



A novel colorimetric and “turn-on” fluorimetric chemosensor for selective recognition of CN^- ions based on asymmetric azine derivatives in aqueous media

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ABSTRACT

A novel chemosensor 2-((Z)-((E)-quinolin-2-ylmethylene)hydrazono)methyl)phenol **PX** has been successfully designed and synthesized, which showed both colorimetric and “turn-on” fluorescence responses for CN^- in DMSO/ H_2O (3:2, v/v; pH = 7.20) solution. The sensor could respond effectively to the stimulation of CN^- ions via deprotonation and sensing mechanism of intramolecular charge transfer (ICT). Moreover, the sensor **PX** was successfully utilized to detect CN^- in bitter almond, and the detection limit on fluorescence response of **PX** towards CN^- was down to 4.5×10^{-7} M. Test strips containing **PX** were also prepared, which could act as a practical colorimetric tool to detect CN^- in aqueous media.

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1. Introduction

The development of anions sensors have been an interesting and emerging field of research due to the important roles of anions in industrial and biological processes [1,2]. It's well that CN^- ion is one of the most toxic anions in various anions, and its toxicity can damage many functions including the vascular, visual, central nervous, cardiac, endocrine, and metabolic systems [3–6] in human body. According to the World Health Organization (WHO), maximum acceptable amount of cyanide ion in drinking water is 1.9 μM [7]. However, widespread utilization of cyanide salts in various industries such as gold extraction, synthetic fibers, electroplating and so on [8–10] have caused a serious environmental concern. Hence, it is necessary for designing reasonable chemosensor to monitor cyanide concentration in environment.

In the past few decades, a variety of techniques such as ion chromatography, potentiometric, electrochemical methods and titrimetric [11–14] have been reported for CN^- detection. However, those methods usually suffer from a series of problem such as high cost, long response time and sophisticated equipment and so on, which seriously limits its practical application. In contrast, fluorimetric and

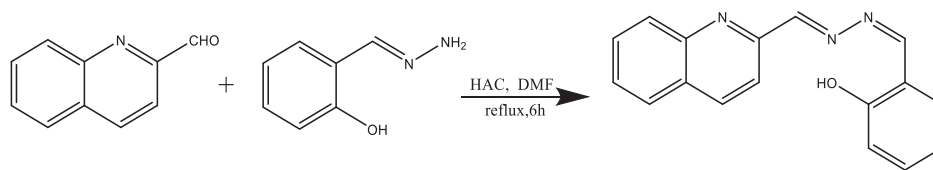
colorimetric sensors due to low cost, simplicity, high selectivity and sensitivity and fast response [15] have gained more attention.

Currently, a great deal of fluorimetric and colorimetric sensors based on various mechanisms (intramolecular charge transfer (ICT) [16–20], excited state intramolecular proton transfer (ESIPT) [21], photo-induced electron transfer (PET) [22], and metal-ligand charge transfer (MLCT) [23,24]) have been synthesized. Among different intelligent strategies in designing sensors, the deprotonation approach is often used to detect CN^- due to easy design and comprehension. In many cases, sensors usually containing groups such as amide, thiourea, pyrrole and hydroxyl could detect CN^- [25].

Our research group has a longstanding interest in molecular recognition [26–34]. Herein, on the basis of the previous work, we designed a novel chemosensor **PX** based on asymmetric azine derivatives, which showed dual-channel response for CN^- in DMSO/ H_2O (3:2, v/v) solution. To the best of our knowledge, the azine chemosensors-based colorimetric and fluorescence “turn-on” process reported so far are very few. Here, the function of sensor **PX** for recognizing CN^- is based on the appended salicylaldehyde hydrazone and quinoline that act as respectively binding sites as well as fluorescent signal group. Moreover, this probe could successfully detect CN^- in bitter almond, and test strips containing **PX** could act as a practical colorimetric tool to detect CN^- in aqueous solution. The recognition mechanism was investigated by mass spectrometry and ^1H NMR.

