Contents lists available at ScienceDirect



Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

A: Chemistry

Development of a sensitive and selective fluorescent probe for Zn^{2+} based on naphthyridine Schiff base



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ARTICLE INFO	A B S T R A C T
Keywords: Fluorescent probe Schiff-base Zinc ion Synthesis Selectivity	In this study, bearing 4-methyl-7-acetamide-1,8-naphthyridyl group as the fluorophore and the receptor, we designed and synthesized a new-type Schiff-base ligand 1 which was identified as a Zn^{2+} fluorescent probe. The excellent selectivity and high sensitivity of this as-synthesized fluorescent probe 1 towards Zn^{2+} over other various biogenic metal ions were observed, for that only Zn^{2+} induced a drastic enhancement by about 63-fold in intensity of fluorescence emission at 504 nm, and the limit of detection (<i>LOD</i>) could reach 7.52 nM. Moreover, the formation of a 2:1 complex between this probe 1 and Zn^{2+} was determined, and the perfect invertibility and renewability of this probe 1 for sensing Zn^{2+} were also demonstrated. As a result, the practical applications of 1 were broadened for sensing and monitoring Zn^{2+} environmentally and biologically.

1. Introduction

More and more attention has been attracted for tracking the concentration levels of transition metals by utilizing fluorescent probes to date because of their crucial roles in various biological processes [1,2]. Among those transition metals, zinc is an element of the secondary content in the human body. Owing to its rich coordination chemistry [3-5], the structure and functionality of diverse proteins were expressed in the gene by utilizing required zinc ion as a cofactor, and zinc ion also exists in many organelles like cytoblast, plastosome and cytolysosome, etc [6-8]. However, when the amount of zinc ion in the human body exceeds the limitation of its maximum level, many severe diseases including Alzheimer's disease, Friedreich's dystaxia and Parkinson's disease can be caused [9-11]. On the other side, impaired cognitive disorders, immune dysfunction, durchfall and death can be induced by the lack of micronutrient zinc ion particularly in under 5year-old children [12,13]. Thus, Zn2+-based compounds have found wide repertoire in the fields of radiation protection, tumor sensitizing, antidiabetic activity, and anti-microbial or anti-tumor agents [14-17]. Therefore, the detection of Zn^{2+} is a significant research topic for exploring its roles in various biological processes.

The development of fluorescent probes have drawn more concerns than other optical probes among scientists due to their intrinsic advantages of high sensitivity, simplicity of operation, and real-time inspection with rapid responses [18-20], which makes the applications of these fluorescent probes broad in various fields of ecology, biology and clinical medicine [21-23]. The design and synthesis of highly selective and sensitive fluorescent probes have been a promising research field in chemistry due to their practicability and utility [24]. To date, a series of Zn^{2+} fluorescent probes with excellent selectivity and high sensitivity have been designed and synthesized on a basis of various fluorophores, including macrocycle, heterocyclic ring, rhodamine, coumarin and quinoline [25-31], but the reports about naphthyridine derived fluorescent probes are extremely few [32]. Moreover, the majority of reported Zn²⁺ fluorescent probes encounter hardness in differentiating Zn^{2+} from Cd^{2+} due to their similar chemical properties and comparable fluorescence responses [33–35]. Therefore, it is still a tremendous challenge for designing highly selective (differentiated from Cd^{2+}), temperate and efficient Zn^{2+} fluorescent probes based on naphthyridine derivatives among scientists in the prospects of analytical chemistry, biological chemistry and pharmaceutical science.

In our previous works, we reported the design and synthesis of novel Schiff-base compounds with different fluorophore units and explored their effects on the sensing of metal ions. Generally, the parts of recognition moiety and fluorophore are two units of a fluorescent probe. The building blocks of 8-naphthyridine and its derivatives always form short distances of metallic bonds, thereby applying them widely as bidentate ligands [36,37]. Additionally, an organic structure which

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https://doi.org/10.1016/j.jphotochem.2019.02.024

Received 6 December 2018; Received in revised form 19 February 2019; Accepted 20 February 2019 Available online 20 February 2019 1010-6030/ © 2019 Published by Elsevier B.V.



