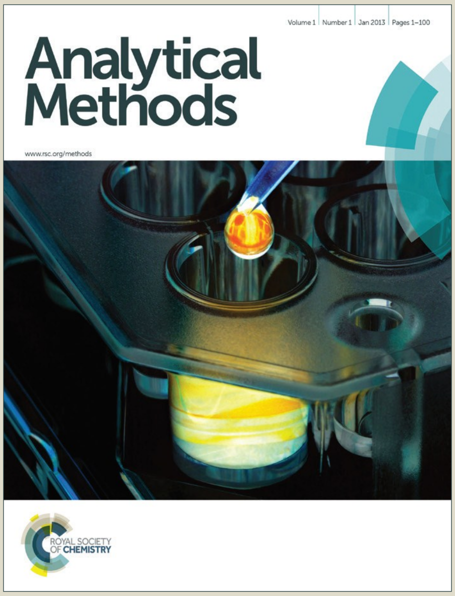
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Selective aqueous fluorescent probe for metal ions based on benzoyl hydrazone derivatives †

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Abstract: Three novel fluorescence compounds were synthesized and employed as fluorescent probes for detecting different metal ions selectively. The naphthol-based probe (**I**) exhibited weak fluorescence in water, which was enhanced during the presence of Al^{3+} ion due to the complexation between **I** and Al^{3+}. In addition, the coumarin-based probe (**II**) and quinolone-based probe (**III**) could selectively detected Cu^{2+} ion and Zn^{2+} ion respectively. Unlike the changes in the fluorescence spectra of **I** and **III** upon Al^{3+} ion and Zn^{2+} ion addition, the fluorescence intensity of **II** decreased dramatically after Cu^{2+} ion was added into the aqueous solution. This is due to the fact that different mechanisms occurred in the recognition process to metal ions. Colorimetric monitoring of these processes was also feasible.

Keywords: fluorescence probe; metal ions; coumarin; naphthol; quinolone.

1. Introduction

The development of fluorescent sensors for the detection of chemical species is currently of significant importance for both chemistry and biology. [1-4] More specifically, sensors for the recognition of heavy and transition metal ions with high sensitivity and selectivity are actively investigated, because these metal ions are significant environmental pollutant and essential trace element in biological systems. [5-7] As the third most abundant metallic element (about 8% by weight) in earth's crust, [8] Aluminum is widely used in chemical industry production and daily necessities. Excess aluminum can cause damages to certain human cells and tissues, resulting in diseases such as Alzheimer’s disease, Parkinson’s disease. [9, 10] Moreover, Cu^{2+} ion is the third most abundant transition metal ions in the human body. The Cu^{2+} disorder in metabolism was proposed to be associated with certain diseases such as Menkes syndrome, Wilson’s disease, and Alzheimer’s disease. [11] Another metal ion, Zn^{2+}, is one of the essential trace elements in biological processes. The zinc deficiency in human organisms leads to growth retardation, the decrease of the immunological defense and some skin diseases. [12] According to the U.S. Environmental Protection Agency (EPA), the acceptable level of three metals in secondary drinking water are 1.0 mg/L (copper), 0.05 to 0.2 mg/L (aluminum) and 5.0 mg/L (zinc), respectively. Therefore, there is considerable interest in developing specific fluorescent sensors for the detection of Al^{3+} ion, [13, 14] Cu^{2+} ion [15, 16] and Zn^{2+} ion.[17, 18]

Although some progress has been made on the detection of Al^{3+}, Cu^{2+} and Zn^{2+}, these methods do suffer from a few practical problems, such as low sensitivity and selectivity, poor water solubility, and difficult to synthesize. Therefore, we are interested in developing fluorescent sensors for metal ions show high sensitivity and selectivity in detection, good water solubility, and simplicity in synthesis.

Benzoyl hydrazone is the ideal recognition functional group for development of fluorescent chemosensors for specific heavy and transition metal ions. Hydrazone derivatives are also found many interesting biological activities, such as anticonvulsant [19] and antimicrobial [20] activities. Particularly, the metal complexes of hydrazone derivatives were shown antibacterial property [21] and inhabitation of DNA synthesis and cell growth [22-24]. Herein, we report the synthese and metal ion recognition properties of three benzoyl hydrazone-based derivatives (Scheme. 1). Combined with hydroxyl of naphthol, carbonyl of coumarin and Nitrogen atom of quinoline, benzoyl hydrazone moiety could coordinate metal ions. In addition, diethylene glycol ammonia moiety was induced to enhance water solubility of these derivatives. Compared with ionic hydrophilic groups, diethylene glycol ammonia moiety has no toxicity so that it can be used in biological samples, and it has no effect on optical properties of fluorophore. The probes exhibit highly selective recognition of Al^{3+}, Cu^{2+} and Zn^{2+} by fluorescent and colorimetric detection in aqueous solution, respectively.

2. Experimental

2.1 Materials and general methods

All chemicals and reagents were purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. and used without further purification. 7-diethylamino-3-formyl-coumarin was synthesized by this group previously. [25] 2-Hydroxy-1-naphthaldehyde and 8-Quinolinecarbaldehyde were purchased from Energy Chemical Technology Co., Ltd. (Shanghai).

