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Original article

A green synthesis of a simple chemosensor that could instantly detect cyanide with high selectivity in aqueous solution

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ABSTRACT

A novel and simple cyanide chemosensor 2-(naphthalen-1-ylmethylene)malononitrile (L) was designed and synthesized *via* a green chemistry method in water without using any catalyst. The chemosensor showed an excellent sensitivity and selectivity for CN^- in aqueous solution. The detection limit could be as low as 1.6×10^{-7} mol/L (0.16 µmol/L), which is far lower than the WHO guideline of 1.9 µmol/L cyanide for drink water.

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1. Introduction

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Cyanide anion (CN⁻) is one of the most toxic and dangerous anions [1-3]. Owing to the extreme toxicity, the maximum permissive level of cyanide in drinking water is set at 1.9 µmol/L by the World Health Organization (WHO) [4]. On the other hand, a large quantity of cyanide anions are widely used in industry for the synthesis of fine chemicals, electroplating and precious metal mining and so on [5]. Therefore, finding methods to detect cyanide at the environmental level has attracted much attention [6-10]. Although previous work has involved the development of a wide variety of chemical and physical sensors for the detection of CN⁻ [6–10], so far, improving the detection selectivity and sensitivity in the context of interference from coexisting anions such as F⁻, AcO^{-} , and $H_2PO_4^{-}$ in the aqueous solution has been challenging. Moreover, most physical methods require expensive equipment, involve time-consuming and laborious procedures that can be carried out only by well-trained professionals and seriously restrict the practical application of these CNsensors [6,7,11,12]. For the purposes of simplicity, convenience and low cost, easily-prepared CN⁻ optical chemosensors [8-10] become an excellent choice. Furthermore, in biological and environmental systems, cyanide-sensor interactions commonly occur in aqueous solutions. Therefore, much attention has been paid to developing CN⁻ optical chemosensors that work in aqueous solutions [13–18].

Several chemosensor systems for cyanide anion detection reported to date are based on the mechanism of coordination [16], hydrogen-bonding interactions [17,18], nucleophilic addition reactions [13,15,19,20] and so on. Among these cyanide sensors, reaction-based sensors display both high selectivity and sensitivity for the cyanide anion. However, most the reaction-based cyanide anion sensors employ sophisticated structures, require complicated synthetic sequences, can only operate in the pure or mixed organic solvent and require high temperature or long reaction time for detection CN⁻. Therefore, simple and efficient CN⁻ optical chemosensors that could instantly detect CN⁻ in the aqueous solution at room temperature are essential. On the other hand, the synthetic procedures of most artificial sensors usually involve rather harsh reaction conditions and often employ hazardous materials such as starting materials, solutions and catalysts, which pose a huge risk to the environment. To minimize the generation and application of hazardous substances, a green synthetic procedure should be encouraged in the synthesis of CN⁻ chemosensors.

With these considerations and our interest in ion recognition in mind [21–23], we here report an efficient optical chemosensor (Scheme 1) that could sense CN^- with high selectivity and sensitivity in aqueous solutions. In addition, the sensor was synthesized *via* a simple, efficient and environmentally friendly route in pure water without using any catalyst.

The strategies for the design of the sensor are as follows. Firstly, in order to achieve the instantaneous detection of cyanide, a



Scheme 1. The green synthesis of L and the CN⁻ sensing mechanism.

dicyanovinyl group was introduced as the binding site. According to the literatures [19,20], vinyl-substituted derivatives display both selective and sensitive responses to various concentrations of the cyanide anion. Additionally, the dicyano substitution on the vinyl group could significantly enhance the sensitivity of the nucleophilic addition reaction between the vinyl group and CN⁻. Secondly, we introduced a naphthyl group as the signal groups. Finally, the sensors were designed to be easily synthesized *via* a green chemistry method.

2. Experimental

2.1. Materials and apparatus

All reagents for synthesis were of analytical grade, commercially purchased and were used without further purification. Tetrabutylammonium (TBA) salts of anions were purchased from Sigma–Aldrich Chemical and stored in a vacuum desiccator. Melting points were measured on an X-4 digital melting point apparatus and were uncorrected. UV–vis spectra were recorded on a Shimadzu UV-2550 spectrometer. ¹H NMR spectra were recorded on a Varian Mercury Plus-400 MHz spectrometer with DMSO- d_6 as solvent and tetramethylsilane (TMS) as an internal reference. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. Elemental analyses were performed by Thermo Scientific Flash 2000 organic elemental analyzer. Electrospray ionization mass spectra (ESI-MS) were measured on a Bruker Daltonics Esquire6000 ESI-ION TRAP system.

