Two Schiff-base fluorescence probes based on triazole and benzotriazole for selective detection of Zn^{2+}

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Abstract: Two novel Schiff-base fluorescence probes based on triazole and benzotriazole were designed and synthesized. Corresponding orbital electron distribution and molecular geometry configurations of the compounds were predicted by density functional theory (DFT). Fluorescence properties of probes were detected by UV-vis and fluorescence spectra. Test results indicated that the probes had specific selectivity and high sensitivity for Zn^{2+} compared with metal ions examined (Ag^+ , Al^{3+} , Cd^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^+ and Pb^{2+}). In addition, the detection limit of the probes toward Zn^{2+} was low down 10^{-9} M. Therefore, the probes should be potential application in both the environment and biological systems for the detecting of Zn^{2+} .

Key words: fluorescence probes, triazole, benzotriazole, Schiff-base

Introduction

Zinc is an important essential trace element (10 to 15 mg each day) in the human body. Many researchers reveal that Zn^{2+} plays a vital role in biological and metabolic function, including regulate catalytic activity of enzymes, neurotransmission, cellular transport, and apoptosis [1-3]. Moreover, Alzheimer's diseases, Parkinson's diseases, epilepsy and Ehlers-Danlos syndrome [4-6] are caused by deviation of Zn^{2+} concentrations in vivo biology. Excess of Zn^{2+} can also cause great damage to human health and environment. Therefore, it is of essential for people to find a simple and accurate method to detect the concentrations of Zn^{2+} in both the biological systems and environment.

Up to now, Some traditional techniques, such as spectrophotometric method with dithizone [7] and ionization mass spectrometry [8], which **needs expensive equipment, cumbersome and time-consuming** are very difficult to detect Zn^{2+} . **Comparing with these techniques,** fluorescence probes have become a popular method for detecting Zn^{2+} because of their high selectivity, **low detection limit and real-time monitoring.** According to some researches [9-14], Zn^{2+} could cooperate with specific receptors of fluorescent probes. Such complexation changes the photophysical properties, and thus realizes high selectivity for Zn^{2+} . Besides, a large number of Zn^{2+} -selective fluorescence probes have been designed and synthesized based on photo-induced electrontransfer (PET) [15], intramolecular charge-transfer (ICT) [16], chelation-enhanced fluorescence (CHEF) [17], and fluorescence resonance energy transfer (FRET) [18] theories, respectively. However, there still exists some drawback among the reported fluorescence probes, e.g. the detection limit of probes is

restricted[19-22], some of the sensors are hard to synthesize [23], “turn-on” responses and selectivity are relatively scarce [24], optical properties are interferenced from other metal ions, such as Cd^{2+} which exhibits highly similar chemical properties as Zn^{2+} . Therefore, to develop some low cost, easily-prepared, high selectivity and sensitivity Zn^{2+} fluorescence probes are expected to remain a challenging.

Herein, more and more researchers focus on the development of Schiff-base fluorescence probes with high selectivity, sensitivity, **low detection limit and real-time monitoring**[25-28]. In view of previous researchers, we find Schiff-base fluorescence probes containing C=N structure with a lone electron pair have good ability to coordinate with metal ions. Compounds with an unbridged C=N structure are often nonfluorescent due to the C=N isomerization. By combining specific metal ions, the C=N isomerization is prevented, specific chelating effect is caused, thereby fluorescent property is enhanced [29]. Therefore, we incorporated a special functional groups of sp^2 nitrogen (-CH=N-) into our probe design. In particular, we expected that fluorescence probes had relatively lower detection limits in the range detected. At the same time, considering that triazole and benzotriazole exhibit excellent photophysical property and low cost [30, 31], we designed two simple Schiff-base fluorescence probes on the basis of them, which played high selectivity and sensitivity for Zn^{2+} compared with other metal ions.

1. Experimental

2.1 Materials and measurements

Unless otherwise stated, reagents and materials were obtained from commercial

suppliers at analytical grade and used without further purification. Triazole, benzotriazole, *p*-fluorobenzaldehyde and *p*-phenylenediamine were purchased from Sinopharm Chemical Reagent Co., Ltd. Distilled water was used throughout the experiment. Metal ions used in fluorescence analysis were prepared from the corresponding inorganic salts.