The ^1H and ^{13}C nuclear magnetic resonance (NMR) were recorded on a Bruker DRX-400

AVANCE spectrometer, DMSO-d_6 and $CDCl_3$ were used as solvents. Steady-state fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer. UV-vis absorption spectra were measured on a Shimadzu UV-3390 spectrophotometer. Elemental analysis was obtained on a Vario MAX CHN apparatus. Mass spectra (EI-MS) were obtained by use of an Agilent 7890A-5975C GC-MC spectrometer. Fluorescence lifetimes were measured on an EI FLS920 Steady state and transient state fluorescence spectrometer.

2.2. Synthesis of benzoyl hydrazone-based derivatives

The synthetic route of benzoyl hydrazone-based derivatives is shown in Scheme 1.

4-N-((2-ethoxy)ethanolmethylamino)methyl benzoate

4-N-((2-ethoxy)ethanolmethylamino)methyl benzoate was synthesized according to the reported method. [26] Methyl 4-formylbenzoate 1.64 g (10 mmol) and 2-(2-aminoethoxy) ethanol 3.20 g (30 mmol) were dissolved in 25 mL ethanol and the solution was stirred for 5 h at room temperature. The mixture was evaporated under reduced pressure and dichloromethane (50 mL) was added to the flask. Then sodium triacetoxyborohydride 6.55 g (30 mmol) was added to the reaction mixture portion wise over a period of 3 h, the progress of reaction was monitored by TLC. The reaction was quenched with 20 mL of water and then extracted with dichloromethane, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (CH_2Cl_2 : C_2H_5OH = 100 : 1, v / v) to obtain a colourless liquid (1.21 g, 47.8% yield).

^1H NMR (400 MHz, $CDCl_3$): δ(ppm) =8.00 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H), 3.88 (s, 2H), 3.71 – 3.76 (m, 2H), 3.64(t, J = 5.2 Hz, 2H), 3.57 – 3.61 (m, 2H), 2.83 (t, J = 5.2 Hz, 2H), 2.20 (s, 2H). Analytically calculated for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53%. Found: C, 61.54; H, 7.59; N, 5.55%.

4-N-((2-ethoxy)ethanolmethylaminobenzoyl hydrazine

4-N-((2-ethoxy)ethanolmethylaminobenzoyl hydrazine was synthesized according to the reference with a minor modification. [27] A mixture of 4-N-((2-ethoxy)ethanolmethyl amino)methyl benzoate 0.76 g (3 mmol) and 80% hydrazine hydrate 1.47 g (30 mmol) in ethanol (15 mL) was heated under reflux for 24 h. After cooling, the solvent was removed under vacuum and crude product was subjected to column chromatography (silica gel C_2H_5OH: $NH_3\cdot H_2O$ = 400 : 1, v / v) to obtain a colorless liquid (0.68 g, 87.2% yield).

^1H NMR (400 MHz, $CDCl_3$): δ(ppm) =7.70 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.33 (s, 1H), 3.87 (s, 2H), 3.69 – 3.77 (m, 2H), 3.64 (t, J = 5.2 Hz, 2H), 3.57 – 3.61 (m, 2H), 2.83 (t, J = 5.0 Hz, 2H). Analytically calculated for $C_{12}H_{19}N_3O_3$: C, 56.90; H, 7.56; N, 16.59%. Found : C, 56.88; H, 7.54; N, 16.46%.

2-hydroxy-1-[4'-N-((2-ethoxy)ethanol)ethylaminobenzoyl hydrazone]methylnaphthalene. (I)

Compound **I** was synthesized according to the reference with a minor modification. [28] 2-hydroxy-1-naphthalenecarbox aldehyde 0.18 g (1mmol) and 4-N-((2-ethoxy)ethanol methylaminobenzoyl hydrazine 0.13 g (0.5 mmol) were dissolved in EtOH (10mL). The mixture was stirred at 95 ℃ for 6 h. After cooling to room temperature, the reaction solution was concentrated under reduced pressure. The residue was purified by silica gel column chromatography. The yellow colored fraction was collected then the solvent was removed under reduced pressure to yield the yellow brown compound **I** (0.08 g) at 40% yield.

^1H NMR (400 MHz, DMSO): δ(ppm) =9.55 (s, 1H), 8.23 (d, J = 8.8 Hz, 1H), 7.85 – 8.05

(m, 4H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 3.87 (s, 2H), 3.47 – 3.56 (m, 4H), 3.37 – 3.46 (m, 2H), 2.68 – 2.75 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d6): δ (ppm) =162.78, 158.47, 147.25, 147.22, 133.18, 129.45, 128.80, 128.34, 128.27, 128.22, 128.05, 124.01, 121.07, 119.40, 109.01, 72.66, 69.73, 60.70, 52.52, 48.31. Analytically calculated for $C_{23}H_{25}N_3O_4$: C, 67.98; H, 6.13; N, 10.56 %. Found: C, 67.80; H, 6.18; N, 10.31 %. ESI-MS: m/z: calcd: 408.1935, found: 408.1923 [M+1].

