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Short communication

Studies on transition metal ions recognition properties of 1-(2-benzothiazole)-3-(2-thiophene)-2-pyrazoline derivatives

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Abstract

Spectroscopic studies revealed that 1-(2-benzothiazole)-3-(2-thiophene)-2-pyrazoline derivatives have rather strong affinity toward divalent transition metal ions. In the case of 1-(2-benzothiazole)-3-(2-thiophene)-5-(4-dimethylamine-phenyl)-2-pyrazoline, enhancement of the fluorescence intensity was observed upon addition of the Zn^{2+} ion ($[Zn^{2+}]/L2 = 100$), while most of the other transition metal ions caused complete quenching.

Keywords: Pyrazoline; Benzothiazole; Recognition; Divalent transition metal ions

1. Introduction

1,3,5-Triaryl-2-pyrazolines are well known fluorescent compounds with high quantum yields and are widely used as whitening or brightening reagents [1–6]. In addition, these compounds have been utilized as fluorescence probes in some elaborated chemosensors [7–9]. In most, such sensors contained an acceptor (=ligand) and a fluorophore (=pyrazoline). The fluorescent 3-(2-pyridyl) analogues [10–12] of triaryl pyrazolines themselves can serve as *N*, *N*-type bidentate ligands for metal ions. In these intrinsic fluorescent ligands, the metal ion binding may affect intramolecular charge transfer and consequently induce spectral changes both in absorbance and in emission. The foregoing may also be applicable to the sensing of metal ions. Recently, Wang et al. [13] reported that 3-(2-pyridyl)-2 pyrazoline derivatives are potential compounds used for developing efficient fluorescent Zn^{2+} chemosensors.

In prevenient study, we have synthesized a series of novel benzothiazoyl pyrazoline compounds containing aromatic heterocycles [14]. They all have stronger fluorescence. In this paper, we investigated their recognition properties to metal ions. To the best of our knowledge, 1-(2-benzothiazole)-3-(2-thiophene)-2-pyrazoline derivatives' interactions with metal ions have not been reported.

2. Experimental

2.1. Materials

All the solvents were of analytical grade and materials were obtained from commercial suppliers except for the fluorescent probes shown in Scheme 1, which were prepared as previously reported [14].

2.2. Methods

The hydrochloric acid salts of Zn^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} ions were used to evaluate the metal ion binding properties of **1a–b**. Stock solutions (10^{-2} M) of the hydrochloric acid salts

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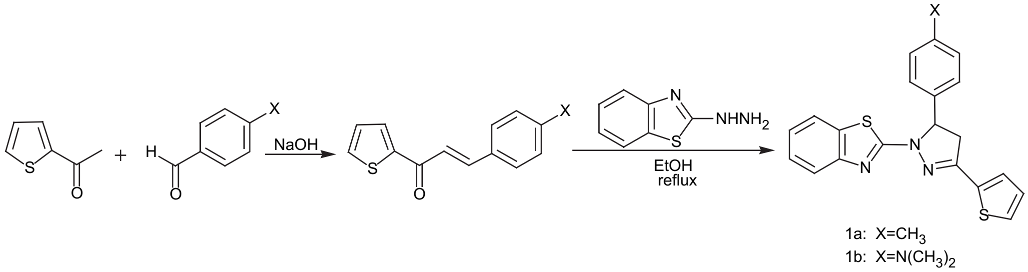

Scheme 1. Synthesis of 1-(2-benzothiazole)-3-(2-thiophene)-2-pyrazoline derivatives.

of the metal ions in THF:H_2O = 4:1 were prepared. A stock solution of the host (10^{-3} M) in THF:H_2O = 4:1 was also prepared. The test solutions were prepared by placing 0.1 mL of the probe stock solution into 10 mL volumetric flasks, adding the appropriate aliquot of each metal stock, and diluting the solution to 10 mL with THF:H_2O = 4:1. Fluorescence spectra were measured using a conventional quartz cell (10 × 10 × 45 mm) at 25 °C with the excitation and emission slits of 1 nm width for **1a–b**. The sample solutions at a host concentration of approximately 1×10^{-5} mol/L were excited at 365 nm for **1a** and 366 nm for **1b** to give a strong emission, and fluorescence spectra were similarly obtained on a Varian Eclipse spectrofluorometer.

3. Results and discussion

Binding affinities of 1-(2-benzothiazole)-3-(2-thiophene)-2-pyrazoline derivatives **1a–b** toward divalent transition metal ions, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, were evaluated by fluorescent spectroscopy measurements. Upon addition of these metal ions, the fluorescent spectrum of derivatives **1a** changes in a similar manner as shown in Fig. 1. The addition of metal ions causes a decrease in optical density of the fluorescence maximum (457 nm for **1a**), probably because there is an electron or energy transfer between metal cation and fluorophore, which is known as the fluorescence quenching mechanism [9]. These results indicate that derivatives **1a** have high binding affinity toward these metal ions.

