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## **Graphical Abstract**

# A novel colorimetric and fluorescent probe based on indolium salt for detection of cyanide in 100% aqueous solution

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2	detection of cyanide in 100% aqueous solution
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10	Abstract : We reported a novel indolium salt -based colorimetric and fluorescent
11	probe N1 for cyanide. The probe N1 showed a bleaching solution and fluorescence
12	quenching toward $CN^{-}$ in 100% aqueous solution over other anions. In UV-vis and
13	fluorescent spectrometry method, a large blue shift (261 nm), color bleaching and
14	fluorescence quenching was observed. The minimum detection limit on fluorescence
15	response of the probe N1 towards CN <sup>-</sup> was $3.34 \times 10^{-7}$ mol/L. This probe N1 operates
16	via intramolecular charge transfer (ICT) mechanism, because the nucleophilic
17	attacking of CN <sup>-</sup> to the indol C=N, the ICT progress was blocked with color changed
18	and fluorescence quenched, which is further confirmed by <sup>1</sup> H NMR, MS and DFT
19	studies. Therefore, the synthesized probe would be a promising device for the
20	detection of cyanide.

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21 Keywords: cyanide; water soluble; intramolecular charge transfer; nucleophilic
22 addition

#### 23 1. Introduction

Cyanide plays a critical role in several industries such as organic synthesis, metallurgical engineering, electroplating technology and other fields due to its special characteristics. However, it is still extremely damaging to human beings even at very low concentrations for 0.5 mg per kilogram of body weight, which leads to cellular asphyxiation and death [1-5]. Hence, in human terms, it's very urge to develop reliable and efficient approaches to detect cyanide in environmental systems [6, 7].

30 Up to now, several traditional detection methods, such as titrimetric, electrochemistry and spectroscopy [8-11], have been devised for the detection of CN. With the 31 development of analytical instruments, the devised and prepared probes for 32 colorimetric and fluorescent detection of cyanide have gained increasing attention 33 because of their outstanding properties [12, 13]. Compared with various traditional 34 approaches, colorimetric and fluorescent probes are regarded as the powerful tools for 35 36 detection method owing to their simplicity, high sensitivity and naked eye detection [14-17]. And lots of fluorescent probes have been reported for CN<sup>-</sup> detection so far. 37

The above probes had been designed on the basis of various chemical reaction mechanisms, nucleophilic addition reaction [18-23], supramolecular self-assembly [24], hydrogen bonding motifs [25-28], cyanide complexation addition[9], electron deficient alkenes [14, 29, 30], and so on. However, the majority of these probes are inclined to poor solubility in water [31-35]. Thereby, there is a significant challenge

43 to develop the CN<sup>-</sup> probes in 100% aqueous solution in biological and environmental
44 systems.

45 Herein, we synthesized a novel colorimetric and fluorescent dual-channel probes N1 with carboxylated indole as an electron-withdrawing group and dimethylamine as an 46 electron-donating group (Scheme 1), which showed highly sensitive detection for CN<sup>-</sup> 47 48 in 100% H<sub>2</sub>O solution (0.01 M Tris-HCl buffer, pH 7.2). The mechanism of detection for CN<sup>-</sup> was mainly based on the nucleophilic addition reaction, which collapsed the 49  $\pi$ -conjugation and interrupted the ICT process to form a sensitive colorimetric and 50 fluorescent turn-on response. The possible mechanism of the probe N1 sensing CN 51 was confirmed by the measurements of <sup>1</sup>H NMR, MS and DFT. Therefore, the 52 synthesized probe would be a promising device for the detection of cyanide. 53

54

#### Scheme 1

#### 55 2. Materials and methods

56 2.1 Chemicals and Apparatus

All reagents and solvents were analytical grade and obtained commercially without further purification. The ultrapure water was used throughout the experiment. Tetrabutylammonium salt of anions (CN<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, Ac<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>) were purchased from Sigma-Aldrich. Sodium salts (S<sup>2-</sup>, SCN<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) was obtained from Energy Chemical (Shanghai, China). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were carried out on a 500 MHz, and TMS was used as an internal standard. A Shimadzu UV-2550 spectrometer was performed to get UV-vis spectra. Fluorescent 64 spectra was achieved by use of a Shimadzu RF-5301 fluorescence spectrophotometer.