7-diethylamino-3-[4'-N-m((2-ethoxy)ethanol)ethylamino benzoylhydrazone]methyl coumarin (II)

Following general procedure of compound **I**, orange solid (32.7%, 0.11g): ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) =11.86 (s, 1H), 8.51 (s, 1H), 8.37 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 9.2 Hz, 1H), 6.58 (s, 1H), 3.84 (s, 2H), 3.45 – 3.60 (m, 8H), 3.39 – 3.44 (m, 4H), 2.61 – 2.79 (m, 2H), 1.14 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): *δ* (ppm) = 163.14, 161.29, 156.99, 151.79, 145.54, 142.65, 139.04, 132.05, 131.29, 128.25, 127.99, 113.18, 110.21, 108.57, 96.91, 72.65, 70.44, 60.75, 53.00, 48.62, 44.72, 12.83. Analytically calculated for $C_{26}H_{32}N_4O_5$: C, 64.98; H, 6.71; N, 11.66%. Found: C, 64.87; H, 6.69; N, 11.69%. EI-MS: m/z: calcd: 481.2451, found: 481.2458 [M+1].

8-[4'-N-((2-ethoxy)ethanol)ethylaminobenzoylhydrazone] methylquinoline (III).

Following general procedure of compound **I**, yellow brown solid (45%, 0.17g): ^{1}H NMR (400 MHz, DMSO): δ(ppm) = 12.13 (s, 1H), 9.78 (s, 1H), 9.00 (d, *J* = 3.6 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 7.6 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.64 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 3.87 (s, 2H), 3.46 – 3.58 (m, 4H), 3.38 – 3.46 (m, 2H), 2.67 – 2.79 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d6): δ (ppm) = 163.34, 150.84, 145.84, 145.09, 143.76, 137.17, 132.37, 131.76, 130.49, 128.72, 128.53, 128.15, 127.05, 126.10, 122.38, 72.66, 60.69, 52.44, 48.22. Analytically calculated for $C_{22}H_{24}N_4O_3$: C, 67.58; H, 6.13; N, 104.06 %. Found: C, 67.33; H, 6.16 ; N, 14.28 %. ESI-MS: m/z: calcd: 393.1932, found: 393.1927 [M+1].

3. Results and discussion

3.1. Fluorescence titration of chemosensors with metal ions

The interaction between benzoyl hydrazone-based derivatives and metal ions were investigated by using UV-vis and fluorescence spectrometries. Fig. 1a showed that upon the continuous addition of Al^{3+} ion from 0 to 2.02 equiv., the fluorescent intensities of **I** centered at 470 nm was gradually increased. Compared with compound **I**, addition of Cu^{2+} ion (0-1.06 equiv) induced obvious fluorescence quenching of compound **II** (Fig. 2 a). And for compound **III**, upon the continuous addition of Zn^{2+} ion from 0 to 7.0 equiv., the fluorescent intensities of **III** centered at 503 nm was gradually increased (Fig. 3 a). These results suggested that the fluorescent intensity of benzoyl hydrazone-based derivatives was changed by addition of metal ions.

3.2. Selective recognition of chemosensors with metal ions

Fig. 1b shows the fluorescence spectra (ex = 380 nm) of **I** (10 μM) measured in aqueous solution with the addition of respective metal ions (2.02 equiv.). Compound **I** showed only a very weak fluorescence without the absence of metal ions. The addition of Al^{3+} resulted in remarkably enhanced fluorescence intensity. Under the same condition, additions of other metal ions including Sn^{2+}, Cd^{2+}, Mn^{2+}, K^+, Na^+, Mg^{2+}, Cu^{2+}, Ca^{2+}, Zn^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+}, and

Co^{2+} did not cause any discernible changes. These observations indicated that compound **I** could selectively recognize Al^{3+} in aqueous solution.

However, addition of 1.06 equiv. Cu^{2+} ions resulted in an obvious decreased fluorescence intensity of compound **II** in aqueous solution than other metal ions Fig. 2b, which indicated compound **II** had higher binding affinity toward Cu^{2+} ion than other surveyed metal ions. Following the same method, addition of 7.0 equiv. Zn^{2+} ions resulted in remarkably enhanced fluorescence intensity of compound **III**. And additions of other metal ions did not cause any enhanced fluorescence intensity Fig. 3b. These results indicate that compound **II** and compound **III** could selectively recognize Cu^{2+} and Zn^{2+} in aqueous solution, respectively.

Colorimetric monitoring of these processes was also feasible with the excitation of UV lamp. It was found that Al^{3+} (2.02 equiv) produced an instant bright blue color of **I** in aqueous solution. In contrast, no change in color with the addition of other metal ions was observed (Fig. 1b). Cu^{2+} (1.06 equiv.) triggered a green fluorescence quenching of compound **II** in aqueous solution, whereas other metal ions did not lead to a change in fluorescence (Fig. 2b). As depicted in Fig. 3b, none of the other metal ions exhibited any significant fluorescence enhancement to the aqueous solution of **III** except Zn^{2+}. The stability of benzoyl hydrazone-based probes in aqueous solution was exemplified by time dependent fluorescence spectra and different changes were observed after exposed under visible light for 72 h. The stability of the probes followed the order of **II** > **I**> **III**. (Fig. S 1-3). † These results indicate that three benzoyl hydrazone-based derivatives show potential as practical colorimetric and fluorescent chemosensors for Al^{3+}, Cu^{2+} and Zn^{2+} with a high selectivity in aqueous solution.