Scheme 1. Synthetic route of compound 1.

contains a rigid and conjugate moiety is an ideal choice for the unit of fluorophore. Based on this mechanism, compound 1 called 7-acetamidyl-4-methyl-2-formyl-1,8-naphthyridine trihydroxybenzoyl hydrazone was designed and synthesized, bearing 4-methyl-7-acetamide-1,8-naphthyridyl group as the fluorophore and the receptor for sensing Zn^{2+} (Scheme 1). A C=N bond was linked between 4-methyl-7-acetamide-1,8-naphthyridyl moiety and trihydroxybenzoyl hydrazine unit, leading to the formation of a fluorescent-sensing molecule for sensing metal cations potentially. From the experimental processes, we could observe that this compound 1 showed significant fluorescence emission enhancement with addition of Zn^{2+} , and could be recognized as an efficient probe for zinc ion detection. In addition, excellent selectivity of 1 towards Zn^{2+} over other metal cations, especially Cd²⁺, was confirmed.

2. Experimental

2.1. Materials and instrumentation

All reagents and raw materials were of analytically pure quality, originated from chemcats, and utilized as received with no further depuration needed. A microscopic melting point apparatus labeled as Beijing XT4-100x was utilized for determining melting points with no correction. Utilizing TMS (tetramethylsilane) as an interior label and DMSO-d₆ as a solvent, we utilized JNM-ECS 400 MHz instruments spectrometers for recording ¹H NMR spectra. A Bruker Esquire 6000 spectrometer was used to record mass spectra of the final product in ethanol solution. A VERTEX-70 spectrometer with KBr disks was utilized for acquiring FT-IR spectra (4000-400 cm⁻¹). A VarioEL Cube V1.2.1 analyzer was used to perform elemental analyses. A spectro-photometer labeled as Shimadzu UV-240 equipped with a 1 cm length quartz cells of optical path was utilized to obtain UV-vis absorption spectra. A Hitachi RF-5301 fluorimeter was used for measuring fluorescence emission spectra at 298 K.

2.2. Synthesis

Synthesis of 7-amidyl-2,4-dimethyl-1,8-naphthyridine (2), 7-acetamidyl-2,4-dimethyl-1,8-naphthyridine (3) and 7-acetamidyl-4-methyl-1,8-naphthyridine-2-aldehyde (4) was reported according to the previous method [38]. Synthetic route of the probe 1 was outlined in Scheme 1.

2.2.1. Synthesis of compound 1 (7-Acetamidyl-4-methyl-2-formyl-1,8naphthyridine trihydroxybenzoyl hydrazone)

Trihydroxybenzoyl hydrazine was synthesized on a basis of the method reported previously [39]. An 10 mL of ethanolic solution of trihydroxybenzoyl hydrazine (0.454 g, 1.00 mmol) was introduced into

another 30 mL of ethanolic solution containing 7-acetamidyl-4-methyl-1,8-naphthyridine-2-aldehyde (4) (0.229 g, 1.00 mmol). Then the mixture was heated to refluxing under agitation for 12 h in the atmosphere of liquid nitrogen. After completing the reaction and cooling the reaction mixture to 0 °C, the sediment was isolated by filtration, washing with absolute ethanol $(3 \times 5 \text{ mL})$ to afford compound 1 as a gray white solid (Scheme 1). Yield: 0.44 g (66.17%). m.p.: at least 300 °C. ¹H NMR (400 MHz, DMSO-d₆) (Fig. S1): δ 10.18 (s, 1H, -NH-), 9.41 (s, 1H, -NH-), 7.37 (s, 1H, H₈), 7.35 (s, 1H, H₉), 7.22 (d, *J* = 7.2 Hz, 1H, H₇), 6.86 (d, J = 7.2 Hz, 1H, -CH=N-), 6.51 (d, J = 5.7 Hz, 2H, H₆), 6.47-6.30 (m, 15H, H_{1, 2, 3, 4, 5}), 4.68 (s, 6H, $-OCH_2-$), 2.69 (s, 3H, $-COCH_3$), 2.24 (s, 3H, $-CH_3$). MS (ESI) (Fig. S2): $m/z [M + H^+]^+$ calcd 666.7043, found 666.0867; [M + Na⁺]⁺ calcd 688.6862, found 688.0592; [M + K⁺]⁺ calcd 704.7947, found 704.0249. FT-IR (KBr pellet, cm⁻¹) (Fig. S3): 3435 (s), 3065 (w), 2924 (w), 1699 (w), 1653 (m), 1612 (m), 1585 (m), 1501 (w), 1425 (w), 1404 (w), 1371 (w), 1344 (m), 1329 (m), 1240 (w), 1153 (w), 1117 (m), 1078 (w), 999 (w), 804 (w), 750 (w), 696 (w). Anal. Calcd. for C₄₀H₃₅N₅O₅ (%): C, 72.17; H, 5.30; N, 10.52; O, 12.01. found: C, 71.11; H, 5.08; N, 10.32; O, 13.49.

