



# A novel reaction-based colorimetric and ratiometric fluorescent sensor for cyanide anion with a large emission shift and high selectivity



Shaodan Wang<sup>a</sup>, Xiaoliang Fei<sup>a</sup>, Jing Guo<sup>a</sup>, Qingbiao Yang<sup>a,\*</sup>, Yaoxian Li<sup>a</sup>, Yan Song<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, Jilin University, Changchun 130021, PR China

<sup>b</sup> College of Materials Science and Engineering, Jilin University of Chemical Technology, Jilin 132022, PR China

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## ABSTRACT

A hybrid carbazole-hemicyanine dye (**Cac**) has been developed as a novel colorimetric and ratiometric fluorescent sensor for cyanide detection. Upon treatment with cyanide, **Cac** displayed a remarkable fluorescence ratiometric response, with the emission wavelength displaying a very large emission shift (214 nm). The detection of cyanide was performed via the nucleophilic addition of cyanide anion to the indolium group of the sensor, which resulted in the blocking of the intramolecular charge transfer (ICT) process in the sensor, inducing a ratiometric fluorescence change and simultaneously an obvious color change. Furthermore, competitive anions did not show any significant changes both in color and emission intensity ratio ( $I_{381}/I_{595}$ ), indicating the high selectivity of the sensor to  $\text{CN}^-$ .

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## 1. Introduction

Cyanide ( $\text{CN}^-$ ) is a well-known highly toxic material and is very harmful to living beings [1]. A small amount of cyanide can result in extremely lethal poisoning because of its inhibition of cellular respiration in cells via its binding to a heme unit in the active site of cytochrome  $a_3$ , leading to vomiting, convulsion, loss of consciousness, and eventual death [2]. According to the World Health Organization (WHO), the maximum acceptable level of cyanide in drinking water is only 1.9  $\mu\text{M}$  [3]. Nevertheless, the use of cyanide cannot be avoided due to its extensive utilization in many industrial processes, such as electroplating, gold mining and plastics manufacturing [4]. Thus, there is considerable interest in the development of easy and affordable methods for highly selective and sensitive detection of cyanide anion.

In the past few years, a variety of colorimetric or fluorescent sensors for cyanide have been reported according to several common approaches [5–7]. Some of the sensors rely on hydrogen bonding interactions [8,9] or deprotonation [10,11], however, the poor selectivity over other competitive anions limited their application. Other cyanide chemosensors which were developed by employing cyanide complexes based on the strong coordination ability of cyanide, such as Cu (II) complex [12–14], Zn (II) complex [15,16], boronic acid derivatives [17,18] and gold nanoparticles functionalized polyacetylenes [19] were also involved, but they only offered an indirect way to detect cyanide anion. Recently,

reaction-based sensors [20,21] for cyanide anion were also used by taking advantage of its nucleophilic character, which enable the design of recognition systems with features such as direct detection, analyte-specific response and reduction of the interference by the aqueous media. Effective reaction based sensors have been exploited using oxazines [22], pyrylium [23,24], indolium [25,26], salicylaldehyde [27], dicyanovinyl derivatives [28,29], trifluoroacetamide derivatives [30,31] and other highly electron deficient carbonyl groups [32,33].

However, most of the reported fluorescent sensors for cyanide were based on fluorescence quenching [34,35] or enhancement [36,37] which means that the only detection signal is the fluorescence intensity at a single wavelength and could be significantly influenced by the sensor concentration, instrumental efficiency and environmental conditions. By contrast, ratiometric fluorescent sensors can overcome the drawbacks of the intensity based sensors, since they enable the measurement of emission intensities at two different wavelengths, thus increasing the dynamic range of fluorescence measurements and providing a built-in correction for environmental and concentration factors. Unfortunately, up to now, only a few ratiometric fluorescent sensors for  $\text{CN}^-$  have been reported in the literature [38,39]. In general, either a fluorescence resonance energy transfer (FRET) [40] or an intramolecular charge transfer (ICT) [41,42] mechanism can be adopted to design a ratiometric fluorescence sensor. Compared to the former, ICT-based ratiometric sensors are structurally simple.