3.3. Job plot of chemosensors with metal ions

To further determination stoichiometry between compound **I** and Al^{3+}, Job's plot analyses were used (Fig. 1 c). A maximum fluorescence was observed when the mole fraction of Al^{3+} reached 0.43, which is indicative of a 1:1 stoichiometry complexation between **I** and Al^{3+}. And the stoichiometry complexation between **II** and Cu^{2+} (Fig. 2 c), **III** and Zn^{2+} (Fig. 3 c) are 2:1 and 1:1 respectively.

3.4. Calculation of luminescence quantum yields and fluorescence lifetimes.

The luminescence quantum yields of **I**-Al^{3+} and **III**-Zn^{2+} increased when compared to that of free compounds. However, the luminescence quantum yields of **II** decreased significantly after Cu^{2+} ion was added to the aqueous solution (Table 1). We also measured the fluorescence lifetimes before and after metal ions were added to the benzoyl hydrazone-based derivatives solution (Table 1). The fluorescence lifetimes of three complexes are longer than that of their free compounds (Fig. S 4-9). † These results suggested the formation of **I**-Al^{3+}, **II**-Cu^{2+} and **III**-Zn^{2+}. The calculation methods of luminescence quantum yields and fluorescence lifetimes are given in the electronic supporting information†.

3.5. UV–vis titration of chemsensors with metal ions

The binding properties of **I** with Al^{3+} were also studied by UV-vis titration in aqueous solution (Fig. 1d). Upon addition of increasing amount of Al^{3+} (0-2.02 equiv.), the absorption bands at 324 and 362 nm decreased gradually with blue shift to 335 nm and 402 nm, respectively. The blue shifted absorption indicated that the proton at phenol was not deprotonated. [29] Moreover, there were three isosbestic points at 331, 340 and 380 nm, and the presence of three different isosbestic points for the sensor suggested the formation of a complex between **I** and Al^{3+} ion.

Compared with compound **I**, addition of Cu^{2+} ion (0-1.06 equiv) to the solution of compound **II** induced gradual decrease at 307 nm, 456 nm and gradual increase around 352nm, 485 nm (Fig. 2d). Three clear isosbestic points were observed at 325 nm, 376 nm, and 454 nm respectively. And for compound **III**, Zn^{2+} treatment caused a progressive decrease in 323 nm, and a new absorption band appeared at 355 nm (Fig. 3d). Absorbance at 323 nm continued to decrease, and the 355nm band increased with an increase in Zn^{2+} concentrations up to 7.0 equiv. One isosbestic point was observed at 343 nm. These results indicate the formation of complexes **II**-Cu^{2+} and **III**-Zn^{2+}.

3.6. Calculation for detection limit

To obtain the detection limit of benzoyl hydrazone-based derivatives for metal ions, **I**, **II** and **III** were treated with Al^{3+}, Cu^{2+} and Zn^{2+}, respectively. The detection limits were calculated to be at least as low as 165 nM (Al^{3+}), 170 nM (Cu^{2+}) and 366 nM (Zn^{2+}) (Table 2).

3.7. The proposed detection mechanism

According to the above discussion, the binding mode of benzoyl hydrazone-based derivatives and metal ions were proposed in this paper, as shown in Scheme 2. The fluorescence enhancement of compound **I** induced by Al^{3+} is attributable to the photoinduced electron transfer (PET) mechanism and C=N isomerization. [30] When the amino group interacts with Al^{3+}, PET process from N atom to naphthol is hindered and free rotation of C=N bond is locked, and a large enhancement of fluorescence is observed (Scheme 2a). Compound **II** owns three metal binding sites (O, N, O atoms), which can bind with Cu^{2+} and result in an enhanced ICT (intramolecular charge transfer) process from the electron-releasing group (N, N-diethylamino) to Cu^{2+}.[31] This charge transfer process induced a remarkable fluorescence quenching of compound **II** in aqueous solution (Scheme 2b). Similar to compound **I**, it is likely Cu^{2+} induced fluorescence enhancement of compound **III** due to the PET process from N atom to quinoline and C=N isomerization prevented in the excited state after binding sites (N, N, O) interacting with Zn^{2+} (Scheme 2c).

In order to verify the configurations of **I** to Al^{3+}, **II** to Cu^{2+} and **III** to Zn^{2+}, density functional theory (DFT) calculations were undertaken. The optimized configurations are shown in Fig. 4, which show that the Al^{3+} ion is well chelated with one **I** molecule through six coordination sites. As the crisscross joint, Cu^{2+} ion is chelated with two **II** molecules through six coordination sites. Similar to Al^{3+} ion, Zn^{2+} ion is chelated with one **III** molecule and forms nearly a planar structure. These calculation results support well proposed binding mode (Scheme 2). The DFT calculation methods and results are given in the electronic supporting information (Fig. S 10-12). †

Conclusions

In conclusion, we have developed three benzoyl hydrazone-based fluorescent sensors for Al^{3+}, Cu^{2+} and Zn^{2+}, respectively. These sensors can be easily operated in aqueous environment with high sensitivity. The complexation modes were elucidated by Job plot and calculated by DFT. In addition, sensors **I**, **II** and **III** could detect corresponding metal ions with high selectivity by color changes. It is proposed that the recognition processes involve the benzoyl hydrazone moiety and hydroxyl of naphthol (**I**), carbonyl of coumarin (**II**) and Nitrogen atom of quinolone (**III**). Our research should be valuable for developing new diagnosis regent for metal ions and designing metal ions assay array by introducing different functional groups beside N=C- of benzoyl hydrazone. Future study will focus on enhancing the emission wavelength of fluorophore and their potential applications in biological chemistry.

