



# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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## A new Schiff base based on vanillin and naphthalimide as a fluorescent probe for $\text{Ag}^+$ in aqueous solution

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### ARTICLE INFO

#### Article history:

Received 14 September 2011

Received in revised form

19 November 2011

Accepted 24 November 2011

#### Keywords:

Schiff base

Naphthalimide

Vanillin

 $\text{Ag}^+$ 

### ABSTRACT

A new Schiff base based on vanillin and naphthalimide was designed and synthesized as fluorescent probe. The probe showed high selectivity for  $\text{Ag}^+$  over other metal ions such as  $\text{Pb}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  in aqueous solution. A new fluorescence emission was observed at 682 nm in the presence of  $\text{Ag}^+$  ion. The fluorescence intensity quenched with increasing the concentration of  $\text{Ag}^+$  at 682 nm. The method of job's plot confirmed the 1:2 complex between  $\text{Ag}^+$  and probe, and the mechanism was proposed.

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### 1. Introduction

Fluorescent chemosensors are very important in chemistry, biology and medicine. There are several strategies in the design of environment-sensitive fluorophores agents based on these donor–acceptor systems like 4-dimethylamino phthalimide and 4-amino-1,8-naphthalimide [1]. It is well known that 1,8-naphthalimide derivatives are sensitive to the environment because of the substituted functional groups, especially aromatic groups. Because of their strongly fluorescence and good photostability, 1,8-naphthalimide derivatives have been used in a number of areas, including polymer materials [2,3], anticancer agents [4,5], fluorescent markers in biology [6], fluorescence probes [7–11] and light emitting diodes [12].

Schiff bases are a large class of organic compounds being from condensation reaction of aromatic aldehyde and amine [13]. Vanillin was used as a flavoring agent in foods, but there was only a few reports about its ability of combined with metal ions [14]. Herein, our job designed and synthesized a Schiff base based on vanillin and 1,8-naphthalimide.

The structure was characterized by FTIR, Mass and  $^1\text{H}$  NMR spectra analysis. Then the influence of solvents and pH on its absorption spectra was investigated. The coordination of metal ions and the probe was investigated by fluorescence emission in aqueous solu-

tion. The probe showed high selectivity for  $\text{Ag}^+$ , and the job's plot confirmed the formation of 1:2 between  $\text{Ag}^+$  and probe.

### 2. Experimental

#### 2.1. Reagents

All the chemicals and organic solvents were of analytical grade. The solution of metal ions was prepared from their nitrate salts and chloride salts of analytical grade. The value of pH was adjusted by HCl ( $0.1 \text{ mol L}^{-1}$  and  $1 \text{ mol L}^{-1}$ ) and NaOH ( $0.1 \text{ mol L}^{-1}$  and  $1 \text{ mol L}^{-1}$ ) at room temperature.

#### 2.2. Apparatus

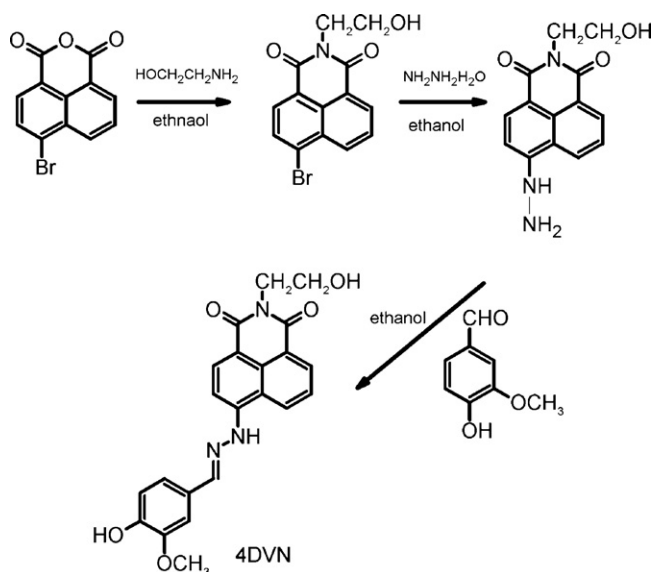
IR spectra were recorded on Nicolet AVATAR360 infrared spectrometer and pellets were made by using KBr. The MS spectra were performed on Bruker ESQUIRE LC–MS.  $^1\text{H}$  NMR spectra were recorded using Bruker AVANCE-400 spectrometer operating at 400 MHz. UV–vis spectra were recorded using Hitachi U-4100 Spectrophotometer. The fluorescence spectra were taken on Hitachi F-7000FL Spectrophotometer.

#### 2.3. Synthesis of the probe of 4DVN

The synthesis of 4DVN was shown in Scheme 1.

4-Bromo-*N*-hydroxyethyl-1,8-naphthalimide: It was synthesized by 4-bromo-1, 8-naphthalimide and ethanolamine followed the

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Scheme 1. Synthesis of 4DVN.

literature [15]. Yield: 94%. m.p. 199–201 °C. IR(KBr pellet,  $\text{cm}^{-1}$ ): 3387, 1698, 1568, 1375, 778.

**4-Hydrazine-N-hydroxyethyl-1,8-naphthalimide:** 4-Bromo-N-hydroxyethyl-1,8-naphthalimide (2.00 g) and 12.5 mL 80% hydrazine hydrate in 30 mL ethanol were heated under reflux for 4 h. After cooling to room temperature, the precipitated product was filtered, washed with ethanol and dried, 1.63 g orange crystal obtained [16]. Yield: 96%. m.p. 197–199 °C. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3475, 3376, 1578, 1631, 1390, 775.