2.2. General procedure for the UV-vis experiments

A solution of sensor L (2.0×10^{-4} mol/L) in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilutions. Solutions of 1.0×10^{-2} mol/L TBA salts of the respective anions (F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻ and ClO₄⁻) were prepared in H₂O, and the sodium salts of CN⁻, NO₃⁻, S²⁻ and SCN⁻ were prepared in H₂O. Any changes in the UV-vis spectra of sensor L were recorded upon the addition of salts while keeping the concentration of sensor L (2.0×10^{-5} mol/L) constant in all experiments.

2.3. General procedure for ¹H NMR experiments

For ¹H NMR titrations, sensor **L** was prepared in DMSO- d_6 , NaCN was prepared in D₂O. Sensor **L** in DMSO- d_6 was added into an NMR tube, then 0.2, 0.5, 1.0 and 1.5 equiv. of CN⁻ anion was added sequentially. All solutions were mixed directly in the NMR tube.

2.4. Synthesis of sensor L

Naphthaldehyde (0.468 g, 3 mmol) and malononitrile (0.234 g, 3 mmol) were combined in 20 mL of pure water. The solution was stirred at 90 °C for 2 h. After cooling to room temperature, the yellow precipitates were collected by filtration, washed with 75% ethanol three times, and then recrystallized in ethanol to obtain the yellow powdery product **L**. Yield: 82%, mp 173–174 °C, ¹H-NMR (400 MHz, DMSO- d_6 ,): δ 9.38 (s, 1H, C–H), 8.27 (m, 2H, Ar–H), 8.20 (t, 1H, *J* = 7.2 Hz, Ar–H), 8.09 (t, 1H, *J* = 7.2 Hz, Ar–H), 7.70 (m, 3H, Ar–H). IR (KBr, cm⁻¹): ν 2224 (C \equiv N), 1562 (C=C), 1506 (C=C), 1456 (C=C). Anal. Calcd. for C₁₄H₈N₂: C 82.33, H 3.95, N 13.72; found: C 82.41, H 4.02, N 13.64. APCI-MS: Calcd. for C₁₄H₈N₂: 204.1, found: 204.0.

3. Results and discussion

Sensor **L** was synthesized by the Knöevenagel reaction as depicted in Scheme 1. Usually, the Knöevenagel reaction is carried out in polar aprotic solvents such as DMF or CH₃CN and catalyzed by such bases as piperidine, or sodium hydroxide [19]. We, however, attempted to synthesize the sensor **L** in pure water under the catalyst free conditions to avoid the use of organic solvents and catalyst and prevent environmental contaminations. It is exciting that the naphthaldehyde could undergo the Knöevenagel reaction with malononitrile in pure water without using any catalyst to give 2-(naphthalen-1-ylmethylene)malononitrile (**L**) in high yields. The proposed reaction mechanism involves the ionization of malononitrile, the nucleophilic addition of dicyanomethyl carbanion to naphthaldehyde followed by a dehydration condensation process (Scheme 2) [24]. This is an excellent green chemistry method for the preparation of these kinds of fine chemicals.

The sensing ability of **L** toward various anions, such as F^- , Cl^- , Br^- , I^- , Ac^- , $H_2PO_4^-$, HSO_4^- , ClO_4^- , SCN^- , N_3^- , $SO_4^{-2}^-$, NO_3^- , S^{2-} and CN^- was investigated by UV–vis spectroscopy. With the aim of excluding the possible influence of pH fluctuation, we carried out experiments in DMSO/H₂O (8/2, v/v), HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) (10 mmol/L) buffered solutions at pH 7.04. Upon adding 50 equiv. of CN^- to the solution, the absorption at 369 nm disappeared immediately. To validate the selectivity of **L**, the same tests were applied to other anions and no such changes were observed (Fig. 1). It was confirmed that **L** could selectively and instantly detect CN^- in DMSO/H₂O binary solution.

To further explore the utility of sensor **L** as an ion-selective chemosensor for CN^- , competitive experiments were carried out in the presence of 50 equiv. of CN^- and 50 equiv. of various other anions (F⁻, Cl⁻, Br⁻, I⁻, Ac⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻, SCN⁻,



Scheme 2. The proposed reaction mechanism for the condensation between malononitrile and naphthaldehyde.



