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A highly selective fluorescent chemosensor for CN^- based on a novel bis(salamo)-type tetraoxime ligand

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ABSTRACT

The optical properties of a novel chemosensor for cyanide anions based on a symmetric bis(salamo)-type ligand (H_3L) were investigated by UV–Vis and fluorescence spectroscopy in MeOH/H_2O (1:1 v/v) solution. Sensor H_3L can selectively sense CN^- based on prominent color changes among other anions. The chemosensor exhibits an apparent fluorescence enhancement at 482 nm to CN^- which because cyanide ions interact with C═N bonds. Combining the corrected Benesi-Hildebrand formula, the binding constant of the formed host-guest complex was calculated as $2.42 \times 10^5\ M^{-1}$. Meanwhile, the detection limit of the sensor toward CN^- was 8.91×10^{-7} M. It is worth noting that the designed sensor can be used for rapid detection of cyanide anions in basic pH range, and has great practical value.

1. Introduction

Cyanide anion is widespread in nature, especially in biology, and is the most important anion in industrial production. It can react with heavy metal ions and soft acids to form a strong combination. Based on this, cyanide is widely used in wet smelting of gold and silver [1–3]. Unfortunately, cyanide has a greatly harmful to the environment and human body. When it enters the organism, it inhibits the activity of the enzyme in the tissue and paralyzes the body [4]. Therefore, it is necessary for the detection of cyanide anion. In recent years, the development of fluorescent chemosensors for quantitative analysis of CN^- has become extremely important for organism and environment [5–7]. The fluorescent sensor for CN^- according to the different mode of action is generally divided into hydrogen bonding type CN^- sensor [8,9], deproton type CN^- sensor [10,11], Coordination [12,13] and nucleophilic addition type CN^- sensor [14,15]. CN^- has very strong nucleophilic properties, which can react with some compounds containing electrophilic groups, such as carbonyl compounds and schiff base etc. The researchers have designed and synthesized some sensor molecules using the characteristics of CN^-. In the former work, a large number of fluorescence chemosensors for CN^- based on schiff base were reported [16–20]. These molecules are the addition reaction of using the strong nucleophilicity of cyanide anion and C═N bond, thus affecting the spectral changes, to achieve the detection of the CN^-. Development of new schiff base receptors for the detection of cyanide anion simultaneously is emerging as an area of great interest [21]. However, the cyanide anion fluorescence detector based on salamo-type ligand have not been reported [22–25]. Herein, in this research, a new fluorescent chemosensor is reported for monitoring cyanide anion based on a bis(salamo)-type tetraoxime ligand, which can detect CN^- based on the obvious color changes among a series of anions.

2. Experimental

2.1. Materials and Physical Measurements

All reagents were of the best available analytical reagent grade. Aqueous solutions were prepared using double distilled deionised water. All chemicals were of analytical reagent grade and were used without further purification. C, H, and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. Melting points were obtained by use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were determined by German Bruker AVANCE DRX-400 spectrophotometer. UV-Vis absorption and fluorescence spectra were recorded on a Shimadzu UV-2550 and Perkin-Elmer LS-55 spectrometer, respectively.

2.2. Preparation of Receptor Molecule H_3L

The synthetic route to the bis(salamo)-type tetraoxime ligand (H_3L) is shown in Scheme. 1. The novel bis(salamo)-type tetraoxime ligand H_3L was synthesized according to an analogous method reported earlier [27].

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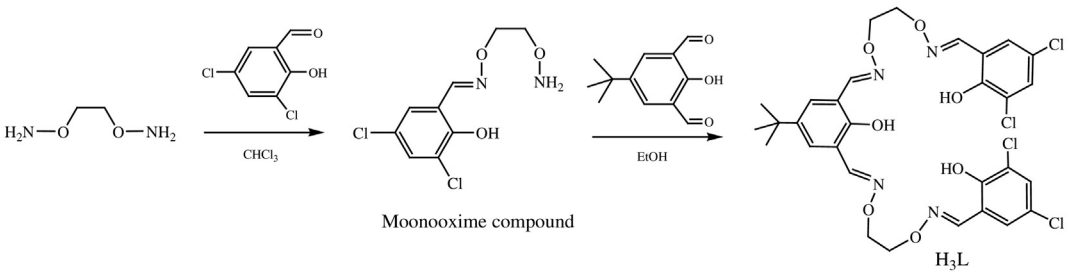

Scheme 1. Synthetic route to the receptor molecule H_3L.

1,2-Bis(aminooxy)ethane was synthesized according to an analogous method reported earlier [26]. (Yield: 80.5%); *Anal.* calcd. for $C_2H_8N_2O_2$ (%): C, 25.28; H, 8.56; N, 30.42. Found (%): C, 24.98; H, 8.92; N, 30.28.

Monooxime compound 2-[*O*-(1-ethyloxyamide)]oxime-4,6-dichlorophenol was prepared by the reaction of chloroform solution of 3,5-dichlorosalicylaldehyde with 1,2-bis(aminooxy)ethane.

