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Rational design, green synthesis of reaction-based dual-channel chemosensors for cyanide anion

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ABSTRACT

Chemosensors **CF1**–**CF3** were designed and synthesized via a simple green chemistry procedure. **CF3** could instantly detect cyanide anion in aqueous solution by dual-channel model. The detection limit of CF3 for CN- is 10 nM. Test strips based on **CF3** could act as a convenient and efficient CN^- test kit.

Cyanide anion (CN^-) is known to be an extremely toxic anion[1] and can directly lead to the death of human beings in several minutes because it strongly binds cytochrome-c, disrupting the mitochondrial electron-transport chain and leading to decreased oxidative metabolism and oxygen utilization.[1,2] Therefore, the maximum permissive level of cyanide in drinking water is set at 1.9 μM by the World Health Organization (WHO).[3] On the other hand, large quantities of cyanide anions are widely used in industry for the synthesis of fine chemicals, electroplating, and precious metal mining.[2a] In addition, a higher level of cyanide could also be accumulated through the consumption of certain foods and plants.[4] All things considered, the rational design and synthesis of efficient sensors to selectively detect CN^- at the environmental and biological levels have attracted much attention. Although previous work has involved the development of a wide variety of chemical and physical sensors for the detection of CN^-,[5] so far, it is still a challenge to improve the detection selectivity and sensitivity in the context of interference from coexisting anions such as F^-, AcO^-, and $H_2PO_4^-$ in the aqueous solution. Moreover, most of physical methods require expensive equipment, involve time-consuming and laborious procedures that can be carried out only by well-trained professionals, and seriously restrict the practical application of these CN^- sensors.[5a,b,6] For purposes of simplicity, convenience, and low-cost, easily-prepared CN^- colorimetric and/or fluorometric chemosensors[5c–e] become an excellent choice. Furthermore, in biological and environmental systems, cyanide–sensor interactions commonly occur in the aqueous solution, therefore, much attention has been paid to develop CN^- optical chemosensors that work in the aqueous solution.[7]

Several chemosensor systems for cyanide anion detection reported to date are based on the mechanism of coordination,[7d,8] hydrogen-bonding interaction,[7e,f] nucleophilic addition reaction,[7a,c,9] and so on. Among these cyanide sensors, reaction-based sensors display both specific selectivity and high sensitivity to the cyanide anion. However, most of the reaction-based cyanide anion sensors often employ sophisticated structures, require complicated synthetic steps, high temperature or long reaction time for detection of CN^-, and can only be operated in the pure or mixed organic solvents. Therefore, simple and efficient CN^- optical chemosensors which could instantly detect CN^- in the aqueous solution at the room temperature are essential. On the other hand, the synthesis procedures of most artificial sensors usually involve rather harsh reaction conditions and often employ hazardous materials like reaction raw materials, solutions, and catalysts which cause a huge risk to the environment. To minimize the generation and application of hazardous substances, a green synthetic procedure should be encouraged in the synthesis of CN^- chemosensors.

With these considerations and our interest in ion recognition,[10] we here report a series of efficient optical chemosensors (Scheme 1) which could sense CN^- with specific selectivity and high sensitivity in aqueous solutions. In addition, these sensors were synthesized

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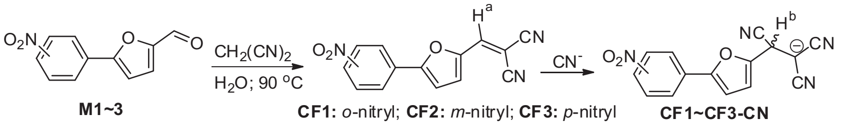

Scheme 1. The green synthesis of **CF1**–**CF3** and the CN^- sensing mechanism.

via a simple, efficient, and environmentally friendly route in pure water without using any catalyst.