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Scheme 1. The synthetic procedure for sensor **PX**.

2. Experimental

2.1. Reagents and Apparatus

All reagents and solvents were obtained from the commercial sources without further purification. Double-distilled water was used throughout the experiment. Tetrabutylammonium salts of anions (F^- , Cl^- , Br^- , I^- , CO_3^{2-} , S^{2-} , PO_4^{3-} , NO_2^- , AcO^- , $H_2PO_4^-$, HSO_4^- and ClO_4^-) and sodium salts of anions (CN^- and SCN^-) were purchased from Alfa-Aesar Chemical Reagent Co. and stored in vacuum desiccators. 1H NMR and ^{13}C NMR spectra were respectively recorded on a Mercury-400BB spectrometer at 400 MHz and 100 MHz, and chemical shifts were recorded in ppm (DMSO d_6 as solvent). Melting points were performed on an X-4 digital melting point apparatus and were uncorrected. Fluorescence measurements were made using a Shimadzu RF-5301 fluorescence spectrophotometer. UV–Vis absorption spectra were measured on a Shimadzu UV-2550 spectrometer. ESI-MS was measured on an Agilent 1100 LC-MSD-Trap-VL system.

2.2. Synthesis of Chemosensor **PX**

The synthesis of chemosensor **PX** is shown in Scheme 1. 2-quinolinecarbaldehyde (0.236 g, 1.5 mmol) was added to the DMF solution (10 mL) of salicylaldehyde hydrazone (0.204 g, 1.5 mmol). The reaction mixture was stirred and refluxed for 6 h with acetic acid as catalyst. After cooling to room temperature, the precipitate was filtered, and recrystallized with DMF to get pale yellow compound **PX**. Color: yellow solid, mp: 164–166 °C. 1H NMR (DMSO d_6 , 400 MHz, ppm) δ : 11.07 (s, 1H), 9.03 (s, 1H), 8.75 (s, 1H), 8.48(t, $J = 8.62$ Hz, 1H), 8.22 (dd, $J = 8.33$ Hz, 1H), 8.09 (m, 1H), 8.04(t, $J = 8.33$ Hz, 1H), 7.82(t, $J = 6.45$ Hz, 1H), 7.73(t, $J = 7.45$ Hz, 1H), 7.67(t, $J = 6.97$ Hz, 1H), 7.41(t, $J = 7.24$ Hz, 1H), 6.97(dd, $J = 7.99$ Hz, 2H). ^{13}C NMR (DMSO d_6 ,

100 MHz, ppm) δ : 164.39, 162.47, 157.30, 153.25, 147.96, 137.41, 134.01, 131.43, 130.72, 129.68, 128.77, 128.50, 128.40, 120.01, 118.80, 118.62, 117.03.

3. Results and Discussion

The colorimetric and fluorimetric sensing ability of **PX** were investigated with various anions (F^- , Cl^- , Br^- , I^- , CO_3^{2-} , S^{2-} , PO_4^{3-} , NO_2^- , AcO^- , $H_2PO_4^-$, HSO_4^- , ClO_4^- , SCN^- and CN^-) in DMSO/ H_2O (3:2, v/v; pH = 7.20) solution. When 50 equiv. various anions were respectively added into the solution of **PX** (2.0×10^{-5} M), only CN^- induced a dramatic color change from colorless to yellow, which was easily distinguished by naked eyes. In the corresponding UV–Vis spectra, an obvious red shift from 350 nm to 435 nm was observed (Fig. 1). However, other examined anions (F^- , Cl^- , Br^- , I^- , CO_3^{2-} , S^{2-} , PO_4^{3-} , NO_2^- , AcO^- , $H_2PO_4^-$, HSO_4^- , ClO_4^- and SCN^-) didn't induce any dramatic color and spectra change. These results suggested that **PX** displayed an excellent selectivity for CN^- over all other anions tested.

