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A high selective fluorescent sensor for Ni(II) ion in acetonitrile

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ABSTRACT

In this paper, a high selective fluorescent sensor for nickel ion based on boron-dipyrromethene (BODIPY) has been studied. Upon addition of Ni(II) ion, the fluorescence of sensor (compound 1) would be quenched, and the selectivity towards Ni(II) ion over Ag(I), Cd(II), Cu(II), Fe(III), Hg(II), Pb(II), and Zn(II) is good in acetonitrile, there is almost no interference from other heavy metal ions. The stoichiometry of complexation for compound 1 with Ni(II) ion is 1:1, and the quenching process could be reversed by triethanolamine.

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1. Introduction

Nickel is commonly found in hydrogenated oils, milk, milk products and etc. Moreover, nickel is known to cause diseases, like acute pneumonitis, dermatitis, asthma, lung etc. [1,2]. Therefore, monitoring nickel in environment is very important due to its toxic nature and some conventional techniques such as flow injection spectrophotometry, flame and graphite furnace atomic absorption spectrophotometry, ICP-AES, flame photometry and ion-selective electrodes have been developed for the determination of nickel. However, there are some drawbacks for these methods such as require sample pre-treatment, infrastructure backup and high concentration of sample, therefore, not very convenient for analysis of large number of environmental samples and trace analysis [3].

Fluorescent sensors are often used to detect many ions owing to their simplicity and sensitivity [4-6]. Therefore, many fluorescent sensors for sensing metal ions (such as Zn(II) [7], Cd(II) [8], Cu(II) [9], Pb(II) [10], Hg(II) [11] and Cr(III) [12]) have been successfully designed and synthesized. Although some chromogenic sensor for Ni(II) ion have been reported [13], the fluorescent sensor for Ni(II) ions is extremely rare. Recently, Chattopadhyay *et al.* [14] reported a fluorescent sensor for both Zn(II) and Ni(II) ions. But, the drawback for this sensor is that 10-fold increase in fluorescence intensity caused by Zn(II) ion and 7-fold increase caused by Ni(II) ion at pH = 10.96. Thus, it has been a significant challenge to develop a sensitive fluorescent sensor for Ni(II) ion. Herein, we report a simple selectively fluorescent sensor for Ni(II) ion based on boron-dipyrromethene (BODIPY) in acetonitrile (Scheme 1).

2. Experimental

2.1. Instrumentation

All the commercial reagents and solvents were used without further purification. The ^1H and ^{13}C NMR spectra were collected on Jeol JNM-AL300 spectrometer at 300 MHz and 75 MHz, respectively. HRMS spectra were recorded on Jeol JMS-700 spectrometer. UV-vis absorption spectra were obtained on a Shimadzu UV-3100 spectrophotometer. Fluorescence spectra were recorded with a FL-4500 spectrofluorophotometer. Stock solutions (1.00 mM) of metal salts were prepared in CH_3CN. Stock solutions of free **1** (1.00 mM) were prepared in CH_3CN.

2.2. Synthesis

1, 3, 5, 7-Tetramethyl-8-(4'-aminophenyl)-4, 4-difluoro-4-bora-3a,4a-diaza-*s*-indacence [15] (0.1017 g, 0.3 mmol) and 2-pyridinecarbaldehyde (0.0321 g, 0.3 mmol) were placed in ethanol, and the solution was refluxed under nitrogen for 24 h. The organic solvent was removed in vacuum.

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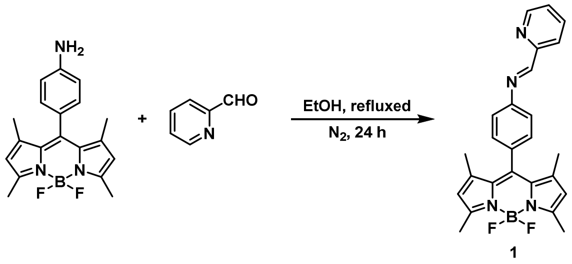

Scheme 1

The crude product was purified by recrystallization to give the title compound as an orange solid (0.1040 g, 80.8%). *N-(4-(5,5-difluoro-1, 3, 7, 9-tetramethyl-5H-4l4, 5l4-dipyrrolo[1, 2-c:2', 1'-f][1, 3, 2]diazaborinin-10-yl)phenyl)-1-(pyridin-2-yl)methane-mine* (**1**): ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.46 (s, 6H, CH$_3$), 2.57 (s, 6H, CH$_3$), 6.00 (s, 2H, Ar-H), 7.33 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.41 (d, 3H, *J* = 8.4 Hz, Ar-H), 7.86 (t, 1H, *J* = 7.8 Hz, Ar-H), 8.23 (d, 1H, *J* = 7.8 Hz, Ar-H), 8.67 (s, 1H, NC-H), 8.75 (d, 1H, *J* = 4.8 Hz, Ar-H). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm) 14.6, 121.2, 121.9, 122.0, 125.5, 129.0, 133.3, 136.8, 143.1, 149.9, 151.7, 154.2, 155.5, 161.7. HRMS (EI, *m/z* (%)) calcd. for $C_{25}H_{23}BF_2N_4$ [M$^+$], 428.1984; found 428.1976.

3. Results and discussion

Initially, metal ion selectivity was examined in acetonitrile. Changes of the fluorescence properties of compound **1** caused by various metal ions including Ag(I), Cd(II), Cu(II), Fe(III), Hg(II), Ni(II), Pb(II), and Zn(II) (10 equiv.) were measured (Figure 1). Only Ni(II) ion produced significant changes in the fluorescent spectra of compound **1** (quenched 95% by 10 equiv.) and Fe(III) ion caused fluorescence intensity of compound **1** quenching a little (quenched 24% by 10 equiv.).

