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An indanedione-based chemodosimeter for selective naked-eye and fluorogenic detection of cyanide

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ABSTRACT

A 1,3-indanedione-based chemodosimeter **1** with both intramolecular charge transfer (ICT) and aggregation-induced emission enhancement (AIEE) characteristics has been developed for the highly selective and sensitive detection of cyanide (CN^-) in a 90% aqueous solution. The colorimetric and ratiometric fluorescent response of the chemodosimeter to CN^- is attributable to the addition of CN^- in the β-conjugated position of the 1,3-indanedione moiety of chemodosimeter **1**, which blocks ICT. The hypothesized sensing mechanism is supported by time-dependent density functional theory (DFT) calculations. Chemodosimeter **1** achieves rapid detection of CN^- in anhydrous THF (a response time less than 1 min), and only 2 equivalents of CN^- is required to reach the spectral saturation. The effect of water on the reaction of the chemodosimeter to CN^- is also examined. The results show that increasing water content results in a longer reaction time due to the solvation of CN^- by neighboring water molecules. Chemodosimeter **1** also exhibits excellent fluorescence responses in the solid state, and **1**-based test strips can be used to conveniently detect CN^- by the naked eye. The detection limit of chemodosimeter **1** (9.4×10^{-7} M) for CN^- is two times lower than the maximum permissible level of CN^- (1.9×10^{-6} M) in drinking water.

1. Introduction

Cyanide (CN^-) is one of the most lethal toxic chemicals to the living environment [1]. However, a large amount of CN^- is extensively used in industrial processes such as electroplating, gold mining, metallurgy, and the synthesis of nylon, fibers, and resins [2]. Thus, there is high demand for the development of simple, low-cost, selective, and sensitive colorimetric and fluorometric chemosensors for detecting CN^- [3]. A number of mechanisms for developing colorimetric and/or fluorometric cyanide-selective sensors have been reported, including those based on intramolecular charge transfer (ICT) [4,5], intramolecular proton transfer (IPT) [6–8], complex formation with metal ions and boron derivatives [9,10], hydrogen-bonding interactions [11], attachment to quantum dots [12], and supramolecular self-assembly [13].

Optical sensors for CN^- [14,15], in which a change in color and/or fluorescence is observed upon detection, have been widely investigated due to their simplicity, high sensitivity, and potential for use with in vivo imaging [16,17]. The conventional fluorescence-based detection strategy, in which the fluorescence intensity is monitored at a single wavelength, is easily overwhelmed by the background noise of the sample media. To overcome this drawback, a ratiometric fluorescent sensing system may be used, which enables measurement of the relative emission intensities at two different wavelengths and provides a precise and quantitative analysis and imaging, even in complicated systems [18,19].

The chemodosimeter approach is one of the most promising for the detection of CN^- due to its high selectivity over other anions [20–52] and its effectiveness in reducing the interference of hydrogen bonding and the acidity of the media. This approach has been successfully utilized in cyanohydrin reactions [53,54], related benzil rearrangements [20,21], and additions to electron-deficient carbon atoms [27–31]. Among these chemodosimeters, the mono- and doubly activated Michael-type acceptors exhibit both selective and sensitive responses to CN^-, with rapid changes in color and fluorescence [55,56]. However, sensors with doubly activated acceptors, which can be operated in either pure organic solvents or solutions containing a large amount of organic solvent, usually have low florescence quantum yields in solution [24,38]. It is especially rare that they operate in aqueous media

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[57]. One major obstacle to ratiometric fluorescent sensing of CN^- in aqueous media is that most organic fluorophores suffer from the aggregation-caused quenching (ACQ) effect and are weakly emissive or even nonemissive in nearly aqueous solution as a result of aggregate formation. The challenge, therefore, is to create ratiometric fluorescent cyanide-selective chemodosimeters that exhibit aggregation-induced emission enhancement (AIEE) and are highly emissive in aqueous media despite the formation of aggregates [58–61].

With these considerations in mind, we herein developed a structurally simple chemodosimeter **1** with both ICT and AIEE characteristics for detecting CN^- that is based on an indole-indanedione conjugate, as shown in Scheme 1. In this molecular design, we chose 1-methylindole as the electron-donating group because it has been found to produce intense fluorescence in the solid state [62]. The 1,3-indanedione moiety was chosen not only because it can act as a strong electron-accepting group and induce an ICT transition but also because it is a cyanide sensing unit. The β-conjugated position of the 1,3-indanedione moiety is electrophilic in nature and because CN^- can easily bind to it. The subsequent intramolecular conformational change prevents the ICT, resulting in a significant change in absorption and fluorescence spectra. Chemodosimeter **1** displays intense fluorescence in an aqueous solvent system consisting of 90% water, which makes it possible for the highly selective, sensitive, and quantitative detection of CN^- in a nearly aqueous solution. Furthermore, chemodosimeter **1** emits an extremely intense yellow light and exhibits excellent fluorescence responses in the solid state, allowing it to be used in practical and efficient CN^- test kits.