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Captions:

Scheme 1. Synthesis method of benzoyl hydrazone based derivatives **I**, **II** and **III**.

Scheme 2. The coordination mode and mechanism of fluorescence changing of **I**-Al^{3+}, **II**-Cu^{2+} and **III**-Zn^{2+}.

Fig. 1 (a) Fluorescence emission spectra of **I** (10 μM) in water with increasing concentrations of Al^{3+} ion excited at 380 nm. (b) Fluorescence intensity and color changes excited by a UV lamp (365 nm) of **I** upon the addition of various metal ions (20.2 mM) in aqueous solution. (Inset) Fluorescence emission plotted vs. lg[Al^{3+}]. (c) Job plot according to the method for continuous variations, indicating the 1 : 1 stoichiometry for **I**-Al^{3+} (the total concentration of **I** and Al^{3+} is 10 μM). (λ_{ex} = 380 nm). (d) Variation of the absorption spectra of **I** (10 μM) in aqueous solution with increasing concentrations of Al^{3+} ion (0 - 20.2 μM).

Fig. 2 (a) Fluorescence emission spectra of **II** (10 μM) in water with increasing concentrations of Cu^{2+} ion excited at 454 nm. (b) Fluorescence intensity and color changes excited by a UV lamp (365 nm) of **II** upon the addition of various metal ions (10.6 mM) in aqueous solution. (Inset) Fluorescence emission plotted vs. lg[Cu^{2+}]. (c) Job plot according to the method for continuous variations, indicating the 1 : 1 stoichiometry for **II**-Cu^{2+} (the total concentration of **II** and Cu^{2+} is 10 μM). (λ_{ex} = 454 nm). (d) Variation of the absorption spectra of **II** (10 μM) in aqueous solution with increasing concentrations of Cu^{2+} ion (0 - 10.6 μM).

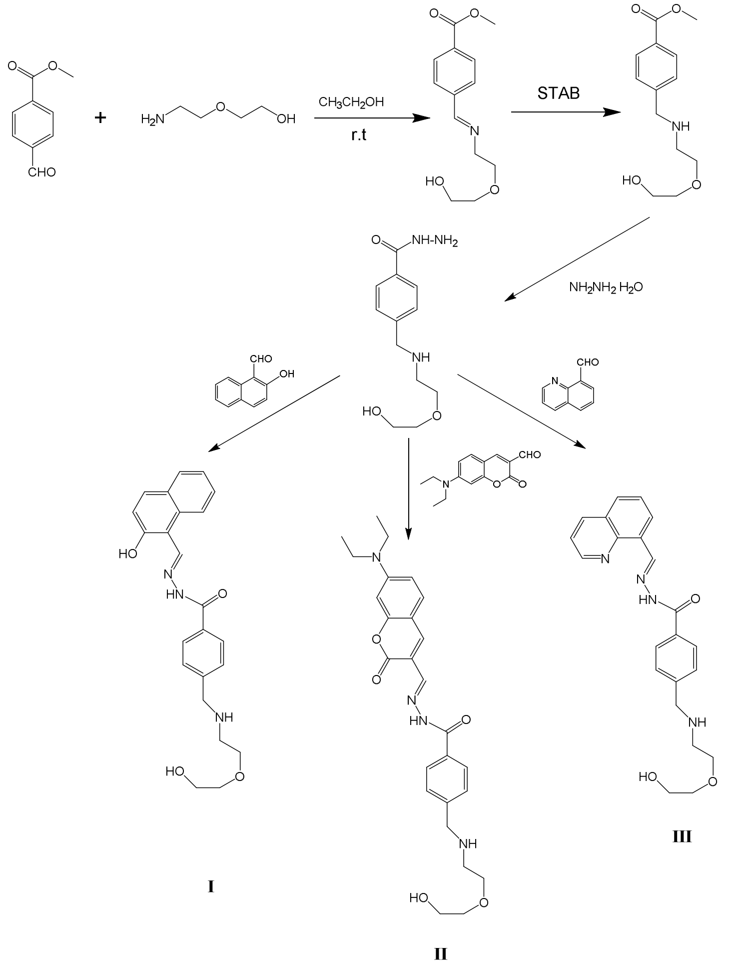
Fig. 3 (a) Fluorescence emission spectra of **III** (10 μM) in water with increasing concentrations of Zn^{2+} ion excited at 343 nm. (b) Fluorescence intensity and color changes excited by a UV lamp (365 nm) of **III** upon the addition of various metal ions (70.0 mM) in aqueous solution. (Inset) Fluorescence emission plotted vs. lg[Zn^{2+}]. (c) Job plot according to the method for continuous variations, indicating the 1 : 1 stoichiometry for **III**-Zn^{2+} (the total concentration of **III** and Zn^{2+} is 10 μM). (λ_{ex} = 343 nm). (d) Variation of the absorption spectra of **III** (10 μM) in aqueous solution with increasing concentrations of Zn^{2+} ion (0 – 70.0 μM).