Fig. 1. UV-vis absorption of sensor $L(2 \times 10^{-5} \text{ mol/L})$ with various anion in DMSO/ H₂O (8/2, v/v), HEPES (10 mmol) at room temperature, other anions are F⁻, Cl⁻, Br⁻, I⁻, Ac⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻, SCN⁻, N₃⁻, SO₄⁻², NO₃⁻, S²⁻.



Fig. 2. UV-vis absorption of sensor **L** $(2 \times 10^{-5} \text{ mol/L})$ with miscellaneous anions exist in DMSO/H₂O (8/2, v/v), HEPES (10 mmol/L) at room temperature, other anions are F⁻, Cl⁻, Br⁻, I⁻, Ac⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻, SCN⁻, N₃⁻, SO₄²⁻, NO₃⁻, S²⁻.

 N_3^- , SO_4^{2-} , NO_3^- , S^{2-}) in a HEPES-buffered solution of sensor **L**. The optical absorbance of sensor **L** with CN^- (Fig. 2) was not influenced by the subsequent addition of competing anions, which indicated that **L** had shown specific selectivity for CN^- .

The UV-vis titration of L with CN^- is carry out in DMSO solutions (Fig. 3). The inset shows a good linear dependence of the



Fig. 3. UV-vis titration of sensor $L~(2\times 10^{-5}~mol/L)$ with CN^- (0–1.8 equiv.) in DMSO solution.

absorbance at 369 nm as a function of $[CN^-]/[L]$. The plot of the decrease in absorbance at 369 nm reached the saturation point at the ratio of $[CN^-]/[L]$ of 1.2, indicating a 1:1 stoichiometry between L and CN^- ions. Furthermore, the detection limit of the UV-vis changes calculated on the basis of $3\sigma B/S$ [25] is 1.6×10^{-7} mol/L for CN^- , which is far lower than the WHO guideline of 1.9 μ mol/L cyanide.

To further elucidate the binding mode, ¹H NMR-titration experiments of sensor **L** were conducted in DMSO- d_6/D_2O (Fig. 4). Sensor **L** was dissolved in DMSO- d_6 and NaCN was dissolved in D₂O. Before adding CN⁻, the ¹H NMR chemical shift of the vinylic proton (H^a) on sensor **L** was at 9.38 ppm. After the addition of 0.2 equiv. CN⁻, it was obvious that the intensity of the vinylic proton (H^a) at 9.38 ppm decreased and a new signal grew at 5.26 ppm corresponding to the α -proton (H^{a'}). With the addition of 1.0 equiv. of CN⁻, the peak at 9.38 ppm disappeared completely. Meanwhile, the proton signals on naphthyl displayed an upfield shift due to the loss of the conjugation between vinyl and naphthyl groups. These observations clearly indicated that the cyanide anion was added to the vinyl group and suggested 1:1 reaction between **L** and CN⁻ ions (as showed in Scheme 1).

The results of APCI-MS experiments also support this hypothesis. In the APCI-MS spectra, the peak of **L** appeared at 204.0 (Calcd. for $C_{14}H_8N_2$: 204.1). However, when 1 equiv. CN⁻ was added to the solution of **L**, the [**L**+CN]⁻ peak appeared at 230.5, coinciding well with that for the species [**L**+CN]⁻ (calcd. for $C_{15}H_8N_3^-$: 230.1) and indicating the formation of the stabilized anionic species **L**-CN.



Fig. 4. CN⁻¹H NMR titration of sensor L(10.0 mmol/L) in DMSO-d₆: (a) Lonly, (b) L + 0.2 equiv. of CN⁻, (c) L + 0.5 equiv. of CN⁻, (d) L + 1.0 equiv. of CN⁻ and (e) L + 1.5 equiv. of CN⁻.

4. Conclusion

In conclusion, an easy-to-make chemosensor **L** was designed and synthesized *via* a green chemistry method. The sensor **L** could instantly detect CN⁻ in water solution at room temperature with high selectivity and sensitivity. The investigation of the recognition mechanism indicated that the sensor **L** recognized CN⁻ by forming a nucleophilic addition adduct. The coexistence of other anions did not interfere with the CN⁻ recognition process. Moreover, the detection limit of the sensor **L** toward CN⁻ was 1.6×10^{-7} mol/L (0.16 µmol/L), which indicated that the sensor **L** may be useful as a chemosensor for monitoring CN⁻ levels in physiological and environmental systems.

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