2. Experimental

2.1. General information

The starting materials, including 1-methylindole-5-carboxaldehyde (**2**), 1,3-indanedione (**3**), piperidine, and tetrahydrofuran (THF) were purchased from Merck, ACROS and Sigma–Aldrich. Reagent grade solvents were used for synthesis, and spectroscopy grade solvents were used for spectral measurements. Column chromatography was performed using silica gel Merck Kieselgel si 60 (40–63 mesh). ^1H and ^{13}C NMR spectra were recorded in deuterated tetrahydrofuran (THF-d_8) on a Bruker 400 MHz spectrometer. Mass spectra were recorded on a VG70-250S mass spectrometer. Absorption and emission spectra were measured using a Jasco V-570 UV–vis spectrophotometer and a Hitachi F-7000 fluorescence spectrophotometer, respectively.

A solution of chemodosimeter **1** (1.0×10^{-5} M) was prepared in aqueous solution (THF:H_2O = 1:9 [v/v], containing 0.01 M HEPES, pH = 7.3). Titration experiments were carried out in 1-cm quartz cell at room temperature. Anions (as the tetrabutylammonium salt) in aqueous solution were added to the host solution and used for the titration experiments.

The kinetics of the reaction was monitored by UV/Vis absorption spectroscopy. A freshly prepared cyanide solution was added in excess (20 equiv.) to a solution containing chemodosimeter **1** (THF/H_2O (1:9, v/v, containing 0.01 M HEPES, pH = 7.3)), and the absorbance was recorded with time. The rate constant was calculated using the following equation: $[A_t] = [A_0]\,e^{-kt}$, in which $[A_0]$ = initial concentration of A, $[A_t]$ = concentration of A at time t, k = rate constant, and t = elapsed time.

The test strips were prepared by immersing filter papers ($2 \times 1\ cm^2$) in the THF/H_2O (1:9, v/v) solution of chemodosimeter **1** (1.0×10^{-6} M) and subsequently drying them in air. A tetrabutylammonium cyanide stock solution of 2.0×10^{-5} M was diluted to different concentrations with deionized water, and test strips coated with chemodosimeter **1** were immersed in aqueous solutions of CN^- with different concentrations for colorimetric/fluorometric response studies.

2.2. Synthesis and characterization

Chemodosimeter **1** was synthesized by stirring a mixture of 1-methylindole-5-carboxaldehyde (159 mg, 1.0 mmol), 1,3-indanedione (146 mg, 1.0 mmol), a catalytic amount of piperidine, and THF (20 mL) at room temperature for 6 h. The solution was extracted with dichloromethane–water. Further purification via column chromatography (silica-gel column, hexane/dichloromethane = 1/2) gave chemodosimeter **1** (yellow powder, 243 mg, 85%). M.p. 203–204 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.47 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 8.05 (d, J = 1.6 Hz, 1H), 7.98 (m, 2H), 7.76 (m, 2H), 7.39 (d, J = 8.8 Hz, 1H), 7.09 (d, J = 3.2 Hz, 1H), 6.65 (d, J = 3.2 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 189.7, 149.7, 142.4, 139.9, 139.6, 134.8, 134.6, 130.6, 130.3, 128.9, 128.6, 125.7, 125.4, 122.9, 109.5, 103.7, 33.1; IR (KBr): 3045, 2951, 1674, 1570, 1477, 1334, 1215, 1149, 725 cm^{-1}; MS (EI) m/z (relative intensity) 287 (M^+, 90); HRMS calcd. for $C_{19}H_{13}NO_2$ 287.0946, found 287.0953.

2.3. Theoretical approach

The Gaussian 03 program was used to perform the *ab initio* calculation of the molecular structure [63]. The molecular structures of chemodosimeter **1** and **1-CN** in the ground state were optimized at the density functional theory (DFT) level using the B3LYP functionals with 6-31 + G* basis sets. The nature of all stationary points was confirmed by harmonic frequency analysis. The electronic excitation energies calculated by time-dependent DFT (TD-DFT) at the B3LYP/6-31 + G* level for the optimized ground-state structures combined with the corresponding oscillator strengths yield the UV–vis absorption spectra. Bulk solvent effects were included, using the linear response conductor-like polarizable continuum model (CPCM), and water was considered as the solvent to approximate the experimental medium.

3. Results and discussion

3.1. Design and synthesis of chemodosimeter 1

Chemodosimeter **1** is composed of an electron-donating 1-methylindole moiety to which a 1,3-indanedione group is attached to act as an electron-withdrawing group and induce ICT. The electrophilic nature of the β-conjugated position of 1,3-indanedione moiety can be modulated by CN^-, which interrupts the π-conjugation, and hence blocks the ICT (Scheme 1). The synthesis of chemodosimeter **1** is readily performed through the condensation of 1-methylindole-5-carboxaldehyde (**2**) with 1,3-indanedione (**3**) in the presence of piperidine. Detailed synthetic procedures and product characterizations are provided in the Section 2 and Supplementary data.

3.2. Optical properties of chemodosimeter 1

Fig. 1 shows the absorption and fluorescence spectra of chemodosimeter **1** in solvents of varying polarity, and the relevant photophysical data are given in Table 1. The longest wavelength absorption band of chemodosimeter **1** appears at ~415 nm, which is assigned to an ICT transition. This assignment can be supported by density functional theory (DFT) calculations (Table S1). Unlike the typical small shifts in absorption spectra seen with changes in solvent, the emission spectra of chemodosimeter **1** are largely red-shifted with any increase in the solvent polarity, which demonstrates strong ICT characteristics for the excited states of the sensor.