- 65 2.2 Synthesis of the probe N1
- 66 The schematic illustration of synthesis methods for probe N1 is shown in Scheme 1. 67 5-carboxy-1-ethyl-2,3,3-trimethyl-3H-indol-1-ium iodide (1) was prepared by 68 references [36]. Compound 5-carboxy-1-ethyl-2,3,3-trimethyl-3H-indol-1-ium iodide 69 (1) (0.72g, 2 mmol), p-dimethylaminobenzaldehyde (2) (0.33 g, 2.2 mmol) and 70 piperidine (3 drop) were dissolved in ethyl alcohol (20 mL), stirred and refluxed for 71 12 h. After the above reaction cooled to ambient temperature, we removed the solvent 72 and refined the left residue with column chromatography to get N1 as a black red powder. 73

1: Yield 75%, <sup>1</sup>H NMR (500 MHz, DMSO) δ 13.20 (s, 1H), 8.39 (s, 1H), 8.14 (d, J =
32.0 Hz, 2H), 4.53 (s, 2H), 2.90 (s, 3H), 1.58 (s, 6H), 1.45 (s, 3H). <sup>13</sup>C NMR (126
MHz, DMSO) δ 196.38, 171.47, 149.00, 141.11, 140.05, 125.85, 120.25, 114.23,
53.72, 42.67, 21.27, 20.54, 13.37, 12.09.

**N1**: Yield 65%, <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  13.21 (s, 1H), 8.42 (d, J = 15.3 Hz, 78 79 1H), 8.31 (s, 1H), 8.25 – 7.94 (m, 3H), 7.79 (d, J = 8.3 Hz, 1H), 7.27 (d, J = 15.4 Hz, 1H), 6.92 (d, J = 8.5 Hz, 2H), 4.54 (d, J = 6.5 Hz, 2H), 3.21 (s, 6H), 1.79 (s, 6H), 1.38 80 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  180.28, 167.18, 156.38, 155.58, 81 144.78, 143.30, 131.00, 129.74, 124.21, 123.07, 113.54, 112.96, 104.51, 51.14, 41.00, 82 40.50, 40.33, 40.16, 40.00, 39.83, 39.67, 39.50, 38.93, 26.88, 13.50. MS m/z [M]<sup>+</sup> 83  $C_{23}H_{27}N_2O_2^+$  363.2073;  $C_{23}H_{26}N_2O_2Na^+$  385.1892. FT-IR: (KBr, cm<sup>-1</sup>) v = 3465.12 84 (-COOH), 3049.25 (C–H), 1700.41 (C=O), 1613.18 (C=C) 85

86 2.3 Theoretical approach of the probe N1 and N1-CN

The Gaussian 09 program was performed. The optimization of the molecular configurations of N1 and N1-CN in the ground state and excited state were implemented using the density functional theory (DFT) with the b3lyp methodology containing 6-31G(d) basis sets.

#### 91 **3. Results and discussion**

Compound N1 was synthesized by the aldol 92 condensation reaction of 93 5-carboxy-1-ethyl-2,3,3-trimethyl-3H-indol-1-ium iodide (1)and p-dimethylaminobenzaldehyde (2) in ethanol (Scheme 1). The N1 was prepared to 94 contain a strong electron withdrawing carboxylated indole derivatives and carboxyl 95 96 and an electron donating dimethylamine, which were linked via an ethylene. Carboxyl was selected because it is an excellent fluorophore with 97 group good electron-withdrawing property and a good water-soluble group. Therefore, N1 can be 98 99 detected the CN<sup>-</sup> in water.

#### 100 3.1. UV-vis and Fluorescence spectroscopic studies of N1

In order to obtain the optical properties of N1 for detection of anions, the UV-Vis and fluorescence titration experimentations of N1 were performed. The absorbance of N1 in H<sub>2</sub>O (0.01 M Tris-HCl buffer, pH 7.2) exhibited one absorption bands at 569. In the UV-Vis spectrum, the significant changes were discovered of N1 in the presence of CN<sup>-</sup> compared to the other anions, including F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, Ac<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, S<sup>2-</sup>, SCN<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, Cys and GSH. Upon the addition of 50 equiv.CN<sup>-</sup> into the H<sub>2</sub>O solution

of N1 (20μM), the absorption band at 569 nm disappeared and a new band started to
grow at 308 nm (Fig. 1a). In the fluorescence spectrum, the probe N1 displays a
strongly fluorescence peak at 603 nm. By addition of CN<sup>-</sup>, the fluorescence band at
603 nm disappeared (Fig. 1b). However, the addition 50 equiv. of other anions, the
absorption band and fluorescence did not remarkable change, which show the fact that
probe N1 possesses a reasonable selectively in respect of cyanide anion.