With these considerations in mind, we present herein a hybrid carbazole-hemicyanine dye (**Cac**) as a new reaction-based

\* Corresponding authors.

colorimetric and ratiometric fluorescent sensor for cyanide based on a novel  $\text{CN}^-$  reaction site, indolium group. Obstruction in the intramolecular charge transfer (ICT) process by the nucleophilic addition of a cyanide anion to the indolium group induces spectral changes as well as the change in color [43]. Importantly, the sensor exhibits large emission wavelength shift (up to 214 nm) upon treatment with cyanide and shows high sensitivity and selectivity to  $\text{CN}^-$  over other anions in aqueous media.

## 2. Material and methods

### 2.1. Materials

1,2,3,3-tetramethyl-3H-indolium iodide, carbazole and tetrabutylammonium (TBA) salts were purchased from Sigma-Aldrich and used without further purification. Reagents with analytical grades and deionized water were used for preparing the solutions. Stock solutions of  $\text{CN}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , were prepared from their TBA salts;  $\text{NO}_3^-$ ,  $\text{HSO}_3^-$ ,  $\text{SCN}^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{AcO}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HS}^-$ ,  $\text{N}_3^-$  were prepared by direct dissolution of proper amounts of sodium salts. Aqueous Tris-HCl buffer (pH=7.4, 10 mM) solution was used as buffer to keep pH value.

### 2.2. Instruments

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured on a Bruker AV-400 spectrometer with chemical shifts reported as  $\delta$  [in  $\text{CDCl}_3$ , tetramethylsilane (TMS) as internal standard]. Absorption and fluorescence spectra were carried out on a Shimadzu UV 2100 PC UV-visible spectrophotometer and a Hitachi F-4500 fluorescence 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  $(298.0 \pm 0.2)$  K.

### 2.3. Synthesis and characterization

**Cac** was conveniently synthesized via the condensation of 9-ethyl-9H-carbazole-3-carbaldehyde (**a**) with 1,2,3,3-tetramethyl-3H-indolium iodide (**b**) in ethanol. 9-ethyl-9H-carbazole-3-carbaldehyde (**a**) was synthesized according to the reported procedure [44]. Compound **a** (0.893 g, 4.0 mmol), compound **b** (1.204 g, 4.0 mmol) and piperidine (0.4 ml, 4.0 mmol) were dissolved in 30 ml ethanol. The reaction mixture was refluxed with stirring for 12 h under nitrogen. After cooling the solid was collected, washed with anhydrous ethanol and dried. The residue was purified by column chromatography on silica gel ( $\text{CH}_2\text{Cl}_2/\text{ethanol}$ , 20:1 v/v) to give **Cac** as an orange red solid (1.27 g, Yield: 83.6%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.00 (s, 1 H), 8.51–8.44 (m, 2 H), 8.39 (d,  $J = 15.8$  Hz, 1 H), 7.98 (d,  $J = 15.8$  Hz, 1 H), 7.58–7.49 (m, 5 H), 7.46 (dd,  $J = 13.5, 7.8$  Hz, 2 H), 7.36 (t,  $J = 7.1$  Hz, 1 H), 4.45 (s, 3 H), 4.38 (q,  $J = 7.2$  Hz, 2 H), 1.87 (s, 6 H), 1.47 (t,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  181.62, 155.62, 143.67, 143.43, 142.42, 140.87, 129.49, 129.33, 129.10, 127.46, 126.27, 125.42, 123.63, 123.27, 122.87, 121.28, 121.02, 115.03, 110.73, 110.68, 109.76,

52.17, 38.02, 34.61, 26.30, 14.33. HRMS (ESI):  $m/z$ , Calcd. 379.2169, found 379.2105 for  $[\text{M}+\text{H}]^+$ .