3. Results and discussion

3.1. UV-vis analysis

Firstly, the spectroscopic methods of UV–vis absorption and fluorescence emission were utilized for investigating the coordinative properties of compound **1** towards cations in ethanol. For UV–vis absorption method shown in Fig. 1, two strong absorption bands of compound **1** originally appeared at 353 nm and 367 nm in ethanol, which were probably assigned to π - π * transitions [40–42]. However, upon incremental addition of Zn^{2+} , these two absorption bands decreased gradually with an appearance of a novel characteristic absorption band of n- π * transition which was centered at 431 nm [40–42], inducing a clearly observed well-defined isosbestic point at 376 nm (Fig. 1), which indicated that a stable complex bearing a certain ratio of stoichiometry between compound **1** and Zn^{2+} ion was formed.

3.2. Fluorescence study

Accompanying with these UV-vis absorption changes, the changes in fluorescence emission of compound **1** upon addition of a series of metal cations were also conducted in ethanol, and the corresponding spectra were depicted in Fig. 2 (a). Almost no fluorescence emission emerged in compound **1** alone when it was excited at 431 nm, but an appearance of a new emission band centered at 504 nm accompanied by a sharp enhancement (*ca.* 63-fold) in its intensity was obtained with the addition of Zn^{2+} . Nevertheless, no obvious changes in the emission



Fig. 1. UV-vis absorption spectra of 1 (10 μ M) in the presence of increasing amounts of Zn²⁺ (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 *equiv.*, respectively) in ethanol.

spectra were produced in the cases of other metal cations like Al^{3+} , Ba^{2+} , Ca^{2+} , Cd^{2+} , Cr^{3+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Hg^{2+} , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} and Pb^{2+} under the identical conditions (Fig. 2 (a)), which suggested that the significant enhancement in fluorescence emission was only caused by Zn^{2+} , thereby providing the method of sensing Zn^{2+} by compound 1 with excellent selectivity.

To study the influences of other various metal ions and counteranions on the binding property of compound 1 with Zn²⁺, 1 equiv. of Zn^{2+} mixing with 5 *equiv*. of other metal cations or counter-anions was introduced into the ethanolic solution of **1**. As illustrated in Fig. 2 (b) and Fig. S4, emission quenching of fluorescence was observed upon mixing of Zn^{2+} with Co^{2+} , Cr^{3+} , Cu^{2+} and Fe^{2+} , and the fluorescence emission intensity at 504 nm also decreased to a certain degree in 1- Zn^{2+} solution in the existence of Mg^{2+} , Mn^{2+} and Al^{3+} . Nevertheless, the intensity of fluorescence emission at 504 nm of 1-Zn^{2+} in the existence of other metal cations and counter-anions was nearly identical to that of $1-Zn^{2+}$ alone. As for as Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{2+} and Mn^{2+} , these five metal cations bearing the paramagnetic properties have pronounced quenching effects on fluorophores due to the mechanism about the electron or energy transfer from photoinduced metal cation to fluorophore [43,44]. However, another two metal cations (Mg²⁺ and Al^{3+}) slightly interfered with the detection of Zn^{2+} by compound 1, but



