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A turn-on fluorescent sensor for detection of cyanide in aqueous media

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ABSTRACT

2-Hydroxy-1-naphthaldehyde oxime (receptor **1**) serves as a selective chemosensor for cyanide anion (CN^-). In the presence of CN^-, an enhanced fluorescent intensity and red-shift were observed. The observed complexation between receptor **1** and CN^- may cause by a hydrogen bonding interaction between the OH group of receptor **1** and CN^-.

1. Introduction

Cyanide anion (CN^-) is highly toxic to living animals due to the inhibition of the oxygen utilization by cells and causing the inactivation of cytochrome oxidase [1–3]. Besides, CN^- is widely used in many chemical processes, such as gold mining, electroplating, metallurgy, the syntheses of nylon and other synthetic fibers and resins. Due to the toxicity and industrial use of CN^-, great efforts have been devoted to the development of sensors for the recognition of CN^- [4–17]. However, many of the reported CN^- sensors suffer from the disturbance by anions such as F^- and AcO^-. In addition, only a few chemical sensors that are operating in aqueous media upon the complexation of CN^-. Therefore, reliable and efficient ways of detecting the presence of CN^- are desirable.

Previously, Kim and co-workers reported a sensitive cyanide sensor based on coumarinlyoxime. When CN^- was added to the oxime derivative sensor, it showed dramatic fluorescence and color changes in aqueous solvent [18]. Recently, we have reported that the commercial available 2-hydroxy-1-naphthaldehyde is highly sensitive and selective towards CN^- in MeOH–H_2O (v/v, 95:5) solution [19]. Herein, we reported an oxime derivative (2-hydroxy-1-naphthaldehyde oxime, receptor **1**) which can serve as a selective chemosensor for CN^- in MeOH–H_2O (v/v, 1:9).

2. Experimental

2.1. General information

All reagents were obtained from commercial suppliers and were used without further purification. Analytical thin-layer chromatography was performed using silica gel 60 F254 plates (Merck). The ^1H and ^{13}C NMR spectra were recorded with a Bruker AM 300 spectrometer. Chemical shifts are given in ppm with residual MeOD as reference. Mass spectra were recorded under electron impact (EI) or electron spray interface (ESI) conditions. UV–vis spectra were recorded by using HP-8453 spectrophotometer with a diode array detector, and the resolution was set at 1 nm. Fluorescence spectra were recorded on a Cary Eclipse Fluorescene spectrophotometer.

2.2. Detection of CN^- in real water samples

To evaluate the practicality of the present method, lake water samples were examined. The lake water samples were obtained from the White Sand Lake of Changhua University of Education, Changhua, Taiwan. The lake water samples were filtered through a 0.20 μm filtered membrane and then centrifuged at 12,000 rpm for 10 min.

2.3. Synthesis of receptor 1 (2-hydroxy-1-naphthaldehyde oxime)

To a solution of 2-hydroxy-1-naphaldehyde (100 mg, 0.57 mmol) in distilled water (5 mL) was added sodium acetate (63 mg, 0.77 mmol) and hydroxylamine hydrochloride (60 mg, 0.86 mmol). The reaction

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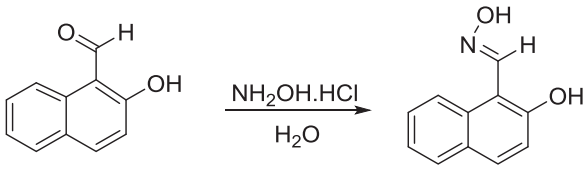

Scheme 1. Synthesis of receptor **1**.

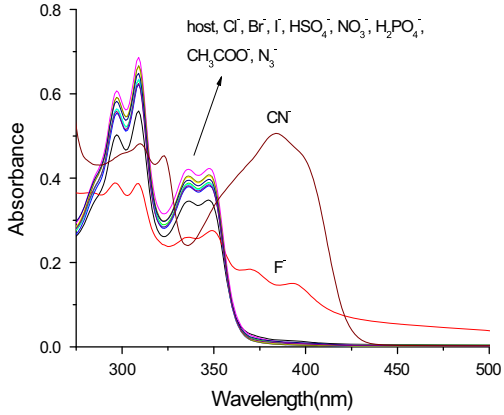

Fig. 1. UV/vis spectra of **1** (70 μM) recorded in MeOH/H_2O=1/9 (v/v) after addition of 10.0 Eq of various anions.