Reactions were monitored by TLC. ¹H NMR spectra were taken on a Bruker Avance 400 MHz NMR Spectrometer with chemical shifts reported in ppm (in DMSO-d₆). Dimethyl sulfoxide (DMSO) was used as the solvent. Elemental analysis was recorded on SGWX-4 micro melting point apparatus. Fourier Transform Infrared (FT-IR) spectra were measured using TENSOR 27 FT-IR spectrometer. Absorption spectra were obtained on a MPC-2600 UV-vis spectrofluorometer. N,N-dimethylformamide (DMF) was used as the solvent. Fluorescent measurements were conducted on F-4500 (Hitachi) spectrofluorometer.

2.2 Synthesis

2.2.1 Synthesis of compound 1

The synthesis route of compound 1 was showed in scheme 1. 1,2,4-Triazole (0.069 g, 10 mmol) and *p*-fluorobenzaldehyde (1.24 g, 10 mmol) were dissolved in DMF solution (20 mL), then anhydrous potassium carbonate (1.66 g, 12 mmol) were added slowly under stirring. The mixture was refluxed under 110°C for 12 h, and then cooled down to room temperature. The precipitate was filtered and the filtrate was extracted three times with 100 mL acetic ether. The combined organic extracts were dried over anhydrous sodium sulfate and left overnight. The soild was filtered and the

concentrate was chromatographed on a silica gel column using methanol: chloroform = 1:9 as an eluent. Yellow powder was dried in vacuum over 6 h to obtain compound 1 (1.02 g, 59%); m.p. 143-146°C; IR (KBr, cm^{-1}): 1689, 1604, 1519, 1207, 981, 837 cm^{-1} ; ^1H NMR (DMSO- d_6 , 400 MHz): δ 10.07 (s, 1H, CHO), 8.67 (s, 1H, triazole H), 8.16 (s, 1H, triazole H), 8.04 (d, 2H, ArH), 7.92 (d, 2H, ArH).

2.2.2 Synthesis of compound 2

The synthesis route of compound 2 was showed in scheme 1. Compound 1 (0.173 g, 1mmol) and *p*-phenylenediamine (0.054 g, 0.5 mmol) were dissolved into DMF (4 mL), and then five drops of glacial acetic acid were added into mixture under stirring. The temperature was maintained at 100°C for 5 h under reflux, and then cooled down to room temperature. Distilled water (20 mL) was added into mixture and obtained precipitate. The yellow precipitate was filtered and washed several times with warm water (50°C). Product was dried in vacuum over 6 h to obtain compound 2 (0.13 g, 63%); m.p. 120-122°C; IR (KBr, cm^{-1}): 1624, 1517, 1406, 1195, 850, 675 cm^{-1} ; ^1H NMR (DMSO- d_6 , 400 MHz): δ 9.42 (d, H, triazole H), 8.29 (d, 2H, ArH), 8.11 (s, 2H, ArH), 8.04-7.94 (m, 2H, ArH), 7.16 (d, H, triazole H), 6.65-6.52 (m, H, HC=N).

2.2.3 Synthesis of compound 3

The synthesis route of compound 3 was showed in scheme 1. Benzotriazole (1.3 g, 8.4 mmol) and anhydrous potassium carbonate (2.3 g, 16.8 mmol) were added to a 50 mL boiling flask-4-neck and dissolved in DMF solution (20 mL). The reaction mixture was stirred under reflux. The temperature was maintained at 80 - 90°C. After reaction for 30 min, *p*-fluorobenzaldehyde (1.04 g, 8.4 mmol) was added into mixture,

and then kept the mixture for 8 - 9 h under the above-mentioned temperature. When the end of the reaction, the mixture was cooled to room temperature, and poured into ice water (50 mL) and left overnight, yellow precipitate was obtained. The precipitate was filtered, washed three times with deionized water and recrystallized with absolute ethanol. Product was dried in vacuum over 6 h to obtain compound 3 (1.69 g, 90%); m.p. 155-157 °C; IR (KBr, cm^{-1}): 1691, 1601, 1510, 1452, 1071, 826, 734 cm^{-1} ; ^1H NMR (DMSO-d_6 , 400 MHz): δ 10.12 (s, 1H, CHO), 8.53 (d, 1H, ArH), 8.21 (d, 4H, ArH), 8.08 (s, 1H, ArH), 7.71 (s, 1H, ArH), 7.55 (s, 1H, ArH).

