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A new colorimetric and fluorescent chemodosimeter for fast detection of cyanide

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ABSTRACT

A new high selective and sensitive fluorescent sensor for the detection of cyanide was developed based on the conjugated of anthracene and hemicyanine. By the nucleophilic attacking of CN^- to the indolenium C-2 atom of the sensor, the ICT progress (Intramolecular Charge Transfer) was blocked with color changed and fluorescence enhanced. The live cell fluorescent experiments demonstrated the value of the sensor in tracing the CN^- in biological systems. Short responding time (less than 1 s) and excellent water-soluble ability (only 20% organic solvents needed in the detection) provided a broader application prospect in the practical application. The sensing mechanism was well rationalized with the aid of TD-DFT (time-dependent density functional theory) calculations.

1. Introduction

Anions play important roles in many areas such as medicinal biological, environmental chemistry and catalysis [1], so the recognition of anions has aroused more and more interest [2–6]. Cyanide as one of the most useful anions, is extensively utilized in many fields such as gold mining, electroplating, metallurgy, synthetic fibers and resins industry [7–11]. But cyanide is a very toxicity anion for the human because it can inhibit cellular respiration in mammals by interacting strongly with a heme unit in the active site of cytochrome a3, leading to vomiting, convulsion, loss of consciousness, and eventual death [12–14]. According to the World Health Organization (WHO), only water with cyanide concentration lower than 1.9 μM is fit to drink [15]. So efficient sensors for cyanide with high sensitivity and selectivity are in great need.

A number of methods are available for the cyanide analysis including spectrophotometric [16–19], titrimetric [20–22], voltammetry [23], electrochemical methods [24,25], ion selective electrodes [26], and chromatographic method [27]. The major limitation of these methods is the use of time-consuming procedures that involve the use of sophisticated instrumentation. Up to now, lots of sensors for CN^- have been invented [28]. The general approaches used for the cyanide detecting are summarized as hydrogen bonding [29,30], nucleophilic addition on the carbonyl moiety [31–34], copper cyanide affinity (displacement approach) [35–37], iminiumsalts [38,39], electron-deficient alkenes [40,41], and so on [42]. But they themselves all have their own drawbacks such as poor solubility in aqueous media, long responding time or poor application in the "naked eye" detecting. So due to its operational simplicity, low cost, and rapid implementation, chromogenic sensor for the detection of cyanide are in great need.

With these considerations in mind, we here developed a new chemodosimetric sensor for the cyanide detection based on anthracene–hemicyanine conjugate as shown in Scheme 1. As its indolenium C-2 atom is an effective target for the nucleophilic analytes, the cyanide can easily combine with it, inducing a remarkable change in spectroscopic properties. With the gradual addition of cyanide, the color of the solution changed from red to colorless which offers the possibility for us to detect the cyanide by "naked eye". Furthermore, short responding time (less than 1 s), great water-soluble ability (20% organic solvents needed) and excellent biocompatibility provide a broader prospect for our sensor in the practical application.

2. Materials and methods

2.1. Materials

9-Anthracenecarboxaldehyde, tetrabutylammonium salts were purchased from Sigma–Aldrich and used without further

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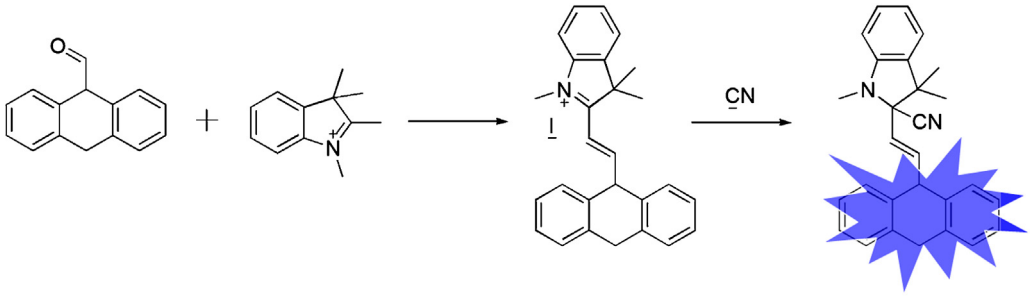

Scheme 1. Synthesis and design concept of fluorescent sensor 1 for CN^-.

purification. All the other reagents were of analytical purity that were used without further treatment. All the solution of anions were prepared by using of tetrabutylammonium salt such as $CH_3(CH_2CH_2CH_2)_4N^+F^-$. Aqueous Tris–HCl buffer (pH = 7.4, 10 mM) solution was used as buffer to keep pH value.