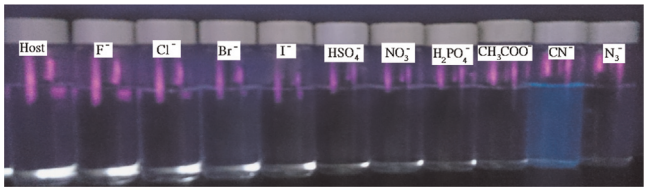

Fig. 2. The color changes of receptor **1** (70 μM) observed under UV light upon addition of 10.0 Eq of various anions in MeOH/H_2O=1/9 (v/v). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

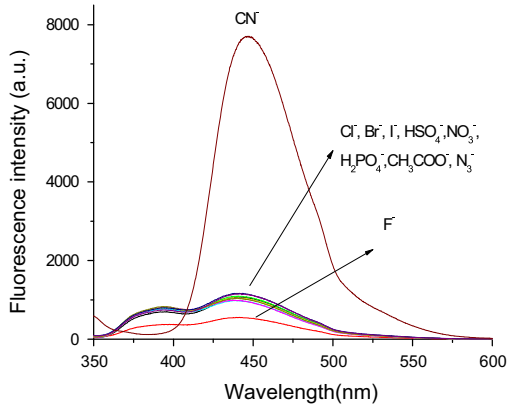

Fig. 3. Fluorescence emission spectra ($\lambda_{ex.}$=319 nm) of receptor **1** (70 μM) in the presence of 10.0 Eq of various anions in MeOH/H_2O=1/9 (v/v).

mixture was refluxing for 1 h. After cooling to room temperature the mixture was filtered. The solid obtained was washed with water and recrystallized from ethanol to afford the white solid. (87 mg, 81%) *Rf*=0.76 (EtOAc/Hexane=1:2); ^{1}H NMR (300 MHz, MeOD) δ 6.93 (d, *J*=9 Hz, 1H), 7.11 (t, *J*=15.9 Hz, 1H), 7.27 (t, *J*=16.8 Hz, 1H), 7.25 (d, *J*=9.3 Hz, 2H), 7.84 (d, *J*=8.7 Hz, 1H), 8.91 (s, 1H); ^{13}C NMR (75 MHz, MeOD) δ: 158.3, 149.4, 133.4, 132.9, 129.9, 129.8, 128.5, 124.6,

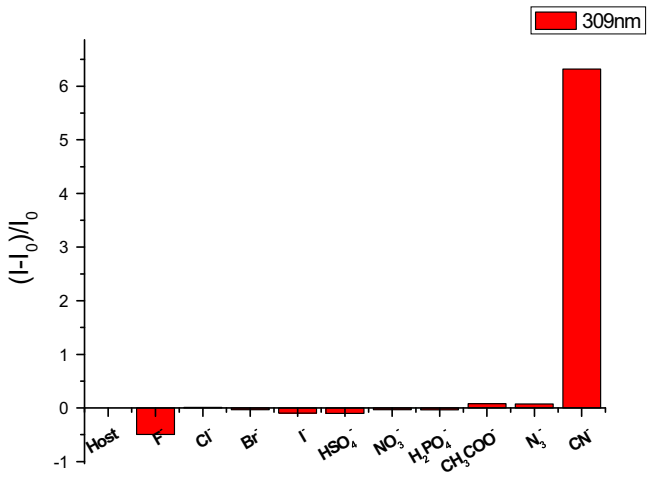

Fig. 4. Variation of the fluorescence intensity at 454 nm ($\lambda_{ex.}$=319 nm) of receptor **1** (70 μM) in the presence of 10.0 Eq of various anions in MeOH/H_2O=1/9 (v/v).

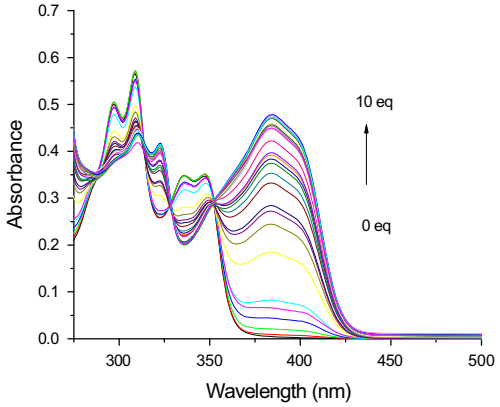

Fig. 5. UV–vis spectra of receptor **1** (70 μM) in MeOH/H_2O=1/9 (v/v) upon addition of increasing concentrations CN^-.

121.8, 119.6, 108.9; HRMS (EI): Calcd for $C_{11}H_9NO_2$ (M^+), *m/z* 187.0633; found *m/z* 187.0634.

3. Results and discussion

3.1. Synthesis of receptor 1

Receptor **1** can be readily prepared by the coupling reaction of 2-hydroxy-1-naphaldehyde and hydroxylamine hydrochloride with 81% yield in H_2O (Scheme 1), and characterized by ^{1}H NMR, ^{13}C NMR and mass spectrometry analysis (Figs. S1 and S2).

3.2. Absorption and fluorescence studies

The sensing properties of receptor **1** for anions (F^-, Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, $H_2PO_4^-$, AcO^-, CN^-, N_3^-) using TBA (tetrabutylammonium salts) as a counter ion were investigated by UV/vis and fluorescence measurements. As shown in Fig. 1, receptor **1** showed two major absorption bands at 315 and 350 nm, respectively. In the presence of CN^-, the absorption spectra of receptor **1** in MeOH–H_2O (v/v, 1:9) showed a major band at 383 nm with a red-shift. The formation of the new low-energy band may be attributed to the interaction of CN^- with receptor **1**. Meanwhile, the solution of receptor **1** showed a dramatic color change from deep blue to light blue which could easily be detected by the