Fig. 3. Change in fluorescence emission spectra of 1 (10 μ M) upon addition of various amounts of Zn²⁺ (0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00 *equiv*., respectively) in ethanol with an excitation at 431 nm.

it was nearly detectable (Fig. 2 (b) and Fig. S4). These results indicated that most of other metal ions and counter-anions did not affect the detection of Zn^{2+} by compound 1, and excellent selectivity of 1 towards Zn^{2+} over most of other environmentally and biologically important metal cations and counter-anions was confirmed, which provided the utility of this compound 1 for practical applications.

Subsequently, we carried out the fluorescence titration experiments for binding compound 1 with Zn^{2+} in ethanol. As illustrated in Fig. 3, negligible emission band of fluorescence was observed in compound 1 alone with excited at 431 nm. However, the gradual addition of Zn^{2+} to compound 1 solution led to an appearance of a new band of emission centered at 504 nm accompanied by the enhancive intensity. Moreover, a plateau was reached in intensity of fluorescence emission at 504 nm with addition of 0.5 *equiv*. of Zn^{2+} (Fig. 3), giving a solid evidence for a 2:1 coordinative stoichiometry of compound 1 with Zn^{2+} . The above fluorescence titration experiments gave an excellent linear dependence between the intensity of fluorescence emission at 504 nm and Zn^{2+} concentration over its range from 0.5 nM to 5.0 nM (R² = 0.9762), from which we calculated the *LOD* value of 1 for the analysis of Zn^{2+} to be 7.52 nM (Fig. S5), and it was sufficiently below the mutable Zn^{2+} amount in human bodies [45]. From the results above, the extremely



Fig. 2. (a) Changes in fluorescence emission spectra of 1 (10 μ M) upon addition of Zn²⁺ (1 *equiv.*) and other respective metal ions (5 *equiv.*) in ethanol with an excitation at 431 nm. (b) Fluorescence responses at 504 nm of 1 (10 μ M) to Zn²⁺ (1 *equiv.*) and other various interfering metal ions (5 *equiv.*) under identical conditions in ethanol. Black bar: 1 + other metal ions (50 μ M), red bar: 1 + other metal ions (50 μ M) + Zn²⁺ (10 μ M). (λ_{ex} = 431 nm, slit: 5.0/5.0 nm).



Fig. 4. A Job's plot for determining the binding stoichiometry between 1 and Zn^{2+} in ethanol ($X_{Zn} = [Zn^{2+}]/([Zn^{2+}] + [1])$), the total concentration of 1 and Zn^{2+} was 20 μ M).

high sensitivity of compound 1 towards Zn^{2+} was concluded for sensing and monitoring Zn^{2+} environmentally and biologically.

A Job's plot method was further utilized for demonstrating the coordinative stoichiometry of compound **1** with Zn^{2+} by keeping the total concentration of **1** and Zn^{2+} homeostasis at 20 µM and changing the Zn^{2+} molar number ratio in complex $1-Zn^{2+}$, and the intensity of fluorescence emission at 504 nm was plotted as a function of Zn^{2+} molar number ratio. As shown in Fig. 4, the maximum was reached in the intensity of fluorescence emission at 504 nm at Zn^{2+} molar number ratio of 0.33, proving a 2:1 coordinative stoichiometry of compound **1** with Zn^{2+} in ethanol. The 2:1 binding stoichiometry encouraged us to calculate the association constant (*K*) between **1** and Zn^{2+} on a basis of nonlinear Benesi-Hildebrand expression from the fluorescence titration experiments, giving the result as $1.14 \times 10^5 M^{-1}$ (Fig. S6), which was within the range $10^3 - 10^9 M^{-1}$ of other Zn^{2+} fluorescent probes reported previously in the literature and suggested good selective nature of compound **1** with Zn^{2+} [46–49].