Fig. 4 Optimized structure of **I-** Al^{3+}, **II**-Cu^{2+} and **III**-Zn^{2+} by DFT calculation.

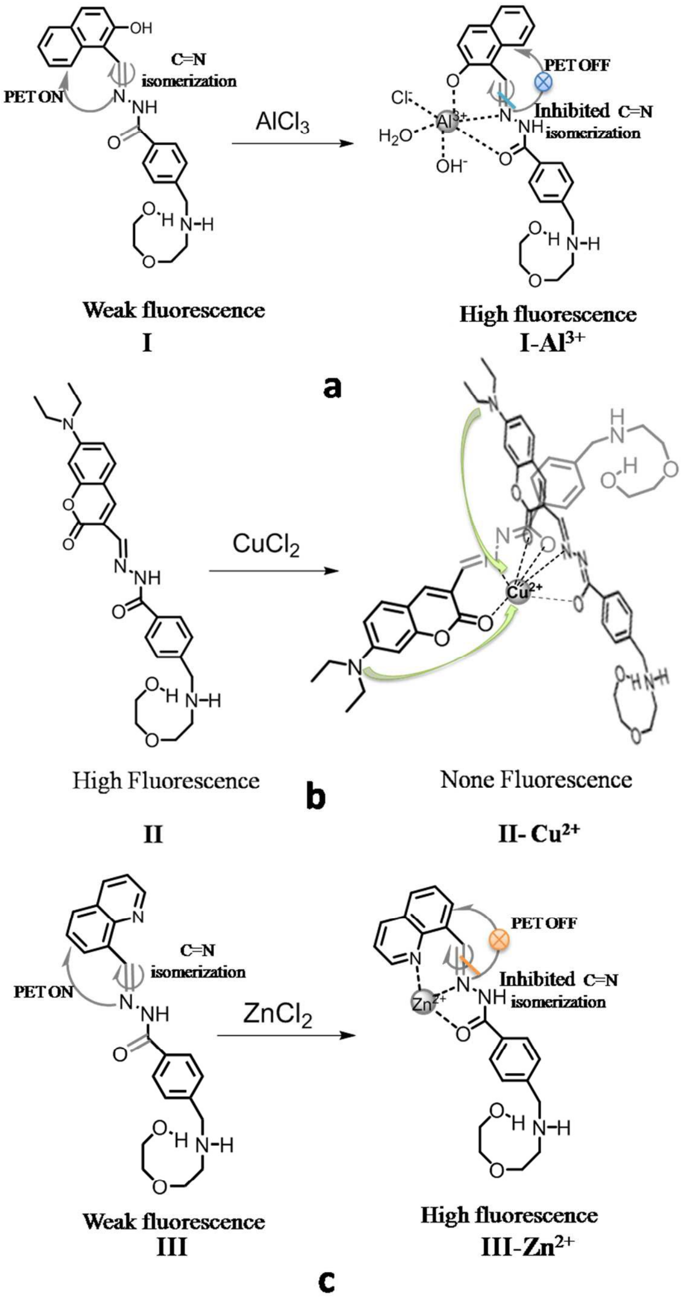
Table 1. Photophysical parameters of benzoyl hydrazone-based derivatives and the metal complexes.

Table 2. The detection limit of benzoyl hydrazone-based derivatives for metal ions

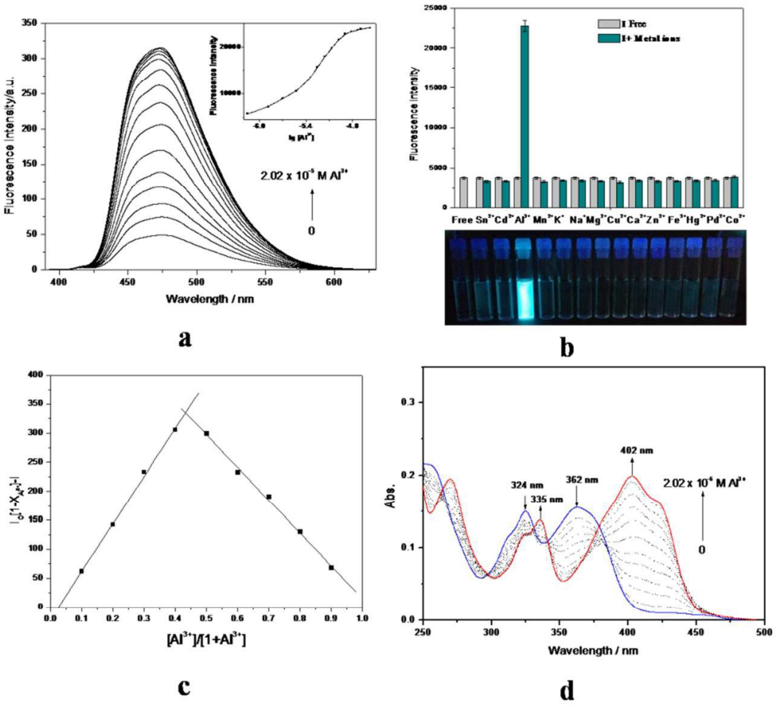
Z. Guo et al.Scheme 1.