The fluorescence spectra of **1b** change significantly upon addition of divalent transition metal ions ([M]/L2 = 100). In the cases of Co^{2+}, Cu^{2+}, Ni^{2+} ions, typical metal-induced fluorescence quenching is observed. However, the fluorescence intensity at 459 nm increased greatly when Zn^{2+} ions ([Zn^{2+}]/L2 = 100) were added (Fig. 2). It may be caused by the Zn^{2+} complex. On the other hand, for **1b**, when we decreased the Zn^{2+} concentration, the fluorescence was quenched obviously (Fig. 3). It indicated that the fluorescence intensity of **1b** may be affected by the concentration of Zn^{2+} ion.

4. Conclusion

In summary, 1-(2-benzothiazole)-3-(2-thiophene)-2-pyrazoline derivatives, especially **1b**, show specific fluorescent behavior toward the Zn^{2+} ion among the divalent transition metal ions. These findings indicate that 1-(2-benzothiazole)-3-(2-thiophene)-2-pyrazoline derivatives **1a–b** are potential compounds for developing efficient fluorescent Zn^{2+} chemosensors, which are of current interest [15–17]. In order to improve the Zn^{2+}-selectivity and provide good water solubility to **1**, further studies are underway.

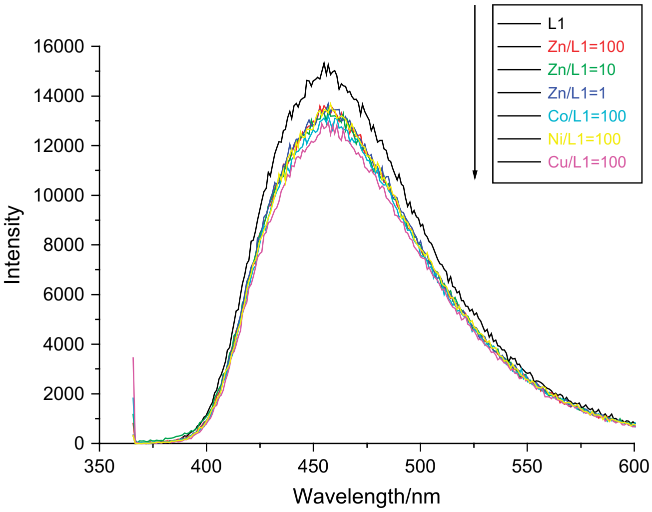

Fig. 1. Fluorescence spectra of **1a** (10^{-5} M) in the presence of various divalent transition metal ions ([M]/[L] = 100) in the solvent of THF:H_2O = 4:1. Excitation wavelength was 365 nm.

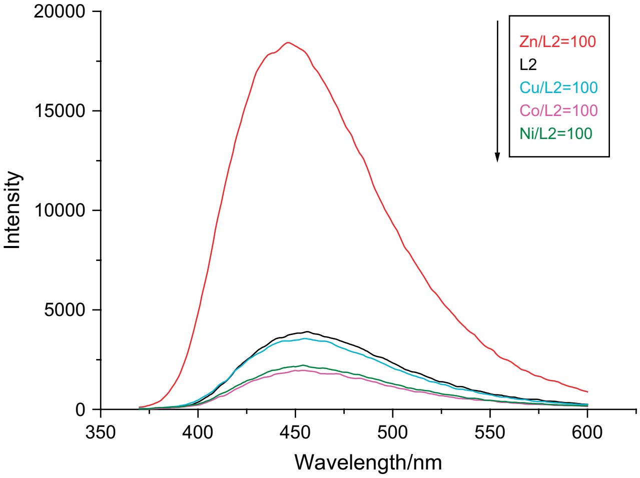

Fig. 2. Fluorescence spectra of **1b** (10^{-5} M) in the presence of various divalent transition metal ions ([M]/[L] = 100) in the solvent of THF:H_2O = 4:1.

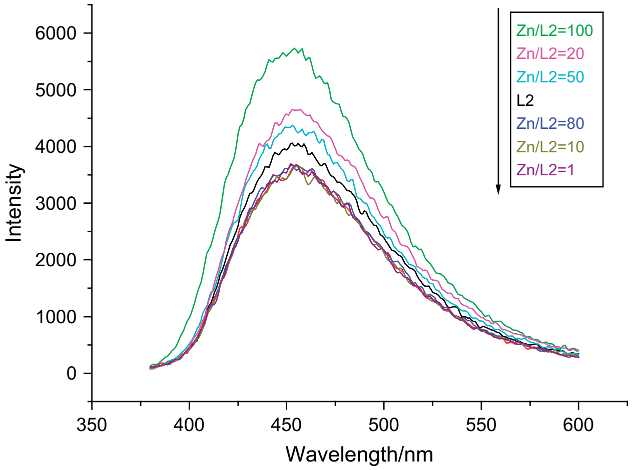

Fig. 3. Fluorescence spectra of **1b** (10^{-5} M) in the presence of increasing Zn^{2+} concentrations in the solvent of THF:$H_2O = 4:1$. Excitation wavelength was 366 nm.

Acknowledgements

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