2.2.4 Synthesis of compound 4

The synthesis route of compound 4 was showed in scheme 1. Compound 3 (0.1 g, 0.45 mmol) and *p*-phenylenediamine (0.024 g, 0.225 mmol) were dissolved in DMF (4 mL) under stirring and reflux. Then four drops of glacial acetic acid were added into mixed solution. The temperature was maintained at 80°C for 2 h, a large number of yellow solid appeared as the reaction process. The mixture was cooled down to room temperature and distilled water (50 mL) was added. The precipitate was filtered, washed thoroughly with warm water (40°C), and then dried in vacuum over 6 h to obtain compound 4 (0.08 g, 65%); m.p. 330-333 °C; IR (KBr, cm^{-1}): 3060, 1601, 1513, 1450, 1244, 836, 745 cm^{-1} ; ^1H NMR (DMSO-d_6 , 400 MHz): δ 8.66 (d, 1H, ArH), 8.21 (d, 4H, ArH), 7.99 (d, 1H, ArH), 7.86 (s, 1H, C=N), 7.63 (s, 1H, ArH), 7.50 (s, 1H, ArH), 7.40 (s, 2H, ArH).

3. Results and discussion

3.1 Design and synthesis of compound 2 and compound 4

As shown in Scheme 1, the compound 2 and 4 can be synthesized in two steps from commercially available chemicals in high yield. Details for synthesis are described in the experiment section. Structures were characterized by ^1H NMR and FT-IR spectrometer.

3.2 Theoretical calculation

The calculation of a wide range of molecular properties with density functional theory makes a close connection between experiment and theory [32]. Through theoretical calculation, the molecular structures of the compounds were optimized, and their performance was predicted by the Gaussian 03 software package. Generally speaking, most of organic molecules exist in the form of lowest energy [33]. Through optimized molecular geometry configurations of the compounds at the DFT (B3LYP/6-31G*) level, we had obtained the initial conformation with lower energy. At the same time, space steric effect was reduced, molecular planarity was enhanced. Through overview literatures, most of compounds containing benzene ring and heterocyclic ring could product fluorescence. The bigger the conjugate system, the stronger the fluorescence intensity. Furthermore, rigid planar structure could result in strong fluorescence [34, 35]. As shown in Fig.1 and 2, compounds 2 and 4 had highly symmetrical rigid planar molecular structures. It could be predicted that compounds could product strong fluorescence.

Corresponding orbital electron distribution of compounds were also predicted in Fig. 1 and 2. Parallel p orbitals on the HOMO and LUMO were almost all over the entire molecular structure, and it could be demonstrated that compound 2 and 4 had

larger delocalized π -bond. As shown in Fig. 1, there were frontier orbital electron density overlaps between LUMO and LUMO+1, between HOMO and HOMO-1, respectively, which shown that compound 2 was very easy to carry out electronic transition. Similar results could be found on compound 4. **Because all the energies are negative, compounds may be combined with metal ions easily.** Energy gap (ΔE) between HOMO and LUMO reflects stability of compounds, the smaller energy gap, the more easily compound is excited [36]. As shown in Table 1, $\Delta E_2 > \Delta E_4$, it could be predicted that maximum absorption wavelength of compound 4 was larger than 2. Therefore, compound 2 and 4 had strong molecular planarity and large conjugated π -bonds, it was expected that the compounds became good fluorescent materials.

3.3 The optical properties of compounds 2 and 4

3.3.1 Reaction time and pH-sensitive investigation

The response time between fluorescence probes and Zn^{2+} was detected with the addition of 10 μM Zn^{2+} , the results were shown in Figure 3. Upon the addition of Zn^{2+} , a fluorescence signal was immediately initiated and the reaction was completed within 10 min. Thus, the reaction of probes and Zn^{2+} should be detected after 10 min. Compared with the majority of Zn^{2+} fluorescent probes which were reported (the response time is 20 min to 2h) [37, 38], compound 2 and 4 could respond to Zn^{2+} more rapidly.