The strategies for the design of these sensors are as follows. Firstly, we introduced the nitrophenyl furan moiety as the signal groups to achieve 'naked-eye' colorimetric and fluorimetric recognition. It is noteworthy that the nitrophenyl furan moiety has seldom been utilized as the signal group for chemosensors. However, this moiety possesses the dual-channel response ability for chemical stimulation. In this moiety, the nitro group is a chromophore and the phenyl furan group is a fluorophore. Moreover, the nitro group is an electron-withdrawing group, which could strengthen the sensitivity of the nucleophilic addition reaction. Secondly, in order to achieve the instantaneous detection of cyanide, a dicyanovinyl group was introduced as the binding site. According to literatures,[9d,f] vinyl-substituted derivates display both selective and sensitive responses to various concentrations of the cyanide anion. Additionally, the dicyano substitution on the vinyl group could significantly enhance the sensitivity of the nucleophilic addition reaction between the vinyl group and CN^-. Finally, the sensors were designed to be easily synthesized via a green chemistry method. In order to estimate the effect of the signal group on the sensor's colorimetric and fluorimetric sensing abilities for CN^-, the *o*, *m*, and *p*-nitro substituted compounds were synthesized respectively.

Sensors **CF1**–**CF3** were synthesized by the Knöevenagel reaction as depicted in Scheme 1.[11] Usually, the Knöevenagel reaction is carried out in dipolar aprotic solvents like DMF or CH_3CN and catalyzed by bases such as piperidine, or sodium hydroxide.[9d] We, however, attempt to synthesize the sensors **CF1**–**CF3** in pure water under the catalyst free condition to avoid the use of organic solvents and catalyst and prevent environmental contamination. It is exciting that 5-nitrophenylfuran-2-carbaldehydes (**M1**–**M3**) could carry out the Knöevenagel reaction with malononitrile in pure water without using any catalyst to give 5-(nitrophenyl)-2-dicyanovinyl-furan (**CF1**–**CF3**) with high yields. These compounds are characterized by ^1H NMR, ^{13}C NMR, IR, EA, and MS, the single crystal structure of **CF2** also confirmed the synthesis results (Fig. 1, CCDC 924675). This is an excellent green chemistry method for the preparation of these kinds of fine chemicals.

In order to investigate the CN^- recognition abilities of the sensors **CF1**–**CF3** in aqueous solution, we carried out a series of Host–Guest recognition experiments. The colorimetric and fluorimetric sensing abilities were primarily investigated by adding pure water solution of various anions to the DMSO/H_2O (7/3, v/v; pH 7.0) solutions of sensor **CF3** respectively. As shown in Figure 2a, the sensor immediately responded with dramatic color changes from yellow-green to pale pink when water solution of CN^- was added to the solution of **CF3** in room temperature. In the corresponding UV–vis spectra, the absorption peak at 410 nm decreased and shifted to 358 nm. However, as shown in Figure 2b, a green fluorescence with one emission band centered at 510 nm appeared when the solution of sensor **CF3** was excited at 437 nm. Upon addition of water solution of CN^-, the fluorescence color instantly changed from green to orange and the emission band decreased remarkably and shifted to 536 nm. However, when water solutions of other anions F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, N_3^-, SCN^-, NO_3^- and ClO_4^- were added to the solution of sensor **CF3** respectively, neither significant color nor fluorescence changes were observed. It was confirmed that **CF3** could selectively dual-channel instantly detect CN^- in DMSO/H_2O binary solution.

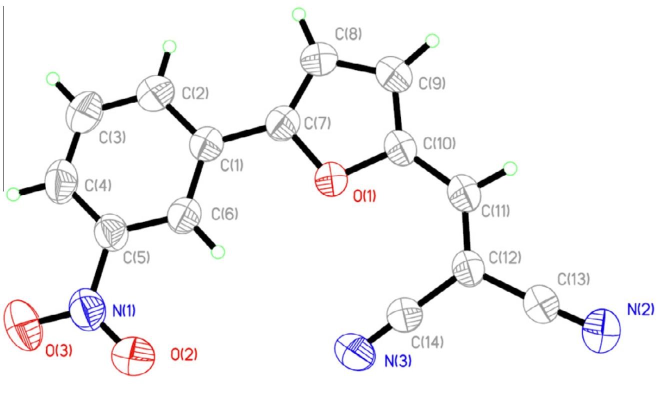

Figure 1. Single crystal structure of **CF2**.