113

#### (Fig. 1)

In order to obtain more information of the N1 with CN, we carried out UV-Vis and 114 fluorescence titration experimentations. By gradual addition of CN, the UV-Vis 115 116 absorption peak at 569 nm declined, while the absorption gradually increased at 308 nm. It is noteworthy that the blue shift of absorption wavelength consistent with a 117 118 pretty evident color change from amaranth to colorless demonstrates that N1 can achieve the goal of detection of CN with visual observation. Meanwhile, the 119 fluorescence titration of N1 with CN<sup>-</sup> was carried out, the emission intensity at 603 120 nm weakens gradually while enhancing CN<sup>-</sup> concentration, along with an obvious 121 fluorescence quenching. The LOD of the N1 was calculated as  $3.34 \times 10^{-7}$  mol/L using 122 the formula  $3\sigma/S$ . Which is far below the WHO standard of  $1.9 \times 10^{-6}$  mol/L cyanide. 123

124

#### (Fig. 2)

To study the selectivity of N1, competition experiments were carried out in the presence of other anions. The addition of 50 equiv. of CN<sup>-</sup> and other anions, the UV-Vis absorption band and fluorescence intensity is not lead to observable changes in absorption at 569 nm and the intensity of emission at 603 nm by the presence of

129	other anions (Fig. 3). These results indicated that the interference of other anions is
130	negligible for the selective detection of CN <sup>-</sup> .

131

#### (Fig. 3)

132 **3.2. Plausible mechanism** 

To examine the possible mechanism of interaction between N1 and CN, <sup>1</sup>H NMR 133 titrations and MS methods have been implemented. <sup>1</sup>H NMR titrations were dissolved 134 in DMSO- $d_6$ . The incremental addition of cyanide to the N1 caused the vanishing of 135 the signal corresponding to the carboxyl OH at 13.21 and all <sup>1</sup>H NMR signals shifted 136 upfield. The peaks belonging to the vinylic protons H exhibited an up-field shift from 137 138 7.79 and 7.27 ppm to 6.85 and 6.57 ppm upon adding 1 equiv. CN<sup>-</sup>. Additionally, the signals in accordance with -N-CH<sub>2</sub>-, i.e. Hc protons presented an up-field shift from 139 140 4.54 to 3.18 ppm. By mass spectral analyses, the peak of N1 was at 363.34 m/z. The CN<sup>-</sup> was dropped into the solution of N1, and then the N1-CN peak arised at 390.37 141 m/z. Therefore, we thus proposed that the suggested mechanism of CN<sup>-</sup> as a 142 proverbial nucleophile is the strong nucleophilic attack of CN<sup>-</sup> to the -C=N group of 143 144 N1.

145

#### (Fig. 4)

146 **3.3. Theoretical studies** 

The geometry of N1 was optimized using Gaussian 09 program, B3LYP methodology,
6-31G(d) basis sets. As shown in Fig. 5(a), the optimized ground-state (S0) structures,
the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular
orbitals (LUMO) of N1 and N1-CN have been showed. The HOMO of probe N1 was

151 mainly distributed on the entire indol and benzene ring, demonstrating the well delocalization of the electron cloud density and the active ICT processes. However, 152 when the N1 was converted to N1-CN, the conjugation is interrupted and the ICT 153 process is blocked. The HOMO-LUMO energy gap of N1 was calculated to be 2.69 154 eV, which is much lower than that of N1-CN (4.04 eV) (Fig. 5b). This building up 155 energy gap is responsible for the blue shift of the UV-vis of N1. The experiment 156 phenomenon was well in line with the theoretical results. Hence, we can summarily 157 conclusion that the N1 detected CN<sup>-</sup> by a nucleophilic addition reaction. 158

159

(Fig. 5)

#### 160 4. Conclusions

161 In this study, we have successfully designed a simple colorimetric and fluorescent probe N1 based on indolium-derived for detection of cyanide in 100% H<sub>2</sub>O (0.01 M 162 Tris-HCl buffer, pH 7.2) solution. The probe performs good anti-interference ability 163 164 and high selectivity toward CN<sup>-</sup> over other anions. The potential or possible mechanism is characterized as a nucleophilic addition reaction by conducting <sup>1</sup>H 165 NMR, MS and DFT measurements. The probe N1 exhibits high selectivity for CN<sup>-</sup> 166 even in the presence other anions and a desirable low LOD of  $3.34 \times 10^{-7}$  mol/L. These 167 unique properties of prepared probe N1 renders its promising application for detecting 168 cyanide in environmental systems. 169