The pH-sensitivity of the fluorescence probes and Zn^{2+} were detected by fluorescence emission spectroscopy. As shown in Figure 4, the fluorescence of compound 2 and 4 was found to be remained stable between pH 6 to 9. In the other

words, it is possible for probes to detect Zn^{2+} in a biological range of pH values.

3.3.2 UV-vis absorption spectra

All UV-vis spectroscopy was obtained after the addition of different metal ions in DMF solution. The concentration of mixture was maintained at 1×10^{-5} M on MPC-2600 spectrometer. As shown in Fig. 5 and 6, in the absence of cations, the maximum absorption wavelength of compound 2 and 4 appeared at 361 nm and 369 nm, respectively. It was caused by $\pi\text{-}\pi^*$ transitions of C=N group. Relative to compound 2, compound 4 had much higher absorbance and showed a red shift, as result of its stronger electron donating ability of introduced benzene ring and stronger conjugate system [39, 40]. In addition, appropriate coordination geometry configuration, metal ions radius and affinity with ligand also affect UV-vis spectrum [41]. With the addition of metal ions (Zn^{2+} , Ag^+ , Al^{3+} , Cd^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^+ and Pb^{2+}), the maximum absorption wavelength of compound 2 and 4 appeared at 365 nm and 372 nm, respectively, and showed a red shift. Above results showed formation of new complex with combination of cations and the lone electron pair of C=N. As Fig 5 showed, upon the addition of Zn^{2+} ion, a significant absorption band in the UV-vis spectra appeared. Compared with Zn^{2+} , other metal ions (Ag^+ , Al^{3+} , Cd^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^+ and Pb^{2+}) at the same concentration showed weaker absorption intensity. Compound 4 also revealed the above-mentioned phenomena in Fig. 6. In summary, the compounds had stronger complexing ability with Zn^{2+} .

3.3.3 Fluorescence spectra

Structures containing electron withdrawing group conjugated to electron donating

group made these compounds as good fluorescent materials. In order to assess the spectroscopic characteristics of probes, a series of experiments were designed to measure fluorescent intensity. The fluorescence spectra of compounds were obtained by exciting at their maximum wavelength, and then results were showed in Fig. 7 and 8. At 1×10^{-5} M, compounds exhibited relatively strong fluorescence emission at 338 nm and 342 nm, respectively. Under the same conditions, relative to compound 2, the higher fluorescence intensity and a red shift of fluorescence emission peak of compound 4 were derived from the higher molecular weight and the stronger molecular conjugate degree of introduced benzene ring. On the other hand, fluorescence were considered to arise from the lowest excited singlet state and terminate in the ground state [42, 43]. Increase of the size of the aromatic conjugated system resulted in decrease of the energy gap between the ground and excited states, so that the compound 4 had larger emission wavelength. As shown in theoretical calculation, the energy difference between HOMO and LUMO of compound 4 was also lower than that of compound 2, which agrees well with the results of fluorescence spectra. As Table 2 shown, the stokes shift has been calculated by the maximum absorption band (λ_{abs}) and the maximum emission band (λ_{em}). The stokes shift is negative, it is anti-stock shift phenomenon.

3.3.4 Selectivity of metal ions

Selectivity of compounds for different metal ions (Zn^{2+} , Ag^+ , Al^{3+} , Cd^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^+ and Pb^{2+}) were detected by a series of experiments. Related fluorescence spectra in the present and absence of metal ions were obtained. The most

important criteria for a selective cationic probe was ability to detect specific cation. As Fig. 7 showed, with the addition of metal ions, the different degrees of enhancement of fluorescence intensity of compound 2 emerged quickly. The isomerisation of C=N double bond resulted in weak or non fluorescence emission. After metal ions were added into the mixture solutions, a selective chelation-enhanced fluorescence (CHEF) effect was observed, a new π -conjugated structure was formed, and then fluorescence enhancement of Schiff-base emerged [44]. In addition, emission change was more sensitive for the addition of Zn^{2+} , in other words, compound 2 had high selectivity to Zn^{2+} . In contrast, no significant changes were observed after adding Ag^+ , Al^{3+} , Fe^{3+} and K^+ because of their low affinity with ligand. Although Hg^+ , Cu^{2+} , Hg^{3+} and Pb^{2+} had a certain degree of fluorescence enhancement, the intensity was smaller compared with Zn^{2+} . Detection limit of fluorescent probe is a very important parameter in ion detecting. As Fig. 9 shown, when the concentration of mixture solution was diluted from 1×10^{-5} M to 1×10^{-9} M, the compound 2 still showed good fluorescence intensity. These data indicated that the compound had potential applications in biological sensing, as concentration of Zn^{2+} in human body was reported to maintain a millimolar level. Thus, compound 2 could be used as an excellent selective fluorescence chemosensor for Zn^{2+} .

