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ORIGINAL PAPER

A Highly Selective and Turn-on Fluorescence Sensor for Detection of Cyanide

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Abstract 2-Hydroxy-1-naphthaldehyde (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 from a formation of phenoxide anion by nucleophilic addition of the CN^- to carbonyl group.

Keywords Chemosensor · Fluorescence · Turn-on · Cyanide

Anions are extensively used in the environmental, industrial, biological, and medical fields [1–7]. Among these anions, cyanide (CN^-) is one of the most toxic anions and harmful to environment or human health. It is acutely toxic to mammals when administered through any route, causing death in minutes [8]. Nevertheless, CN^- is widely used in many chemical processes, such as gold mining, electroplating, metallurgy, and the syntheses of nylon and other synthetic fibers and resins. Thus, the sensitive and selective detection of CN^- is of considerable importance and significant interest. Up to now, a large number of chemosensors for CN^- have been invented [9–12], colorimetric and fluorimetric sensor for the naked-eye detection have attracted considerable interest for their simple and fast implementation as well as their high sensitivity [13–17]. Moreover, one receptor could showing multifunctional activities have been a topic of considerable interest. Previously, we have reported the commercial 2-hydroxy-1-naphthaldehyde (receptor **1**) exhibited a highly sensitively and selectively for Al^{3+} in EtOH-H_2O solution [18]. The receptor **1** has naphthalene group as a fluorescent signal unit and salicylaldehyde functionality as a recognition or reaction unit. Salicylaldehyde is a popular reaction counterpart for nucleophilic addition reactions due to its activated carbonyl group by phenolic hydrogen through an intramolecular hydrogen bond. To the best of our knowledge, utilizing 2-hydroxy-1-naphthaldehyde as fluorescent chemosensor for detection of anions has not been reported. Herein, we reported a colorimetric and fluorescent CN^- selective receptor **1** which can work effectively in a partially aqueous medium. Receptor **1** can detect CN^- via naked eye discernible color change and exhibited a unique "turn-on" fluorescence of high selectivity for CN^- in EtOH-H_2O solution.

The sensing properties of receptor **1** for anions (F^-, Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, $H_2PO_4^-$, AcO^-, CN^-, ClO_4^-) using sodium 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 325 and 360 nm, respectively. In the presence of CN^-, the absorption spectra of receptor **1** in EtOH-H_2O (*v*/*v*, 95:5) showed a major band at 400 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 colorless to light yellow which could easily be detected by the naked-eye (Fig. 2). From the fluorescent spectra (Fig. 3), receptor **1** alone displayed no significant emission. However, upon addition of CN^-, receptor **1** exhibited a prominent fluorescent enhancement accompanied by a red shift of 26 nm from 430 to 456 nm. The fluorescent enhancement efficiency observed at 456 nm was 2.6-fold greater than that of the control in the absence of CN^- ion (Fig. 4). CN^- is expected to be detectable by a nucleophilic attack toward to a carbonyl functional group. Fast proton transfer of the phenol hydrogen to the developing phenoxide anion causes the strong fluorescence of the sensor. It has been

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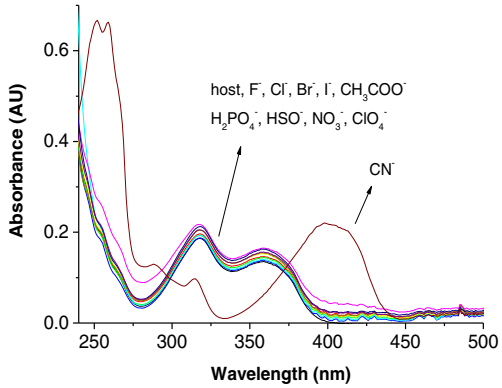


Fig. 1 UV/Vis spectra ($\lambda_{ex.}$ = 317 nm) of receptor **1** (25 μM) in the presence of 10.0 Eq of various anions in EtOH/H_2O (95/5, *v*/*v*)

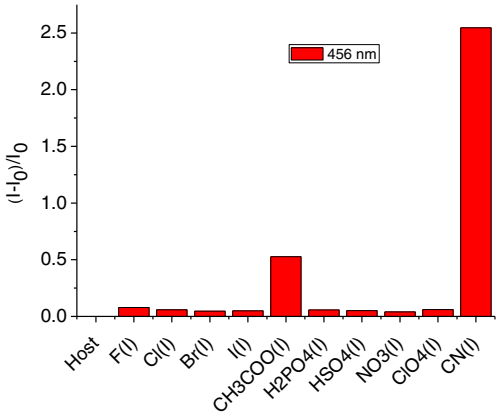


Fig. 4 Variation of the fluorescence intensity at 448 nm ($\lambda_{ex.}$ = 317 nm) of **1** (25 μM) in the presence of 10.0 Eq of various anions in EtOH/H_2O (95/5, *v*/*v*)

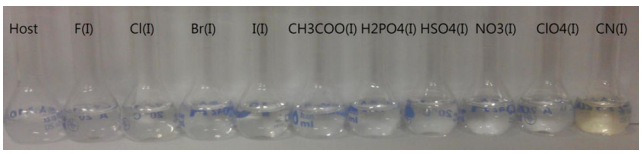


Fig. 2 The color changes observed by naked eye of receptor **1** (25 μM) upon addition of 10.0 Eq of various anions in EtOH/H_2O (95/5, *v*/*v*)

shown that the phenoxide anion formation upon the addition of cyanides created a color change with the red shift [19].