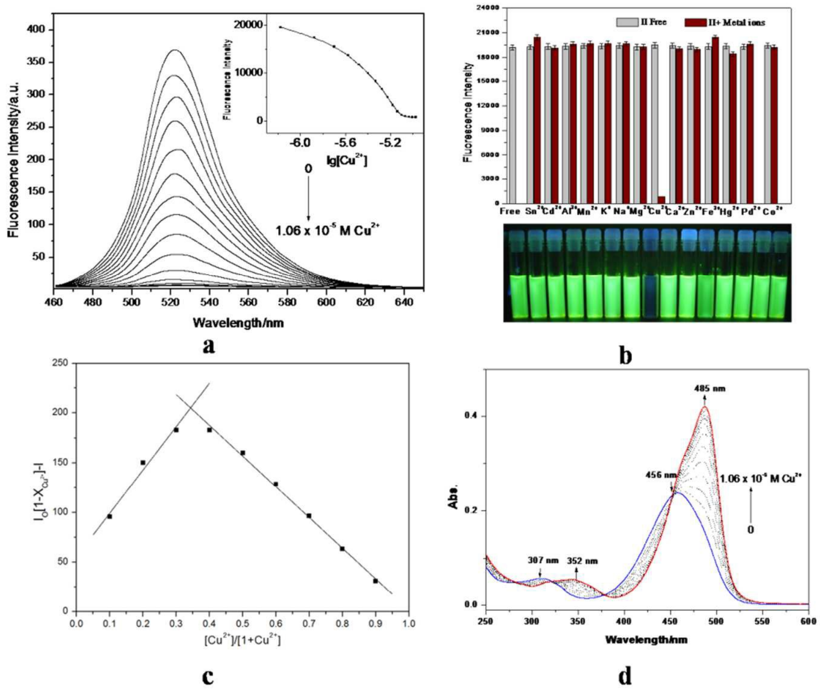
Z. Guo et al.Scheme 2.



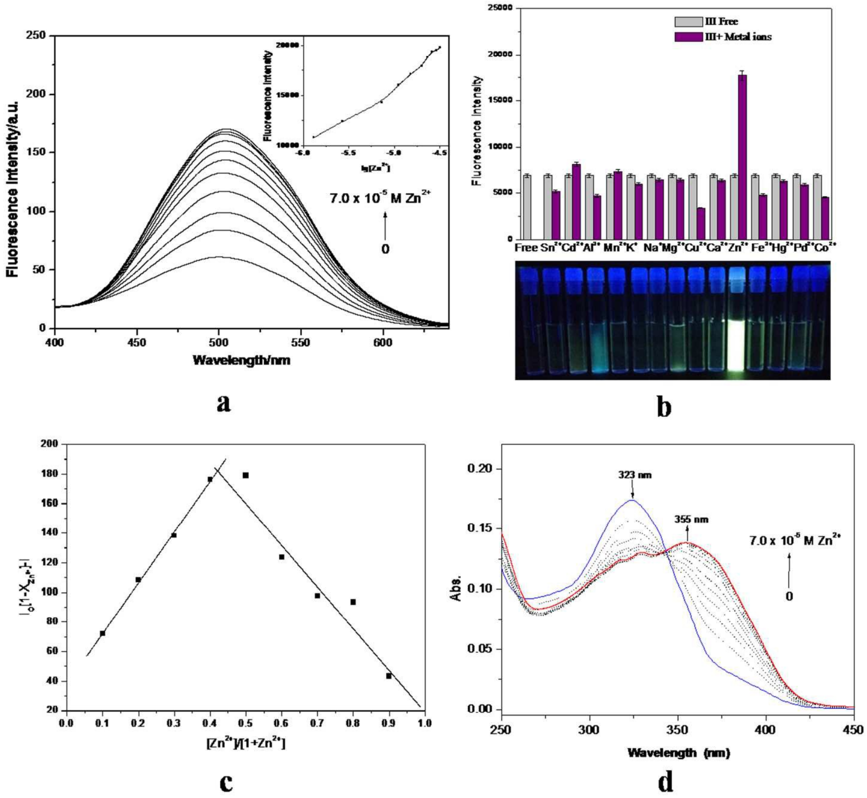
Z. Guo et al. Figure1.