Invertibility and renewability are important characters for broadening a fluorescent probe for actual applicability. So as to explore if good invertibility and renewability of our as-synthesized compound 1 for sensing Zn^{2+} were confirmed, EDTANa₂, which was a perfect chelating agent for binding Zn^{2+} , was introduced into the ethanolic solution of 1 in the existence of Zn^{2+} . From the spectra of fluorescence emission of compound 1 in the existence of Zn^{2+} followed by the addition of EDTANa₂ shown in Fig. 5, we could clearly observe that the fluorescence emission of complex 1-Zn²⁺ quenched significantly with addition of EDTANa₂, which was attributed to the stronger coordination ability of \mbox{Zn}^{2+} with \mbox{EDTANa}_2 than with compound 1, making EDTANa₂ coordinated with Zn^{2+} from complex 1-Zn²⁺ and releasing the free 1. From the results above, we could conclude that perfect invertibility and renewability of our as-synthesized compound 1 for sensing Zn²⁺ were confirmed, which developed 1 for practical applications.

3.3. Binding mode of compound 1 with Zn^{2+}

So as to investigate the binding mode of compound 1 with Zn^{2+} , Fourier Transform Infrared (FT-IR) spectra of compound 1 and complex $1-Zn^{2+}$ were carried out. As can be seen from Fig. S7, the free compound 1 exhibited a characteristic stretching vibration band of C = centered at 1612 cm⁻¹, which was red-shifted to 1585 cm^{-1} upon complexation of 1 with Zn^{2+} . Additionally, a new absorption band centered at 419 cm⁻¹ emerged, which was probably assigned to Zn-N absorption band, but negligible changes in other absorption bands were



Fig. 5. Change in fluorescence emission spectra of compound 1 ($10 \,\mu$ M) upon incremental addition of Zn²⁺ (1 *equiv.*) and EDTANa₂ (1 *equiv.*) in ethanol with an excitation at 431 nm.

observed in the spectra (Fig. S7). From the results above, it was concluded that two nitrogen atoms from the naphthyridine unit in compound 1 participated in the coordination with Zn^{2+} , forming a stable complex $1-Zn^{2+}$.

On a basis of the investigations above, the proposed binding mechanism of compound 1 with Zn^{2+} was deduced in detail. As depicted in Scheme 2, owing to the 2:1 coordinative stoichiometry of compound 1 with Zn^{2+} , 1 formed a stable complex by coordinating four nitrogen atoms from the naphthyridine units in two molecules of 1 with Zn^{2+} , which enhanced the rigidity and coplanarity of this system forming the chelation-enhanced fluorescence (CHEF) effect. Furthermore, the photoinduced electron-transfer (PET) phenomenon from the lone pair electron of nitrogen atom to the naphthyridine unit was inhibited upon complexation of compound 1 with Zn^{2+} (Scheme 2). As a result, significant enhancement in the band of fluorescence emission centered at 504 nm was observed.

4. Conclusion

In conclusion, we designed and synthesized a new-type Schiff-base ligand 1 with 4-methyl-7-acetamide-1,8-naphthyridyl group as the fluorophore and the receptor for sensing Zn^{2+} . This compound 1 showed excellent selectivity towards Zn²⁺ over most of other environmentally and biologically important metal cations, which was because that the remarkable enhancement in fluorescence emission centered at 504 nm was only caused by Zn²⁺, increasing by about 63fold in its intensity, and most of other metal cations did not affect the detection of Zn^{2+} by compound 1. Moreover, the extremely high sensitivity of compound 1 towards Zn²⁺ was concluded, for the LOD value reaching 7.52 nM, and a 2:1 coordinative stoichiometry of compound 1 with Zn²⁺ was ascertained by the experiments of fluorescence titration and a Job's plot method. Additionally, perfect invertibility and renewability of our as-synthesized compound 1 for sensing Zn²⁺ were confirmed, which developed 1 for practical applications. Therefore, the development of novel fluorescent probes might be accelerated by the design and synthesis of compound 1 for detecting various analytes in environmental and biological systems.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21761019) and the Young Foundation of Jinchang (jrc201811).





Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2019.02. 024.

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