2.2. Instruments

All the compounds prepared were characterized by electrospray ionization-mass sepctometry (ESI-MS), proton nuclear magnetic resonance (^{1}H NMR), and carbon nuclear magnetic resonance (^{13}C NMR). ^{1}H NMR spectra of them were measured on a Bruker AV-300 spectrometer with chemical shifts reported as δ [in $CDCl_3$, tetramethylsilane (TMS) as internal standard]. Absorption and luminescence spectra were obtained on a Shimadzu UV 2100 PC UV–visible spectrophotometer and a Hitachi F-4500 luminescence spectrometer, respectively. The pH values of the test solutions were measured with a glass electrode connected to a Mettler-Toledo Instrument DELTA 320 pH meter (Shanghai, China) and adjusted if necessary. All the measurement experiments were performed at about (298.0 ± 0.2) K.

2.3. Preparation and characterization of compounds

The syntheses of the compounds are summarized in Scheme 1. 1-Methyl-2,3,3-trimethyl-3H-indolium 2 were synthesized according to the literature reported procedures [43]. Compound 2 (100 mg, 0.33 mmol) was treated with compound 3 (68 mg, 0.33 mmol) in hydrous ethanol (20 mL). The reaction mixture was then refluxed for 15 h, and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography (CH_2Cl_2/MeOH, 10:1) on silica gel to give the product 1 as a red powder (101 mg, yield: 62.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (d, 1H, J = 16.3 Hz), 8.60 (d, 3H, J = 8.1 Hz), 8.06 (d, 2H, J = 8.4 Hz), 7.80–7.72 (m, 2H), 7.72–7.67 (m, 1H), 7.63–7.54 (5H, m), 7.49 (d, H J = 16.3 Hz), 4.35 (3H, s), 2.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.05, 150.12, 142.89, 141.90, 132.61, 131.26, 130.29, 130.22, 129.76, 129.39, 128.90, 127.83, 126.10, 125.08, 122.69, 121.35, 115.62, 53.06, 37.13, 26.84. ESI-MS m/z $[M]^+$ calc 362.19, obs 362.18.

3. Results and discussion

3.1. Absorption spectral response

The changes of the UV–vis spectra for the sensor 1 in the absence and presence of CN^- were investigated here. Considering environmental applications, we selected the solution of Tris–HCl buffer (pH = 7.4, 10 mM)-ethanol (8/2, v/v) as the testing system to investigate the optical response of 1 at room temperature. As shown in Fig. 1, the sensor 1 showed one main absorption band at 505 nm, which was attributed to intramolecular charge transfer (ICT) transition in sensor. With the gradual addition of CN^-, the absorption intensity at 505 nm decreased evidently, whereas a new absorption band appeared at 405 nm and 280 nm. Eventually, with the CN^- induced to be 1.5 equiv., the absorption intensity was found to be the weakest at 505 nm. Such a strong reduction in the absorption behavior changed the color of the solution from red to colorless as we could see in Fig. 1(A). Upon the addition of increasing amounts of cyanide, the color of the solution with the sensor 1 (30 μM) changed gradually from red to colorless as shown in Fig. 2(A). So this performance allowed the colorimetric detection of CN^- by the naked eyes. The absorbance ratio changes (A_{405}/A_{505}) of sensor 1 upon gradual addition of CN^- (1.5 equiv.) was shown in Fig. S4 in ESI.

The anion sensing property of sensor 1 was also studied in the present of other anions which often showed strong interference to the cyanide detection such as F^-, Cl^-, Br^-, I^-, HS^- and so on. From Fig. 2 (B), we found that the competing anions did not show any considerable changes in the color of the solution as we expected.

3.2. Fluorescence spectral titration of sensor 1 with CN^-

Next, we investigated the concentration dependent changes in the fluorescence spectra upon incubation of sensor 1 (30 μM) with CN^-. As shown in Fig. 3, sensor 1 exhibited a weak fluorescence at 400 nm. With the gradual addition of CN^-, we could find the fluorescence at 470 nm increasing sharply, the addition of 1.5 equiv. of CN^- to sensor 1 induced a nearly 17-folds variation in the fluorescence ratio (I/I_0) (Fig. 4). And from the picture we could see that after the addition of CN^-, under the irradiation of a UV-lamp (365 nm), the fluorescence of sensor 1 changed from dark to green.

Fig. 4 shows the plot of $[I/I_0 - 1]$ vs. the concentration of CN^-, where I_0 and I refer to the fluorescence intensity of aqueous solution for 1 at 470 nm in the absence and presence of CN^-. Interestingly, $[I/I_0 - 1]$ varies almost linearly vs. the concentration of CN^- in the range of 10–45 μM, with the coefficient R = 0.99574. This phenomenon implied that sensor 1 was potentially useful for the quantitative determination of CN^- concentrations.

The detection limit (DL) of 1 for CN^- was determined from the following equation [44]:.

$$DL = \frac{K \times Sb1}{S}$$

where K = 2 or 3 (we take 2 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve. Using this equation, we calculated the detection limit of cyanide with 1 to be 5.885×10^{-8} M. Note that this is much lower than the TLV (10 ppb) set by the EPA.

3.3. Selective and competitive experiments

An important feature of sensor 1 is its high selectivity toward the CN^- over the other competitive anions. Changes of fluorescence