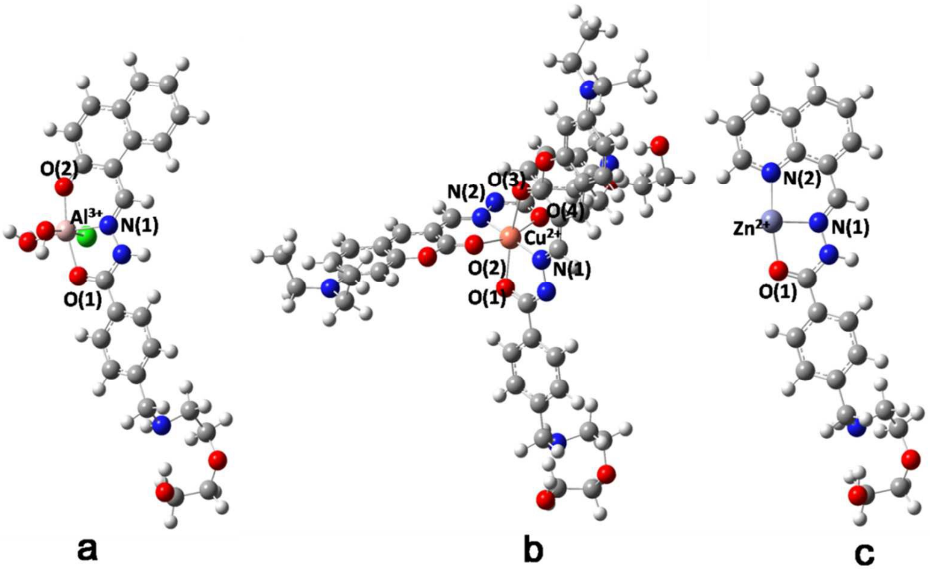
Z. Guo et al. Figure 2.



Z. Guo et al. Figure 3.



Z. Guo et al. Figure 4.



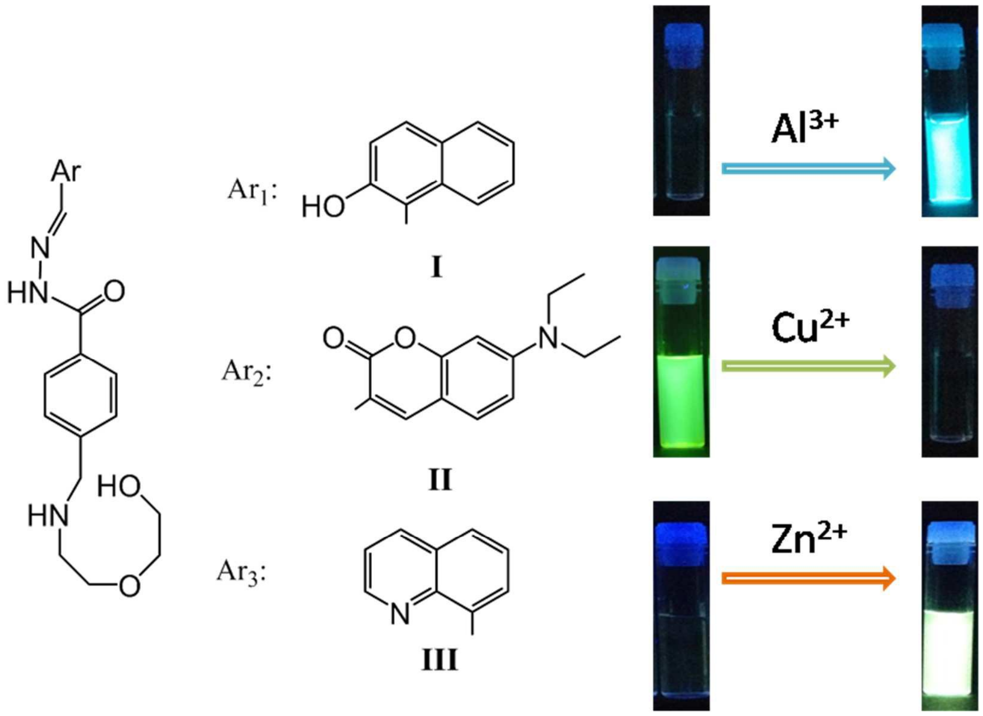
Z. Guo et al. Table 1.

	λ_{abs} (nm)	λ_{em} (nm)	Φ_f	$\tau_F{}^c$ (ns)
I	380	470	0.064[a]	297
I-Al^{3+}			0.570[a]	597
II	454	523	0.970[b]	269
II-Cu^{2+}			0.023[b]	368
III	343	503	0.019[a]	254
III-Zn^{2+}			0.049[a]	359

a. Determined by using quinine sulfate in 0.1 M H_2SO_4(Φ = 0.55) as standard reference; *b*. Determined by using Rhodamine B in ethanol (Φ = 0.65) as standard reference. *c*. Triplet state lifetime, measured by time-resolved transient absorption. 10 μM in aqueous solution.

Z. Guo et al. Table 2.

Complex	**Linear equation**	**Linear relate coefficient (R^2)**	**Detection limit (nM)**
I- Al^{3+}	y= 24.84x + 60.88	0.989	165
II- Cu^{2+}	y= -52.16x + 363.50	0.996	170
III-Zn^{2+}	y= 14.44x + 62.76	0.974	366


Ar
N
HN
O
HN
HO
O
Ar$_1$:
HO
I
Ar$_2$:
O
O
N
II
Ar$_3$:
N
III
Al^{3+}
Cu^{2+}
Zn^{2+}