Cation recognition ability of compound 4 was detected by the above same method. As Fig. 10 shown, fluorescence intensity in the presence of Zn^{2+} was stronger than that in the presence of other ions (Ag^+ , Al^{3+} , Cd^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^+ and Pb^{2+}). Thus, the compound had the strongest chelating ability with Zn^{2+} . Theoretical

calculation showed that the compound 4 had greater energy. With the addition of Zn^{2+} , energy of highest occupied molecular orbital for ligand is decreased, which made it very easy to be excited. On the other hand, compounds containing a covalently bridged C=N double bond structure had a very significant fluorescence enhancement. With the combination of Zn^{2+} and lone electron pair of C=N in Schiff base, the twist angle of structure decreased, the rigidity of system increased, and CHEF emerged. Coordination geometry configuration and conjugate structure have a great influence on the selectivity of compounds [45]. As Fig. 10 shown, when concentration of compound 4 were diluted to 1×10^{-9} M, fluorescent intensity can still be detected. These results exhibited that compound 4 could be useful as a fluorescent probe for selective detection of Zn^{2+} .

3.3.5 The concentration of Zn^{2+} investigation

The stoichiometric ratio of the 1.0 μM probes and Zn^{2+} were researched by fluorescence titration. As shown in Fig.11 and 12, upon the addition of Zn^{2+} (0 - 1.2 μM), the emission intensity was observed and showed a linear enhancement. When the concentration of Zn^{2+} was up to 1.0 μM , emission intensity of probes were found to remain stable which implied the 1:1 binding of probes to Zn^{2+} . Through the above phenomenon, we were able to deduce a possible coordination mode, that is, N atoms from 5-membered heterocyclic and C=N double bonds can form an efficient binding pocket for Zn^{2+} with 1:1 stoichiometry. From the emission intensity by following the modified Benesi-Hidebrand equation, the association constants of compound 2 and 4 were calculated as $4.53 \times 10^6 \text{ M}^{-1}$ and $3.08 \times 10^6 \text{ M}^{-1}$ [46-49]. Detection limits

calculated on the basis of equation $C_L=3S_b/S$ were as low as 3.5×10^{-9} M and 2.8×10^{-9} M respectively. Ideal detection limits were consistent with the experimental values, implying nM range of detection limit is desirable.

Conclusions

In conclusions, two novel fluorescent probes with high selectivity based on triazole, benzotriazole have been designed and synthesized successfully. The investigated results showed that the compounds have specificity for Zn^{2+} compared with metal ions examined. In addition, compared with World Health Organization detection level, the detection limits (10^{-9} M) of compounds were lower. Thus, it can be concluded that compounds 2 and 4 have underlying applications for the detection Zn^{2+} in both the environment and physiological sciences.

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Table. 1. HOMO and LUMO energy and gap of compounds.

Table 2. Photophysical data of compounds 2 and 4.

Scheme. 1. The synthetic routes of compounds 1-4.

Fig. 1. Optimized molecular Structures and corresponding orbital electron distribution of compounds 2.

Fig. 2. Optimized molecular Structures and corresponding orbital electron distribution of compounds 4.

Fig.3. Effect of response time on the fluorescence intensity of compound 2 and 4 (1×10^{-5} M) in the presence of 10 μ M Zn^{2+} .

Fig.4. Effect of pH on the fluorescence intensity of compound 2 and 4 (1×10^{-5} M) in the presence of 10 μ M Zn^{2+} .

Fig. 5. Changes in the absorbance spectra of compound 2 (1.0×10^{-5} M) in the presence of different metal ions (1.0×10^{-5} M) in DMF solution.

Fig. 6. Changes in the absorbance spectra of compound 4 (1.0×10^{-5} M) in the presence of different metal ions (1.0×10^{-5} M) in DMF solution.

