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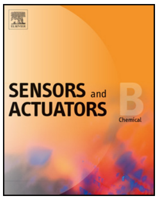

A ratiometric fluorescent probe based on benzo [*e*] indolium for cyanide ion in water

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ABSTRACT

A new ratiometric fluorescent cyanide probe bearing a benzo [*e*] indolium moiety as a fluorophore and binding site was developed. The detection of cyanide was performed *via* the nucleophilic attack of cyanide toward the benzo [*e*] indolium group of the probe, resulting in a prominent fluorescence ratiometric change and a color change. The probe was invested in water with high selectivity and sensitivity for cyanide. A simple paper test strip system for the rapid monitoring of cyanide was developed.

1. Introduction

Cyanide ion (CN^-) is well known for its extremely toxic to mammals with a small amount, and it can be absorbed through the lungs, gastrointestinal track and skin, leading to vomiting, convulsion, loss of consciousness, and eventual death. The highest allowable level of cyanide anion in drinking water is only 1.9 μM according to the World Health Organization (WHO) [1–3]. Nevertheless, CN^- has been produced in large quantities and used in various industrial processes, such as synthetic fibers, resins, herbicide and the gold-extraction [4], which has led to environmental contamination as well. Therefore, efficient detection of CN^- is required from the contaminant sources. Multiple colorimetric and fluorescent probes for CN^- have been developed over past 10 years. One of the common approaches is utilizing hydrogen bonding interactions [5], as well as cyanide complexes with Zn^{2+}-porphyrin [6], Ru^{2+}-pyridine [7], Co^{2+}-salen [8], boronic acid derivatives [9] or CdSe quantum dots [10]. Other strategies, such as displacement method [11] and single-electron transfer reaction have also been developed [12]. Meanwhile, the nucleophilic addition reactions of CN^- with oxazine [13], pyrylium [14], squarane [15], acyltriazene [16], acridinium [17], salicylaldehyde [18], imine group [19], trifluoroacetophenone [20] or trifluoroacetamide derivatives [21] have been reported, in which the interference by other anions, such as F^-, AcO^- and $H_2PO_4{}^-$, can be efficiently minimized.

Among the various chemical sensors, fluorescent chemosensors present many advantages such as high sensitivity, low cost, easy detection, and suitability as a diagnostic tool for biological concerns. However, most of the reported fluorescent probes for CN^- were based on fluorescence quenching or enhancement. As the change in fluorescence intensity is the only detection signal, factors such as instrument efficiency, environmental conditions, and the probe concentration can interfere with the signal output. Ratiometric fluorescent probes which enable the measurement of emission intensities at two different wavelengths, provides an alternative approach that can overcome the drawbacks of intensity-based measurements by built-in correction of the two emission bands and seems to be more favorable for sensing target in comparison with fluorescence intensity-based probes. Nevertheless, only a few ratiometric fluorescence probes for CN^- have been reported till now [11g,19e,f, 21d,22].

Generally, most of the ratiometric fluorescent probes were achieved by intramolecular charge transfer (ICT) and fluorescence resonance energy transfer (FRET). However, to the best of our knowledge, there is no ratiometric fluorescence probe for sensing CN^- that could be performed in pure water. Here, we hope to present a new ratiometric fluorescent probe **1** based on a positively-charged benzo [*e*] indolium fragment with an emission maximum at 580 nm and a relatively large Stokes shift around 155 nm. Probe **1** exhibits a high selectivity and sensitivity to CN^- in pure water, as well as an obvious color change. CN^- is expected to be detectable by nucleophilic attack toward the carbon atom of the C=N group, which is activated by the strong electron-withdrawing feature of the positively-charged benzo [*e*] indolium fragments and the trifluoromethyl group. The nucleophilic attack of CN^- interrupts the

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π-conjugation of probe **1** to make the emission of benzo [*e*] indoline recover. Hence, two well-separated emission peaks before and after the CN$^-$ addition could be obtained due to the distinct emission between the probe **1** and benzo [*e*] indoline.

2. Experimental

2.1. General

All reagents and solvent were purchased from commercial source and used without further purification, if not otherwise stated. All reactions were carried out on the magnetic stirrers and their reaction process was monitored on thin layer chromatography (TLC). Absorption and fluorescence spectra were taken on a Shimadzu UV-1800 spectrophotometer and a Varian Cary Eclipse fluorescence spectrometer, respectively. ^{1}H NMR and ^{13}C NMR measurements were recorded at 600 and 150 MHz on a Brucker Avance 600-MHz spectrometer. Dimethyl sulfoxide (DMSO-d_6) was solvent, and tetramethylsilane (TMS) was used as internal standard. The following abbreviations were used to explain the multiplicities: s = singlet; d = doublet; m = multiplet. ESIMS were taken on a Fourier transform ion cyclotron resonance mass spectrometry (Varian 7.0T).

2.2. Preparation of probe *1*

2.2.1. Preparation of 1,2,3,3-Tetramethylbenz[e]indolium iodide (*2*)

2,3,3-Trimethylbenz [e] indole (10.0 g, 47.78 mmol) was dissolved in acetonitrile (50 mL) then methyl iodide (3.57 mL, 57.34 mmol) was added and the reaction mixture heated at reflux for 1 h with vigorous stir. The reaction was cooled to room temperature and the precipitate was collected by filtration, washed with diethyl ether, and dried *in vacuo*. Product **2** was obtained as a white solid in 86% yield (14.41 g). ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.36 (d, 1H, J = 8.2), 8.29 (d, 1H, J = 8.8), 8.22 (d, 1H. J = 8.2), 8.10 (d, 1H, J = 8.8), 7.78 (m, 1H), 7.72 (m, 1H), 4.09 (s, 3H), 2.87 (s, 3H), 1.75 (s, 6H).