To further investigate the sensing properties of receptor **1**, UV/vis and fluorescent titration of receptor **1** with CN^- were performed. With the addition of increasing amounts of CN^- to a solution of receptor **1** in EtOH-H_2O (*v*/*v*, 95:5), the maximum absorbance at 320 and 363 nm decreased gradually, and concomitantly, a rising new absorbance that peaked at 405 nm appeared as shown in Fig. 5. Two isosbestic points were clearly observed at 300 and 372 nm, respectively, indicating

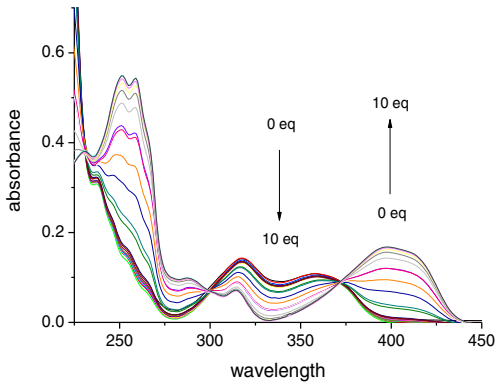


Fig. 5 UV/Vis spectra of **1** (22 μM) in EtOH/H_2O (95/5, *v*/*v*) upon addition of increasing concentrations CN^-

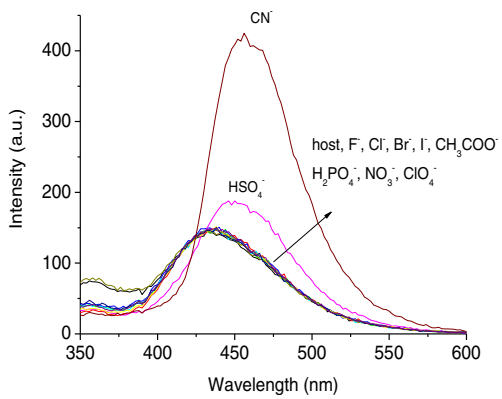


Fig. 3 Fluorescence emission spectra ($\lambda_{ex.}$ = 317 nm) of **1** (25 μM) in the presence of 10.0 Eq of various cation in EtOH/H_2O (95/5, *v*/*v*)

the formation of a new complex between receptor **1** and CN^-. From the fluorescent titration profiles (Fig. S1), the association constant for receptor **1**-CN^- in EtOH-H_2O (*v*/*v*, 95:5) was

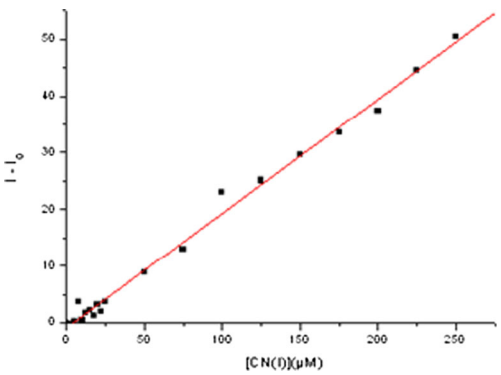


Fig. 6 CN^- concentration dependent fluorescence intensity change

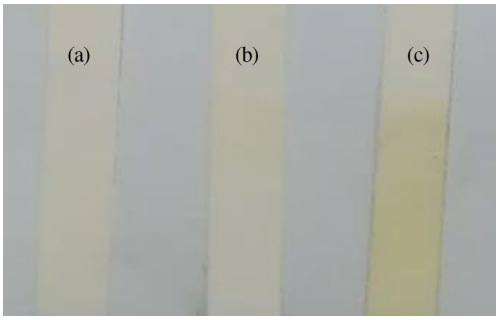
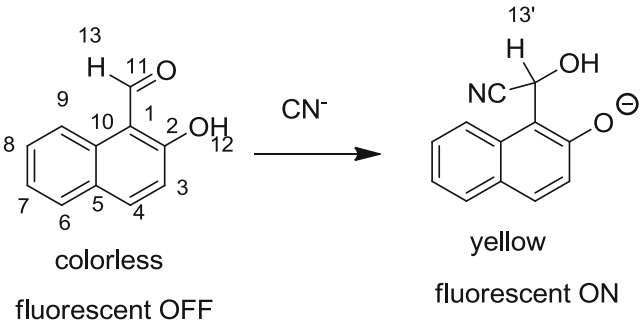


