn “On” state, which further demonstrated the complex formed between **H₂L** and Zn^{2+} was 1:1 stoichiometry. The limit of detection (LOD) for Zn^{2+} was measured to be $1.38 \times 10^{-6} \text{ M}$ (Figure S6).

In order to investigate the coordination configuration of **H₂L** to Zn^{2+} , we carried out theoretical calculations of binding energy of **H₂L** and Zn^{2+} . In theoretical calculations, the geometry of the molecules was optimized with Gaussian 09 package at the B3LYP/6-31G(d) levels for C, H, O, N atoms and LANL2DZ levels for Zn. The minimum nature of the structure was confirmed by frequency calculations at the same computational level. Fig. 5 showed the optimized configurations of binding mode of **H₂L** Zn^{2+} . All atoms of C, N, O were nearly in a plane, which showed that only one Zn^{2+} occupied the coordination centres of **H₂L** well and one cavity was formed by the chemosensor, suitable for coordinating Zn^{2+} , irrespective to the impact of solvent molecule and perchlorate ion. The bond lengths were obtained from the natural bond orbital (NBO) analysis. The Zn–N bond length was 2.043 Å and the two Zn–O bond lengths were 1.856 Å, 1.883 Å, respectively. The interaction energy of between **L²⁻** with Zn^{2+} was $-830.52 \text{ kcal mol}^{-1}$. The result demonstrated the chemosensor can effectively detect Zn^{2+} .

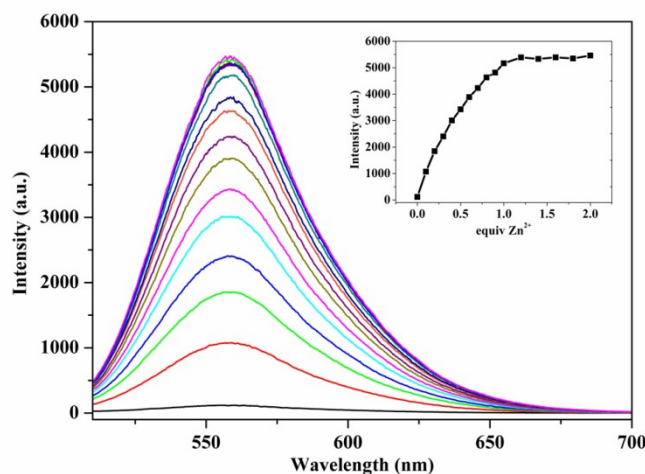


Fig. 4. Fluorescence emission spectra of **H₂L** (50 μM) upon addition of Zn^{2+} (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 equiv) with respect to **H₂L** in Tris–HCl (20 mM, pH 7.36), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v), Excitation wavelength was 490 nm. The inset is the corresponding Zn^{2+} titration profile according the emission at 556 nm.

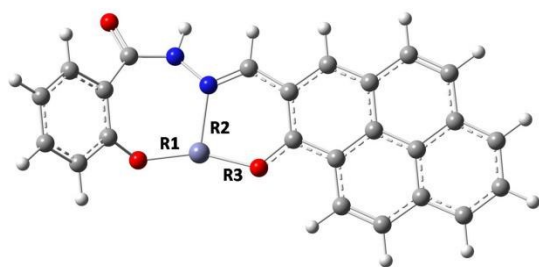


Fig. 5. Calculated energy-minimized structures of complex **L-Zn**.

4. Conclusions

In conclusion, we have successfully developed a new highly selective and sensitive fluorescent chemosensor for Zn^{2+} over other competing cations including Cd^{2+} . DFT calculations also demonstrated that the chemosensor had high selectivity for Zn^{2+} . The fluorescent enhancement may be attributed to chelation-enhanced fluorescence, which is resulted from the strong coordination ability of Zn^{2+} with **H₂L**, the PET process and the inhibition of $C=N$ isomerisation. These results indicated that pyrene group as fluorophore was valuable for designing fluorescent chemosensor.

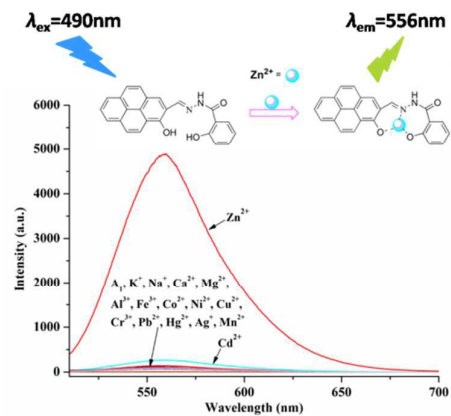
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TOC Image:



A highly selective for zinc ion fluorescent chemosensor H_2L based on pyrene derivative was described. Importantly, this chemosensor can clearly distinguish Zn^{2+} from Cd^{2+} .