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## Rational design, synthesis of reaction-based dual-channel cyanide sensor in aqueous solution



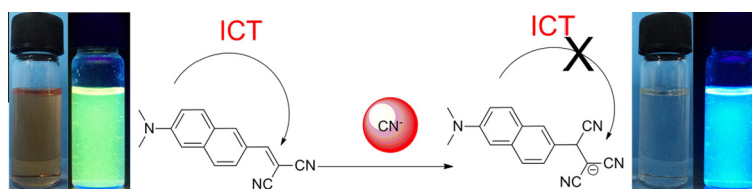
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### HIGHLIGHTS

- A highly selective and sensitive cyanide ion sensor.
- Fluorescent “turn on” response  $\text{CN}^-$  with detection limit as  $1.8 \times 10^{-7}$  mol/L.
- The sensor **L** recognizes  $\text{CN}^-$  selectively in aqueous solution.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A new dual-channel sensor for the detection of cyanide was developed based on the conjugated of naphthalene and malononitrile. Upon the addition of  $\text{CN}^-$ , the sensor displayed very large blue-shift in both fluorescence (80 nm) and absorption (120 nm) spectra. The sensor of cyanide was performed via the nucleophilic attack of cyanide anion to vinylic groups of the sensor with a 1:1 binding stoichiometry and the color changed of the sensor is mainly due to the intramolecular charge transfer process improvement. The intramolecular charge transfer progress was blocked with color changed and fluorescence blue-shift. The mechanism of sensor reaction with  $\text{CN}^-$  ion was studied using  $^1\text{H}$  NMR and mass spectrometry.

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## 1. Introduction

Over the last few decades, the design and synthesis of sensors for the detection of anions have been received extensive attention because such anions play important roles in biological systems and also constitute some pollutants in our environment [1,2]. Among anions, cyanide is widespread in industrial processes, such as gold-extraction, electroplating, the synthesis of fibers and resins [3,4]. But cyanide is a highly toxic anion that is deadly to humans because it can affect many biological functions, such as vascular, visual, central nervous, cardiac, endocrine and metabolic systems [5,6]. It is generally known that 0.5–3.5 mg of cyanide per kg of body weight is fatal for humans [7]. Accordingly, the rational

design and synthesis of efficient sensor to recognize cyanide anion is an important field of supramolecular chemistry.

At present, several sensors systems for cyanide anion detection are based on the mechanism of coordination [8,9], hydrogen bonding interaction [10–13], supramolecular self-assembly [14], nucleophilic addition reaction [15–18], and so on [19,20]. Among these cyanide sensors, reaction-based sensors display both specific selectivity and high sensitivity to the cyanide anion [21,22]. However, most reaction-based cyanide anion sensors often employ sophisticated structures that require complicated synthetic steps, high temperature, or long reaction time for  $\text{CN}^-$  detection [23–26]. As a consequence, developing a simple and efficient optical sensor for  $\text{CN}^-$  in aqueous solution is essential.

As a general rule, fluorescent sensors can be designed mainly according to two mechanisms: fluorescence resonance energy transfer (FRET) and intramolecular charge transfer (ICT) [27]. Compared with the former, ICT-based fluorescent sensors are

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structurally simple [28]. For a typical ICT fluorescence sensor, the tuning of the normal donor- $\pi$ -acceptor (D- $\pi$ -A) structure of sensors would lead to different optical nature and concomitant fluorescent or color changes [29,30].

In this article, we designed a naphthalene-malononitrile compound (**L**) as a fluorescent sensor toward cyanide, in which the two units of donor and acceptor were covalently linked through a double bond. The design focuses on utilizing the nucleophilic addition reaction of  $\text{CN}^-$  with a dicyano-vinyl group as the strategy for sensor design in tracking  $\text{CN}^-$  levels. As a result, sensor **L**, which contains dicyano-vinyl acceptor groups, was designed and synthesized. Considering the dicyano-vinyl acceptor group as electron-withdrawing group in **L**, we introduced an electron-donating group, such as the 4-dimethylamino, thereby changing the initial charge distribution of the sensor. This technique can effectively change the intramolecular charge configurations and construct a molecule that improves intramolecular charge transfer. The electron-withdrawing nature of dicyano-vinyl group can be modulated by cyanide anion, which interrupts  $\pi$ -conjugation through nucleophilic addition reaction. When the reaction starts, this group would rapidly respond to the spectrum change, resulting in very high sensitivity and selectivity. In this research work, a novel colorimetric and fluorescent dual-channel cyanide sensor 2-((6-(dimethylamino)naphthalene n-2-yl)methylene) malononitrile (**L**) was synthesized. The receptor showed good selectivity and fast response to  $\text{CN}^-$ . The mechanism of this process has been investigated by  $^1\text{H}$  NMR and infrared spectroscopy and mass spectrometry.

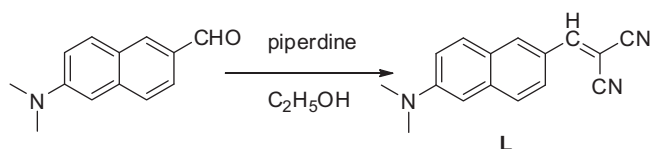
## 2. Experimental

### 2.1. Materials and instruments

Distilled water was used throughout the experiments. All other solvents and reagents were commercially available at analytical grade and were used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded using a Mercury-400BB spectrometer at 500 and 125 MHz, respectively. Chemical shifts were reported in ppm downfield from tetramethylsilane (TMS,  $\delta$  scale with solvent resonances as internal standards). UV-vis spectra were recorded using a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were obtained using a Shimadzu RF-5301 fluorescence spectrophotometer. Melting points were measured on an uncorrected X-4 digital melting-point apparatus. Infrared spectra were obtained using a Digilab FTS-3000 FT-IR spectrophotometer.