Compound **PX** alone displayed a weak fluorescence emission band at 440 nm in DMSO/ H_2O (3:2, v/v; pH = 7.20). Upon addition of 50 equiv. CN^- in aqueous solution, **PX** produced a significant fluorescence enhancement response and shifted towards 516 nm, which responded with a color change from colorless to green under UV lamp. Moreover, other anions (F^- , Cl^- , Br^- , I^- , CO_3^{2-} , S^{2-} , PO_4^{3-} , NO_2^- , AcO^- , $H_2PO_4^-$, HSO_4^- , ClO_4^- and SCN^-) produced a negligible change in fluorescence color and intensity, which indicated that **PX** could detect CN^- with specific selectivity and high sensitivity in DMSO/ H_2O (v/v = 3:2; pH = 7.20) solution (Fig. 2).

To get insight into the CN^- (0.01 M) sensing property of sensor **PX**, UV–Vis absorption titration experiment was carried out in DMSO/ H_2O

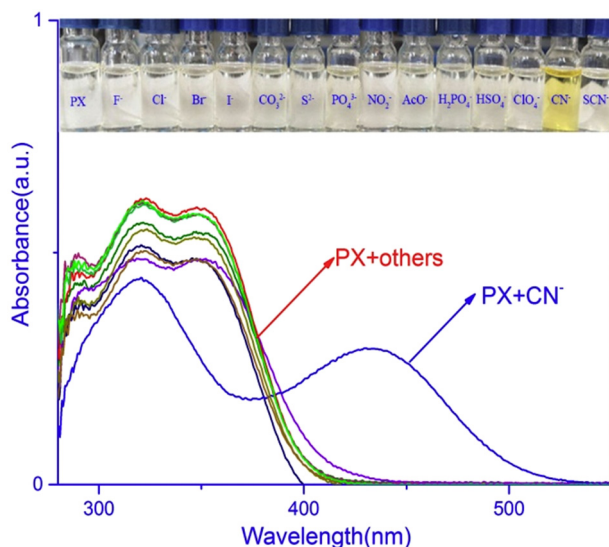


Fig. 1. UV–vis spectra of **PX** (20 μ M) in the presence of 50 equiv. of various anions in DMSO/ H_2O (3:2, v/v; pH = 7.20) solution. Inset: Color changes of **PX** (20 μ M) with various anions (50 equiv.) in DMSO/ H_2O (3:2, v/v; pH = 7.20) solution.

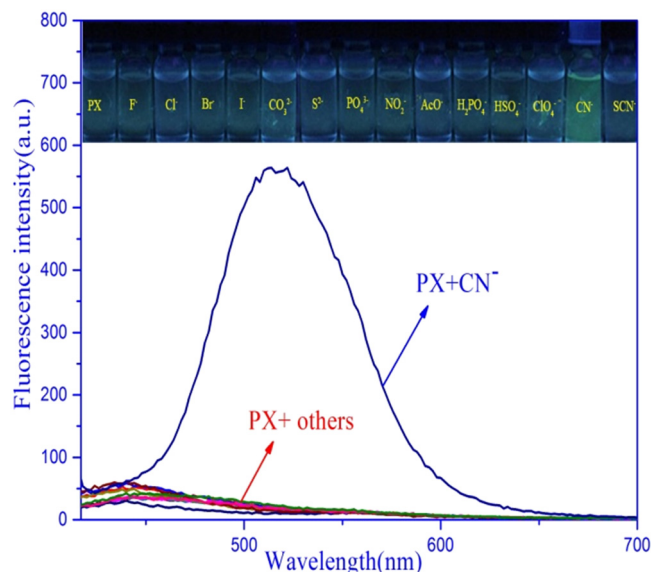


Fig. 2. Fluorescence spectra of **PX** (20 μ M) with various anions (50 equiv.) in DMSO/ H_2O (3:2, v/v; pH = 7.20). Inset: Color changes for **PX** (20 μ M) with various anions (50 equiv.) in DMSO/ H_2O (3:2, v/v; pH = 7.20) solution under the UV lamp.

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