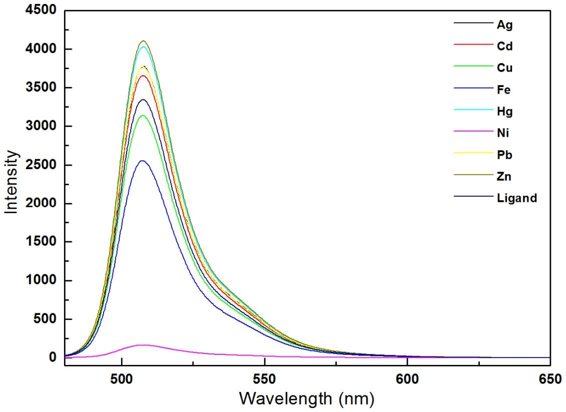

Figure 1. Fluorescence spectra of compound **1** (10 μM) in acetonitrile in the presence of Ni(II) ion and other metal ions (10 equiv., respectively).

Figure 2 depicted the results of competition experiment for compound **1**. As shown in Figure 2, only Fe(III) showed a little interference and other metal ions showed almost no change or a little enhancement in the presence of compound **1** and Ni(II) ion. That proves the selectivity of compound **1** to Ni(II) is good over other heavy metal ions.

The titration of fluoroionophore (**1**) (10 μM) in CH$_3$CN with Ni(II) ion was also studied. Figure 3 exhibited a gradual decrease in the fluorescence intensity (507 nm) with increasing concentration of Ni(II) ion between 0 and 10 μM. That indicates a 1+1 stoichiometry of complexation for compound **1** with Ni(II) ion.

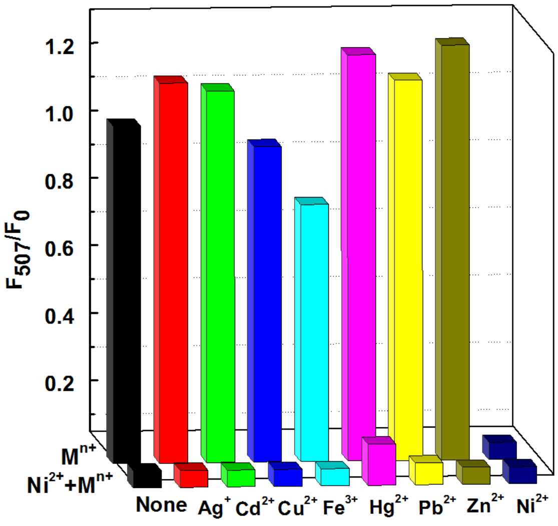

Figure 2. Fluorescence response of compound **1** to various metal ions in acetonitrile. Bars represent the final integrated fluorescence response (F) over the initial integrated emission (F0). First row: Ni(II) + other metal ions; Second row: only metal ion.

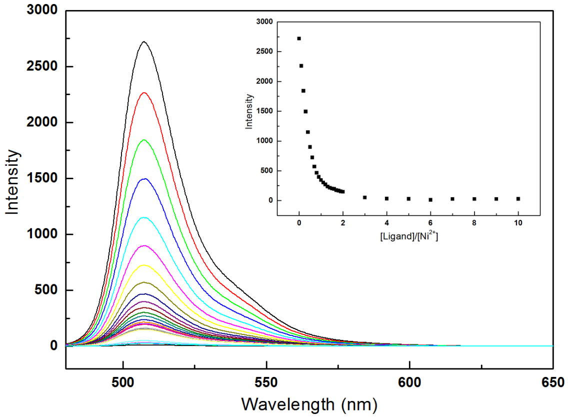

Figure 3. Fluorescence response of compound **1** (10 μM) to Ni(II) in CH$_3$CN (2 mL), the spectra show correspond to free Ni(II) concentrations between 0 and 10 equiv. in acetonitrile.

To examine the reversibility of compound **1**, excess of triethanolamine was added to the compound **1**-Ni(II) complex in CH$_3$CN. As a result, the solution showed strong fluorescence intensity after addition of triethanolamine, indicated that the compound **1**-Ni(II) complex could be reversed by triethanolamine (Figure 4).

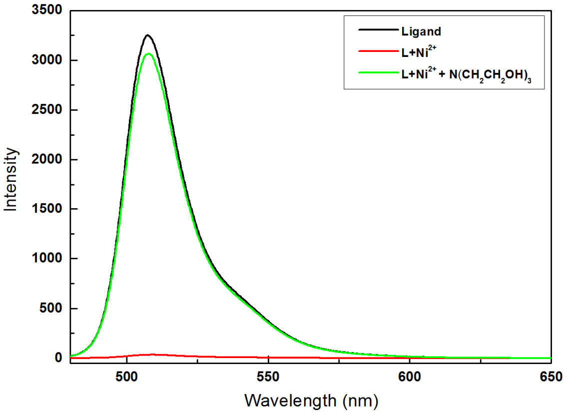

Figure 4. Fluorescence spectra of compound **1** to Ni(II) in CH_3CN (2 mL), triethanolamine can increase fluorescence intensity of the complex.

4. Conclusion

In conclusion, we demonstrated a simple fluorescent sensor for Ni(II) ion in acetonitrile. The selectivity towards Ni(II) ion is good over Ag(I), Cd(II), Cu(II), Fe(III), Hg(II), Pb(II), and Zn(II) ions, almost no interference from other heavy metal ions.

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