The **Cac-CN** product could be conveniently synthesized via the condensation of **Cac** and 1.5 equiv. of TBACN in ethanol at room temperature, and purified by column chromatography on silica gel ( $\text{CH}_2\text{Cl}_2$ ) (yield: 80%). Note: the product is very unstable in the air (Scheme 1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (s, 1 H), 8.13 (d,  $J = 7.6$  Hz, 1 H), 7.63 (d,  $J = 8.4$  Hz, 1 H), 7.50 (t,  $J = 7.4$  Hz, 1 H), 7.41 (t,  $J = 9.2$  Hz, 2 H), 7.35–7.23 (m, 2 H), 7.20 (t,  $J = 7.4$  Hz, 1 H), 7.09 (d,  $J = 7.1$  Hz, 1 H), 6.88 (t,  $J = 7.1$  Hz, 1 H), 6.62 (d,  $J = 7.6$  Hz, 1 H), 6.24 (d,  $J = 16.1$  Hz, 1 H), 4.38 (q,  $J = 6.7$  Hz, 2 H), 2.83 (s, 3 H), 1.57 (s, 3 H), 1.44 (t,  $J = 6.7$  Hz, 3 H), 1.26 (s, 3 H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.88, 140.54, 140.32, 137.15, 136.90, 128.38, 126.52, 126.22, 124.83, 123.41, 122.95, 121.94, 120.71, 120.33, 119.57, 119.44, 119.40, 117.82, 108.97, 108.87, 108.82, 80.85, 77.36, 53.58, 49.21, 37.82, 31.73, 29.84, 24.72, 23.13, 13.95; HRMS (ESI):  $m/z$ , Calcd. 405.2205, found 406.2057 for  $[\text{M}+\text{H}]^+$ .

### 2.4. Titration experiments of Cac

**Cac** was dissolved in DMSO to afford a concentration of 0.1 mM stock solution, which was then diluted to the corresponding concentration (20.0  $\mu\text{M}$ ) with the solution of DMSO-Tris-HCl buffer (10.0 mM, pH=7.4, 6:4, v/v). The TBACN stock solution of 1.0 mM was diluted to different concentrations with buffer solution for spectra titration studies. Changes in the fluorescence intensity were recorded using a fluorescence spectrometer ( $\lambda_{\text{ex}}=340$  nm, slits: 5 nm/5 nm).

### 2.5. Paper test of Cac

The neutral filter paper was dipped in the EtOH solution of **Cac** (1.0 mM) and then drying them in a vacuum oven. Then various solutions of anions (1.0 mM) were dropped individually.

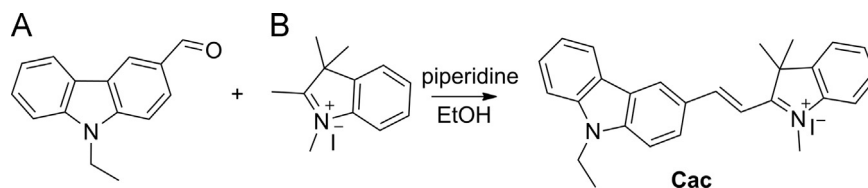
### 2.6. Water samples test

The tap water and distilled water were used directly without further purification and the real lake water collected from a local lake was first filtered through nylon microporous filter (0.45  $\mu\text{m}$ ) to remove any particulate suspension. The Tris-HCl buffer (pH=7.4) was first prepared by samples, and **Cac** was diluted with DMSO:Tris-HCl buffer=6:4 (v/v, pH=7.4). Then different concentrations of cyanide (10  $\mu\text{M}$ , 20  $\mu\text{M}$  and 30  $\mu\text{M}$ ) were added to the solution. The fluorescence intensity ratio ( $I_{381}/I_{595}$ ) of each sample was recorded after 10 min.

## 3. Results and discussion

### 3.1. Effect of reaction time

We first examined the time courses of the fluorescence intensities of the sensor in the presence of 5 equiv.  $\text{CN}^-$  in DMSO:Tris-HCl buffer solution. As shown in Fig. 1, the maximal fluorescence signal at 381 nm and minimal fluorescence signal at 595 nm



Scheme 1. Synthetic route of **Cac**.

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