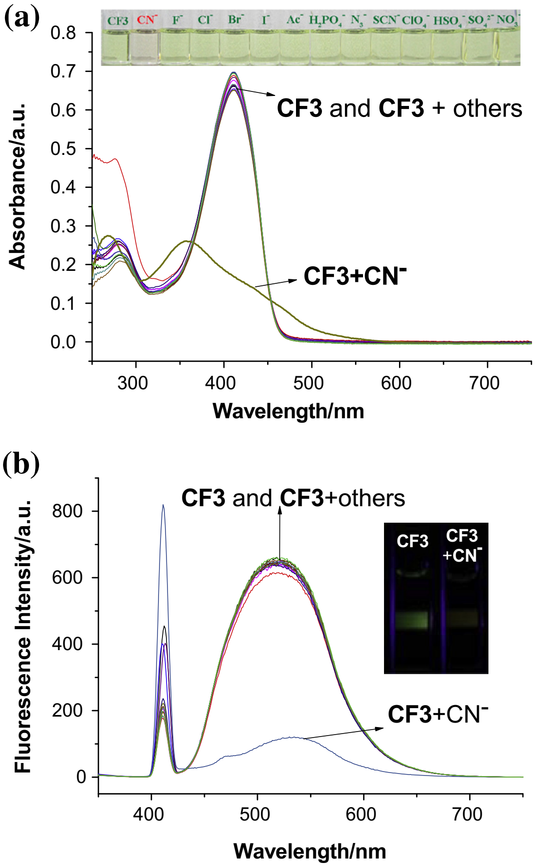

Figure 2. (a) UV–vis spectra of **CF3** with various anions in DMSO/H_2O (7/3, v/v; pH = 7.0) solutions. Inset: color changes of **CF3** with various anions; (b) fluorescence responses of **CF3** with various anions in DMSO/H_2O solution (λ_{ex} = 437 nm). Inset: Fluorescent photograph of **CF3** and **CF3** + CN^-. Concentration of **CF3**: 2.0×10^5 M; CN^-: 1×10^3 M.

The same tests were applied to **CF2** and **CF1**. In this case, when water solution of CN^- was added to the DMSO/H_2O solution of **CF2** and **CF1**, respectively, the colors of the solutions changed from yellow–green to pale pink. In corresponding UV–vis spectra, the absorption peaks at 396 nm (for **CF2**) and 383 nm (for **CF1**) decreased (Fig. S1 in the Supplementary data). While other anions could not cause such color and spectra changes, therefore, the **CF2** and **CF1** could colorimetrically detect CN^- selectively. However, in the corresponding fluorescence spectra of **CF2** and **CF1**, the *meta* or *ortho* position of the phenyl groups of **CF2** and **CF1** is substituted respectively by the nitro group, therefore the fluorescent intensities of **CF2** and **CF1** are very weak (Fig. S2 in the Supplementary data). The addition of CN^- caused very slight responses in the fluorescence emission intensity, which indicated that **CF2** or **CF1** could not fluorescently sense CN^-.

Because **CF3** has properties of dual-channel specific selectivity for CN^-, a series of experiments were carried out to investigate the CN^- recognition capability and mechanism of **CF3**. To gain an insight into the stoichiometry of the CN^-–**CF3** addition reaction, the method of UV–vis titration was used. As shown in Figure 3, upon addition of 1 equiv of cyanide, the UV–vis absorbance of the solution at 410 nm experiences a ca. 4.2-fold (A_0/A) decrease in a manner, that is, inversely proportional and 1:1 stoichiometrically related to the cyanide concentration.