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283

#### 284 Figure & Scheme captions

- 285 Scheme 1 Synthetic procedures for probe N1. (a) AcOH, KOH. (b), CH<sub>3</sub>CH<sub>2</sub>I, acetonitrile,
  286 refluxed,75%. (c) piperidine, EtOH, refluxed. 65%.
- **287** Fig. 1. (a) UV-vis absorption spectra of N1 ( $2.0 \times 10^{-5}$  M) with various analytes in H<sub>2</sub>O [0.01 M
- 288 Tris-HCl buffer, pH 7.2] in the presence of CN', F', Cl', Br', I', Ac',  $SO_4^{2-}$ ,  $H_2PO_4^{-}$ ,  $ClO_4^{-}$ ,  $N_3^{-}$ ,  $S^{2-}$ ,
- 289 SCN<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, Cys and GSH. (b) Fluorescence spectra of N1 ( $2.0 \times 10^{-5}$  M) with various analytes in
- $290 \quad H_2O.$
- **291** Fig. 2. (a) UV-vis spectra of N1  $(2.0 \times 10^{-5} \text{ M})$  in H<sub>2</sub>O [0.01 M Tris-HCl buffer, pH 7.2] upon
- adding an increasing concentration of CN<sup>-</sup>. Inset: Color change. (b) Fluorescence spectra of N1
- 293 upon adding an increasing concentration of CN<sup>-</sup>. Inset: Color change.
- **Fig. 3.** (a)UV-vis spectra of **N1** at 569 nm with addition of CN<sup>-</sup> in the presence of 50 equiv. of
- 295 other anions (0 L1; 1 CN<sup>-</sup>; 2 F<sup>-</sup>; 3 Cl<sup>-</sup>; 4 Br<sup>-</sup>; 5 I<sup>+</sup>; 6 Ac<sup>-</sup>; 7 SO<sub>4</sub><sup>-2-</sup>; 8 H<sub>2</sub>PO<sub>4</sub><sup>-</sup>; 9 ClO<sub>4</sub><sup>-</sup>; 10 N<sub>3</sub><sup>-</sup>; 11 S<sup>2-</sup>;
- 296 12 SCN<sup>-</sup>; 13 CO<sub>3</sub><sup>2-</sup>; 14 Cys; 15 GSH.) inH<sub>2</sub>O (b). Fluorescence of N1 at 603 nm with addition of
- **297**  $\text{CN}^{-}$  in the presence of 50 equiv. of other anions in H<sub>2</sub>O.
- Fig. 4. Suggested mechanism for the N1 to CN<sup>-</sup>. Partial <sup>1</sup>H NMR spectra of N1 and in the
  presence of different equiv. of CN<sup>-</sup>.
- **300** Fig. 5. (a) The optimized ground-state structures of N1 and N1-CN (b) Frontier molecular orbitals
- 301 of N1 and N1-CN obtained from the DFT calculations using Gaussian 09 program.

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Scheme 1 Synthetic procedures for probe N1. (a) AcOH, KOH. (b), CH<sub>3</sub>CH<sub>2</sub>I, acetonitrile,

refluxed,75%. (c) piperidine, EtOH, refluxed. 65%.



**Fig. 1.** (a) UV–vis absorption spectra of **N1** ( $2.0 \times 10^{-5}$  M) with various analytes in H<sub>2</sub>O [0.01 M Tris-HCl buffer, pH 7.2] in the presence of CN<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, Ac<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, N<sub>3</sub><sup>-</sup>, S<sup>2-</sup>, SCN<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, Cys and GSH. (b) Fluorescence spectra of **N1** ( $2.0 \times 10^{-5}$  M) with various analytes in H<sub>2</sub>O.



**Fig. 2.** (a) UV–vis spectra of **N1**  $(2.0 \times 10^{-5} \text{ M})$  in H<sub>2</sub>O [0.01 M Tris-HCl buffer, pH 7.2] upon adding an increasing concentration of CN<sup>-</sup>. Inset: Color change. (b) Fluorescence spectra of **N1** upon adding an increasing concentration of CN<sup>-</sup>. Inset: Color change.



**Fig. 3.** (a)UV–vis spectra of **N1** at 569 nm with addition of  $CN^{-}$  in the presence of 50 equiv. of other anions (0 L1; 1  $CN^{-}$ ; 2 F; 3  $C\Gamma$ ; 4 Br<sup>-</sup>; 5  $\Gamma$ ; 6 Ac<sup>-</sup>; 7  $SO_{4}^{-2}$ ; 8 H<sub>2</sub>PO<sub>4</sub><sup>-</sup>; 9  $CIO_{4}^{-}$ ; 10 N<sub>3</sub><sup>-</sup>; 11 S<sup>2-</sup>; 12 SCN<sup>-</sup>; 13  $CO_{3}^{-2-}$ ; 14 Cys; 15 GSH.) inH<sub>2</sub>O (b). Fluorescence of **N1** at 603 nm with addition of  $CN^{-}$  in the presence of 50 equiv. of other anions in H<sub>2</sub>O.



Fig. 4. Suggested mechanism for the N1 to  $CN^-$ . Partial <sup>1</sup>H NMR spectra of N1 and in the presence of different equiv. of  $CN^-$ 



Fig. 5. (a) The optimized ground-state structures of N1 and N1-CN (b) Frontier molecular orbitals

of N1 and N1-CN obtained from the DFT calculations using Gaussian 09 program.

## Highlights

- 1. A cyanide probe based on a conjugated indolium system.
- 2. The probe recognizes  $CN^{-}$  selectively in 100% aqueous solution
- 3. The detection of cyanide with probe can be performed clearly by color changes