2.2.2. Preparation of probe *1*

2 (1.05 g, 3 mmol) was dissolved in ethanol (5 mL), then 4-trifluoromethyl benzaldehyde (0.52 g, 3 mmol) was added and the reaction mixture heated at reflux for 12 h, then reaction was cooled to room temperature and the precipitate was collected by filtration, washed with cold ethanol, and dried *in vacuo*. Probe **1** was obtained as an orange solid in 80% yield (1.2 g). ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.50 (d, J = 16.6, 2H), 8.44 (d, J = 8.4, 2H), 8.38 (d, J = 8.1, 1H), 8.32 (d, J = 8.9, 1H), 8.25 (d, J = 8.1, 1H), 7.96 (d, J = 7.9, 2H), 7.84 (m, 2H), 7.77 (m, 1H), 4.32 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (150 MHz, DMSO-d_6): δ 186.0, 152.5, 142.8, 142.1, 141.7, 136.8, 134.4, 134.0, 133.4, 131.9, 130.8, 130.0, 129.3, 126.7, 118.9, 116.9, 57.6, 39.2, 28.1. HRMS (ESI) calcd. for [M]$^+$ 380.1621, found 380.1627.

2.3. ^{1}H NMR analysis experiments of *1*

The solution of probe **1** (3×10^{-3} M) in DMSO-d_6 (450 μL) and D_2O (50 μL) was placed in the NMR tube, and potassium cyanide powder was added. All the potassium cyanide powder was soluble.

2.4. Titration experiments of *1*

Deionized water was used as the solvent for titration experiment. The titrations were carried out in 10-mm quartz cuvettes at room temperature. Probe **1** was dissolved in DMF (spectroscopic grade) to afford a concentration of 10 mM stock solution, which was diluted with deionized water. Anions (as their Na$^+$ salt, 10 mM and 100 mM) in deionized water were added to the diluted probe solution and used for the titration and selectivity experiment. The excitation wavelength was 345 nm. The excitation and emission slit width were 5 nm and 10 nm, respectively. The detection was delayed 4 min to ensure complete reaction between **1** and CN$^-$ at room temperature (Fig. 1).

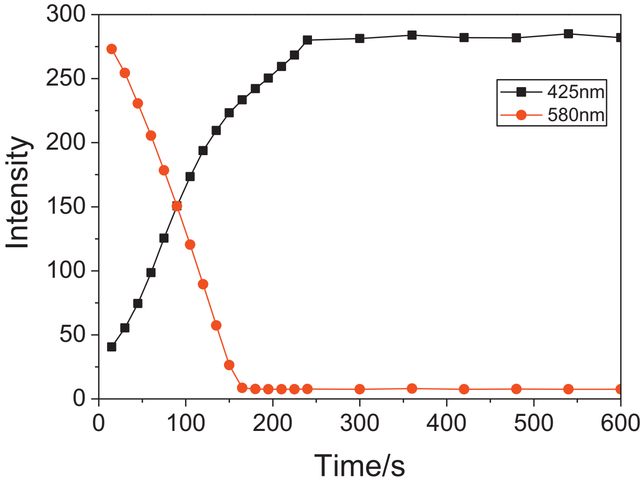

Fig. 1. Time-depended fluorescent intensity changes at 425 nm and 580 nm of **1** (10 μM) in the present of CN$^-$ (10 equiv.).

2.5. Paper test of *1*

The neutral filter paper was dipped in the stock solution of **1** (10 mM) and dried. Then various solutions of anions (1 mM) were seriatim dropped.

3. Results and discussion

3.1. Synthesis

The synthesis route to probe **1** was depicted in Scheme 1. It was easily seen that probe **1** could be conveniently obtained from 2,3,3-Trimethylbenz [e] indole, which were available commercially. The total yield was 68%.

3.2. Cyanide binding studies of *1*

^{1}H NMR analysis was firstly carried out to demonstrate the proposed addition mechanism. As anticipate, after addition of potassium cyanide powder into the solution of **1**, the nucleophilic attack of CN$^-$ toward the positively-charged benzo [*e*] indolium group weakened its electron-withdrawing character and lead all the ^{1}H NMR signals up-field shifted (Fig. 2). It can be seen that the proton signal (H^a, at δ 4.31) of methyl group connected with N$^+$ was dramatically shifted up-field to δ 2.87. Moreover, the proton signal (H^b, at δ 2.03) of two methyl groups was also shifted up-field and divided into two single signals (H$^{b'}$, at δ 1.82 and H$^{b''}$, at δ 1.28), which become non-equivalent after formation of **1**-CN. The unvaried integral intensity ratio between the methoxyphenyl and benzo [*e*] indolium moiety indicates that the formation of **1**-CN keeps them intact. The ^{1}H NMR signals remained essentially unchanged when more than 1 equiv. cyanide was added into the solution, suggesting the 1: 1 binding stoichiometry between **1** and CN$^-$. In addition, the formation of the **1**-CN was further confirmed by mass spectrometry analysis, in which the peak at m/z 445.1283 (calcd. = 445.1294) corresponding to [M+CN+K]$^+$ was clearly observed (Fig. 3).