A solution of 4-tert-butyl-2,6-diformylphenol in ethanol was added dropwisely to a solution of the monooxime compound in ethanol at room temperature. The mixed solution was heated at 55°C for about 10 h. Finally, the solution was concentrated under vacuum, then purified to obtain the symmetric bis(salamo)-type tetraoxime ligand H_3L. (Yield: 79.5%); m.p. 120–121 °C. *Anal.* calcd. for $C_{30}H_{30}N_4O_7Cl_4$ (%): C, 50.89; H, 4.13; N, 7.86. Found (%): C, 51.45; H, 4.32; N, 8.00. ^{1}H NMR (400 MHz, DMSO) δ 10.37 (s, 1H), 10.04 (s, 1H), 8.45 (s, 4H), 8.29 (s, 1H), 7.59 (s, 2H), 7.57 (d, J = 2.6 Hz, 2H), 7.51 (d, J = 2.6 Hz, 2H), 4.44 (s, 8H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 153.22 (C), 151.42 (C), 148.51 (CH), 147.88 (C), 142.69 (C), 130.92 (C), 127.31 (d, J = 12.6 Hz, C), 124.17 (CH), 122.86 (C), 121.26 (=CH), 118.47 (=CH), 73.62 (CH_2), 73.12 (CH_2), 34.48 (C), 31.69 (CH_3).

2.3. UV–Vis and Fluorescence Measurements

The receptor H_3L (0.7 mg) dissolved in MeOH (10 mL) was diluted with 90 mL MeOH to make the final concentration of 0.01 mM. Then, NaCN (4.9 mg, 0.1 mmol) was dissolved in water (100 mL). Fluorescence and UV-Vis measurements were carried out in 1 cm quartz cuvette at room temperature. Simultaneously, any change in the fluorescence intensity using fluorescence spectrometer for monitoring (λ_{ex} = 365 nm with a slit width of 10/10 nm).

3. Results and Discussion

3.1. Fluorescence and Absorption Studies of Receptor H_3L toward CN^- Anion

In order to investigate the receptor H_3L selectivity towards different anions, the identification test was carried out in MeOH/H_2O (1:1 v/v) solution. When cyanide anions were added to the receptor H_3L (1×10^{-5} M), the solution distinctly turned from pale blue to light green, as shown in Fig. 1. The results indicated that receptor H_3L can be used for selective identification of CN^- based on the color changes.

The fluorescence and UV-Vis absorption spectra of receptor H_3L were studied in presence of various anions (Cl^-, I^-, NO_3^-, SO_4^{2-}, $H_2PO_4^{2-}$, AcO^-, CN^- and SCN^-). When the CN^- anion was added to the solution of receptor H_3L, a prominent change in the fluorescence spectroscopy was observed, as shown in Fig. 2a. However, when other anions added, did not cause significant changes of fluorescence spectra. Upon addition of CN^- to the H_3L receptor solution, a pronounced fluorescence enhancement at 482 nm exhibited, compared with the receptor H_3L red shift of 18 nm. The fluorescence profiles at 482 nm of the chemodosimeter showed an apparent selectivity for cyanide over the other anions in MeOH/H_2O (1:1 v/v) solution (Fig. 2b). This significantly enhanced fluorescence intensity may be caused by the CN^- and C=N bond of receptor H_3L in a nucleophilic addition reaction, as shown in Scheme 2.

The sensing phenomena are also monitored by UV-Vis absorption spectroscopy, as shown in Fig. 3. With the addition of the CN^-, resulted in a marked change in the UV-Vis absorption spectra, at 330 nm, the absorption band disappears and shows a new absorption band at 370 nm, compared with the receptor H_3L red shift of 40 nm. This is assumably due to the nucleophilic addition interaction between CN^- with receptor H_3L.

3.2. Fluorescence Titration of Receptor H_3L with CN^-

The CN^- anion was detected by the receptor H_3L in the fluorescence spectra by following the concentration dependent changes. As shown in Fig. 4, with the increase of cyanide anion concentration, the fluorescence spectra of the receptor illustrated a constantly reinforce of the emission intensity of the band at 464 nm. Through the data obtained by fluorescence titration experiment, we have linear fitting the data and get a fitting curve (Fig. 5). Based on the corrected Benesi-Hildebrand formula [28,29], the binding constant for the binding of cyanide to receptor H_3L was calculated as 2.42×10^5 M^{-1}. At the same

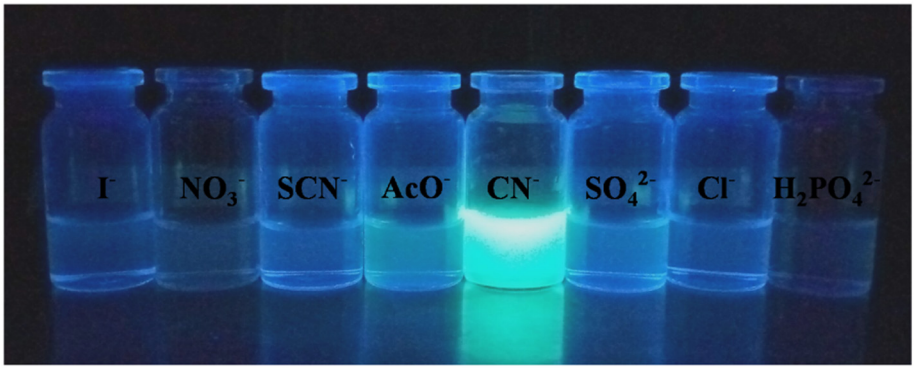

Fig. 1. Change in color of the receptor H_3L under 365 nm UV light.