### 2.2. Synthesis of sensor **L**

To a solution of 0.80 g of 6-(dimethylamino)-2-naphthaldehyde (4 mmol) and 0.26 g of malononitrile (4 mmol) in ethanol was added 20  $\mu\text{L}$  of piperidine, the reaction mixture was stirred at rt for 1 h, a red crystal was formed, and the crystal was filtered and washed by ethanol, yield: 82.0% (m.p.  $170^\circ\text{C}$ – $172^\circ\text{C}$ ), IR: (KBr,  $\text{cm}^{-1}$ )  $\nu$ : 2213 ( $-\text{CN}$ ), 1619 ( $\text{C}=\text{C}$ ).  $^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  8.37 (s, 1H), 8.24 (s, 1H), 7.95 (d,  $J=8.8$  Hz, 1H), 7.85 (d,



Scheme 1. Synthetic procedures for sensor **L**.

$J=9.2$  Hz, 1H), 7.73 (dd,  $J=12.5$ , 6.2 Hz, 1H), 7.30 (dd,  $J=9.2$ , 2.4 Hz, 1H), 6.98 (d,  $J=1.9$  Hz, 1H), 3.12 (s, 6H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz):  $\delta$  160.9, 151.7, 138.4, 136.3, 131.7, 127.5, 127.3, 124.8, 124.6, 117.3, 115.9, 115.0, 105.4, 75.9, 40.88, 40.82; MS  $m/z$  [ $\text{M}$ ] $^+$  Calcd for  $\text{C}_{16}\text{H}_{13}\text{N}_3$  247.1, found 247.4 (See Scheme 1).

### 2.3. General procedures for UV-vis and fluorescence spectrum experiments

All spectrum experiments were performed in solution [0.01 M 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer, pH 7.26, 60% dimethyl sulfoxide (DMSO)]. Any changes in the spectra of the synthesized compound were recorded upon the addition of tetrabutylammonium salts while keeping the ligand concentration constant ( $2.0 \times 10^{-5}$  M) in all experiments. Tetrabutylammonium salt of anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{AcO}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HSO}_4^-$ ,  $\text{ClO}_4^-$  and  $\text{CN}^-$ ) was used for the experiments.

### 2.4. General procedure for $^1\text{H}$ NMR experiments

For  $^1\text{H}$  NMR titrations, the solution of **L** was prepared in DMSO  $d_6$  and the appropriate concentrated solution of the guest was prepared in double distilled water. Aliquots of the two solutions were mixed directly in NMR tubes.

## 3. Results and discussion

To detect the selectivity of **L** towards  $\text{CN}^-$ , we performed a series of absorption spectral experiments, where 50 equiv. of various anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{AcO}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HSO}_4^-$ ,  $\text{ClO}_4^-$  and  $\text{CN}^-$ ) were respectively added to  $2.0 \times 10^{-5}$  M of **L** in DMSO/ $\text{H}_2\text{O}$  solution (6:4, v/v, 0.01 M HEPES buffer, pH 7.26). The sensor immediately responded with obvious color changes from yellow to colorless when  $\text{CN}^-$  water solution was added to the **L** solution at room temperature (Fig. 1). In the corresponding UV-vis spectrum, the absorption peak at 480 nm decreased (Fig. 2). However, a yellow-green fluorescence with one emission band centered at 513 nm appeared when the solution of sensor **L** was excited at 365 nm. Upon the addition of  $\text{CN}^-$  water solution, the fluorescence emission band decreased remarkably and shifted to 433 nm (Fig. 3). A variety of other anions, such as  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{AcO}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HSO}_4^-$  and  $\text{ClO}_4^-$ , did not cause such a significant change.

The UV-vis titration of **L** with  $\text{CN}^-$  is carry out in buffer solutions (Fig. 4). The inset shows a good linear dependence of the absorbance at 480 nm as a function of  $[\text{CN}^-]/[\text{L}]$ . The plot of the decrease in absorbance at 480 nm reached the saturation point at the ratio of  $[\text{CN}^-]/[\text{L}]$  of 1.0, indicating a 1:1 stoichiometry between **L** and  $\text{CN}^-$ . In addition, the detection limit of the UV-vis changes calculated on the basis of  $3\sigma B/S$  [31] is  $1.8 \times 10^{-7}$  mol/L for  $\text{CN}^-$ , which is far lower than the WHO guideline of 1.9  $\mu\text{mol/L}$  cyanide. The sensor has strong fluorescence emission at 513 nm ( $\lambda_{\text{ex}} = 365$  nm,) and yellow-green. The changes in the fluorescence spectra of sensor in the presence of  $\text{CN}^-$  in HEPES buffer solutions are displayed. As it can be seen that the addition of  $\text{CN}^-$  caused changes in the fluorescence spectra: namely, the emission intensity with a 80 nm blue-shift in the emission maximum (from 513 to 433 nm) was observed and the color of solution changed from yellow-green to blue (Fig. 5).

To further exploit the utility of sensor **L** as anion-selective sensor for  $\text{CN}^-$ , competitive experiments were carried out in the presence of 50 equiv. of  $\text{CN}^-$  and other anions in aqueous solution. As shown in Fig. 6, sensor **L** ( $2.0 \times 10^{-5}$  M) shows obvious color change from yellow to colorless upon addition of  $\text{CN}^-$  in solution; the peak at 480 nm disappeared in the UV-vis spectrum and a new signal appeared at 360 nm. It is noticeable that the miscellaneous

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