**4-Vanillin-N-hydroxyethyl-1,8-naphthalimide (4DVN):** Vanillin (0.19 g) and 4-hydrazine-N-hydroxyethyl-1,8-naphthalimide (0.34 g) was added in 40 mL ethanol. Then the mixture solution was stirred and heated under reflux for 6 h. After cooling to room temperature, the solid product was filtered. After purification 0.38 g red powder was obtained [17]. Yield: 75%. m.p. 212–214 °C. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3462, 1578, 1387. Ms:  $m/z$ : 428 ( $[\text{M}+\text{Na}]^+$ ).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ): 9.501 (s, 1H), 8.724 (b, 1H), 8.423 (b, 1H), 8.306 (b, 2H), 7.716 (t, 1H), 7.652 (b, 1H), 7.391 (s, 1H), 7.156 (dd, 1H), 6.873 (d, 1H), 5.749 (s, 1H), 4.119 (t, 2H), 4.801 (t, 1H), 3.896 (s, 3H), 3.606 (q, 2H).

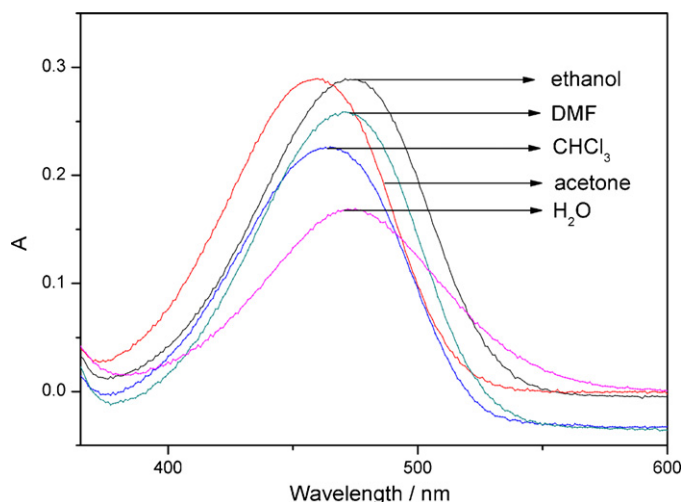
### 3. Results and discussion

#### 3.1. The influence of solvents on UV–vis spectra

The influence of solvents on the absorption spectra was determined. It can be seen clearly from Fig. 1 that the maximum absorption in  $\text{H}_2\text{O}$ , ethanol and DMF were all located at 472 nm. While the maximum absorption in acetone and chloroform has a blue shift in a range of 12 nm, respectively. Taking into account of the economic cost and practical application, the experiments were carried out in aqueous solution.

#### 3.2. The effect of pH on UV–vis spectra

The effect of pH on its absorption spectra was studied in a range from 2 to 12. As shown in Fig. 2, the value of pH played an important role in the absorption spectra. The maximum absorption was located at 475 nm, with the transition from pH 2 to 8. But the maximum absorption has various red shifts after pH 8. The solution took on different colors between pH 8–12, which implied the probe was sensitive to high pH.

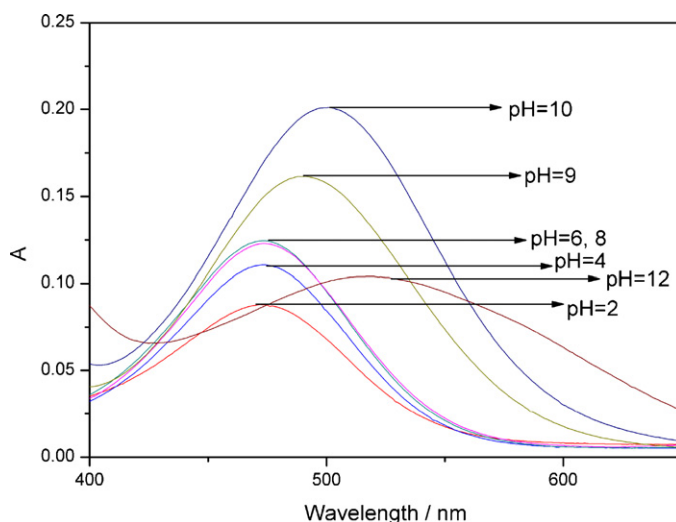
Fig. 1. Absorption spectra of 4DVN in different solvents ( $C = 1.0 \times 10^{-5} \text{ mol L}^{-1}$ ).

#### 3.3. The effect of pH on the fluorescence spectra

The fluorescence spectra of different values of pH were presented in Fig. 3. The fluorescence emission of probe in acidic medium is low with a maximum at 540 nm. During the transition from acidic to alkali pH, the fluorescence intensity increased and the maximum fluorescence emission was shifted by 5 nm [18]. It can be seen that fluorescence kept tiny intensity between pH 2 and 6, but changed sharply after pH 8, which was because the C=N double bond of Schiff base damaged in a low or high pH value [19]. So the experiment followed was carried out in nearly neutral solution of pH 6.8.

#### 3.4. Fluorescence evaluation of metal binding interaction

The photophysical sensitivity of 4DVN towards physiological and environmental relevant metal ions,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  were studied. The fluorescence spectrum of 4DVN displayed at 540 nm ( $\lambda_{\text{ex}} = 455 \text{ nm}$ ) with 1 equiv. metal ions. As can be seen in Fig. 4, the fluorescence profile of the probe remained essentially invariant to added  $\text{Pb}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$ . It implies that there are none or very poor affinities of these metal ions

Fig. 2. Absorption spectra of 4DVN in various pH ( $C = 1.0 \times 10^{-5} \text{ mol L}^{-1}$ ).

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