Fig. 7 **a** Original filter paper; **b** filter paper coated with receptor **1**; **c** filter paper coated with receptor **1** and CN^-



Scheme 1 The proposed reaction mechanism of receptor **1** toward CN^-

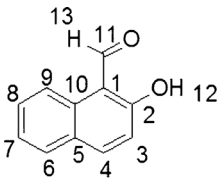
determined as 1.76×10^7 M^{-1} by the Hill equation (Fig. S2). A Job plot indicated a 1:1 complexation stoichiometry between receptor **1** and CN^- (Fig. S3). The detection limit of receptor **1** for the analysis of CN^- ion was determined as 1.6 μM (Fig. 6). Obviously, the detection limit of receptor **1** is lower than the WHO limit (1.9 μM), and suggests that receptor **1** could be an effective sensor for the detection of CN^- in aqueous media [20].

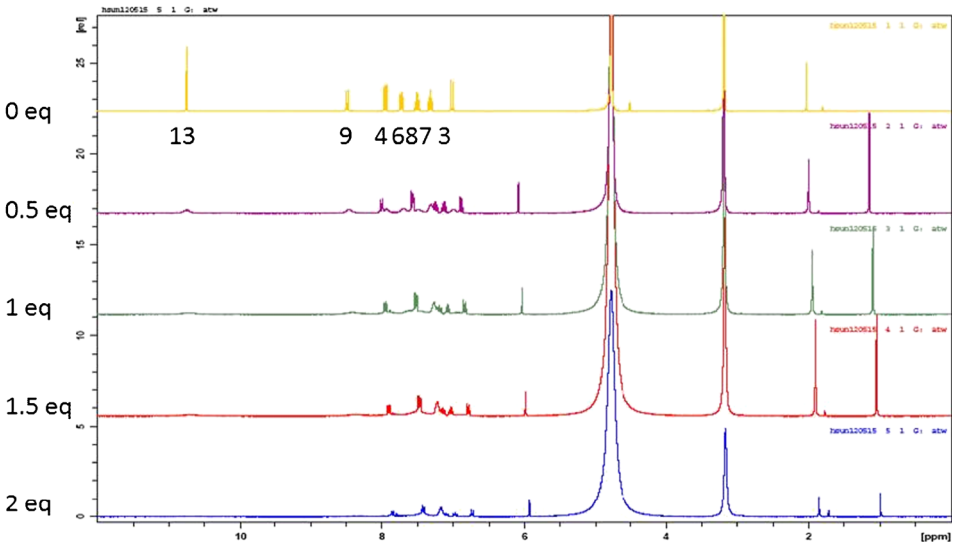
To study the potential of using receptor **1** as ready to use, indicator strips experiments were done using filter paper strips coated with the solution of receptor **1** (Fig. 7). When these coated strips were introduced into the EtOH-H_2O (*v*/*v*, 95:5) solution containing CN^-, the colorless strips were changed to yellow color instantly. Thus receptor **1** can be made into a ready to use strips for detecting the presence of CN^- in aqueous media.

The selectivity toward CN^- was further ascertained by the competition experiment. As shown in Fig. S4, receptor **1** was treated with 10 eq. of CN^- in the presence of other anions of the same concentration. Relatively low interference was observed for the detection of CN^- in the presence of other anions except for HSO_4^-. This result can be due to the lower pH induced the protonation of aldehyde in the presence of HSO_4^-.

To better understand the complexation behavior of receptor **1** with CN^-, ^1H NMR experiments were carried out in CD_3OD. The spectral differences were depicted in Fig. 8. The aldehyde proton (H_{13}) at around 10.7 ppm was disappeared upon the addition of CN^-. Meanwhile, a new signal was appeared at 5.92 ppm, which corresponds to the saturated proton ($H_{13'}$). The protons of naphthalene (H_3, H_4, H_6, H_7, H_8 and H_9) were all shifted up-field by 0.1 to 0.3 ppm. The obvious changes in the above mentioned chemical shifts

Fig. 8 ^1H NMR titration plot of receptor **1** with CN^- in CD_3OD





indicated that the nucleophilic addition of CN^- to the carbonyl group. The proposed mechanism was shown in Scheme 1.

In summary, we employed the commercial salicylaldehyde as a novel differentially selective fluorescent sensor for the detection of selected anions. The receptor **1** displayed dramatic enhanced fluorescent intensity selectively toward CN^- over other ions in EtOH-H_2O (*v*/*v*, 95:5). The significantly red shift in absorption spectrum and enhanced fluorescent intensity were due to CN^- attack toward the carbonyl group leading to phenoxide anion formation.

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Supporting Information Available Supplementary data associated with this article can be found.

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