Fig. 7. Fluorescence spectra response of compound 2 (1.0×10^{-5} M) upon addition of Zn^{2+} , Ag^{+} , Al^{3+} , Cd^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^{+} and Pb^{2+} ions in DMF solution.

Fig. 8. Fluorescence spectra response of compound 4 (1.0×10^{-5} M) upon addition of Zn^{2+} , Ag^{+} , Al^{3+} , Cd^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^{+} and Pb^{2+} ions in DMF solution.

Fig. 9. Fluorescence spectra of compound 2 (1.0×10^{-5} M) in DMF solution at different concentrations of Zn^{2+} . ($[\text{Zn}^{2+}] = 10^{-5}$ - 10^{-9} M).

Fig. 10. Fluorescence spectra of compound **4** (1.0×10^{-5} M) in DMF solution at different concentrations of Zn^{2+} . ($[\text{Zn}^{2+}] = 10^{-5}$ - 10^{-9} M).

Fig.11. The normalized fluorescence spectra of 1.0 μM compound **2** after addition of increasing amounts of Zn^{2+} (0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0, 1.2 μM) at room temperature.

Fig.12. The normalized fluorescence spectra of 1.0 μM compound **4** after addition of increasing amounts of Zn^{2+} (0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0, 1.2 μM) at room temperature.

Scheme. 1. The synthetic routes of compounds **1-4**.

	Compound 2	Energy/eV
Structure
LUMO+1		-0.9
LUMO		-1.5
HOMO		-6.5
HOMO-1		-7.4
HOMO-2		-7.7

Fig. 1. Optimized molecular Structures and corresponding orbital electron distribution of compounds **2**.

Fig. 2. Optimized molecular Structures and corresponding orbital electron distribution of compounds 4.

Fig.3. Effect of response time on the fluorescence intensity of compound **2** and **4** (1×10^{-5} M) in the presence of $10 \mu\text{M Zn}^{2+}$.

Fig.4. Effect of pH on the fluorescence intensity of compound **2** and **4** (1×10^{-5} M) in the presence of $10 \mu\text{M Zn}^{2+}$.

Fig. 5. Changes in the absorbance spectra of compound **2** (1.0×10^{-5} M) in the presence of different metal ions (1.0×10^{-5} M) in DMF solution.

Fig. 6. Changes in the absorbance spectra of compound **4** (1.0×10^{-5} M) in the presence of different metal ions (1.0×10^{-5} M) in DMF solution.

Fig. 7. Fluorescence spectra response of compound **2** (1.0×10^{-5} M) upon addition of Zn^{2+} , Ag^+ , Al^{3+} , Cd^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^+ and Pb^{2+} ions in DMF solution.

Fig. 8. Fluorescence spectra response of compound **4** (1.0×10^{-5} M) upon addition of Zn^{2+} , Ag^{+} , Al^{3+} , Cd^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^{+} and Pb^{2+} ions in DMF solution.

Fig. 9. Fluorescence spectra of compound **2** ($1.0 \times 10^{-5} \text{ M}$) in DMF solution at different concentrations of Zn^{2+} . ($[\text{Zn}^{2+}] = 10^{-5}$ - 10^{-9} M).

Fig. 10. Fluorescence spectra of compound **4** ($1.0 \times 10^{-5} M$) in DMF solution at different concentrations of Zn^{2+} . ($[Zn^{2+}] = 10^{-5}$ - $10^{-9} M$).

Fig.11. The normalized fluorescence spectra of 1 μM compound **2** after addition of increasing amounts of Zn^{2+} (0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0, 1.2 μM) at room temperature.

Fig.12. The normalized fluorescence spectra of 1.0 μM compound **4** after addition of increasing amounts of Zn^{2+} (0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0, 1.2 μM) at room temperature.

Table 1

HOMO and LUMO energy and gap of compounds

Compound	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE(eV)
2	-6.5	-1.5	5.0
4	-3.5	-2.2	1.3

Table 2

Photophysical data of compounds 2 and 4

Compound	$\lambda_{\text{abs}}(\text{nm})$	$\lambda_{\text{em}}(\text{nm})$	I (cm^{-1})
2	365	338	-4569.25
4	372	342	-4240.80

I: Stocks shift = $1/(1/\lambda_{\text{abs}} - 1/\lambda_{\text{em}})$