An important feature of the sensor is its specific selectivity toward the analyte over other competitive species. The variations of UV–vis absorbance, fluorescence, and visual color changes of sensor **CF3** in DMSO/H_2O binary solutions caused by the anions F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, CN^-, N_3^-, SCN^-, NO_3^-, and ClO_4^-, were recorded in Figure 4 and Figure S3 in the Supplementary data. It is noticeable that the miscellaneous competitive anions did not lead to any significant interference. In the presence of these ions, the CN^- still produced similar color and optical spectral changes. These results showed that the selectivity of sensor **CF3** toward CN^- was not affected by the presence of other anions.

The colorimetric and fluorimetric detection limits of sensor **CF3** for CN^- were also tested. As shown in Figure 3, with the gradual addition of CN^-, a sharp decrease in the absorbance at 410 nm and an obvious increase in the absorbance at 480 nm were observed. Simultaneously, the ratio of A480/A410 rises along with the increase in CN^- concentrations, which allows the CN^- concentration to be determined ratiometrically. The detection limit using visual color changes (Fig. 5a) was a concentration of 1.0×10^{-7} M (0.1 μM) while the detection limit of the fluorescence spectra changes calculated on the basis of $3s_B/S$[12] was 1.0×10^{-8} M (0.01 μM) for CN^- anion, which is far lower than the WHO guideline of 1.9 μM cyanide.

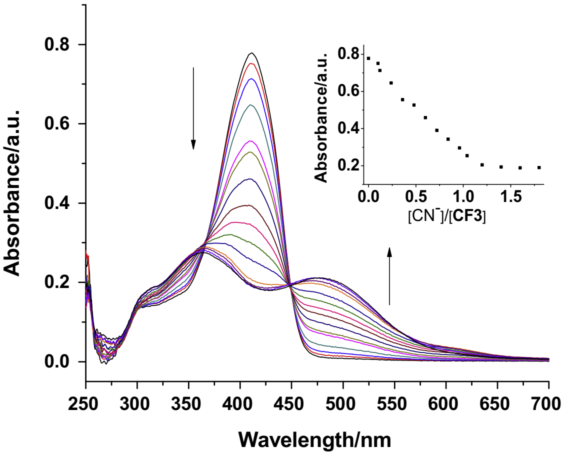

Figure 3. UV–vis titration spectra of **CF3** (20 μM in DMSO/H_2O) upon the addition of CN^- water solution. $[CN^-]$ = 0, 2, 2.4, 4.8, 7.2, 9.6, 12, 14.4, 16.8, 19.2, 20.8, 24, 28, 32, 36 μM. Inset: Plot of absorbance at 410 nm versus number of equivalents of CN^-.

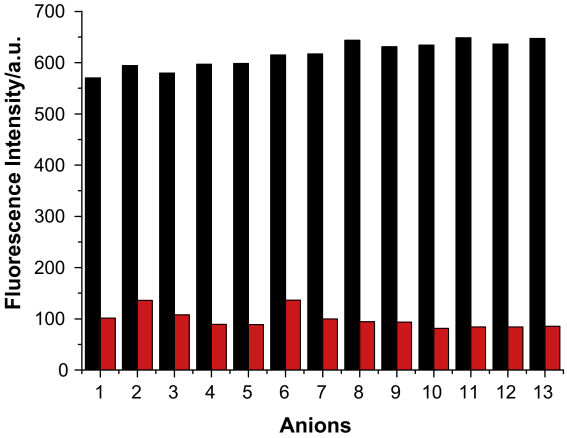

Figure 4. Selectivity of **CF3**. The black bars represent the fluorescence intensity of **CF3** in the presence of other anions (1 mM). The red bars represent the fluorescence intensity that occurs upon the subsequent addition of 1 mM of CN^- to the above solution. From 1 to 13: none, F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^{-}{}^{-}$, HSO_4^-, ClO_4^-, N_3^-, SO_4^{2-} and NO_3^-, SCN^-.

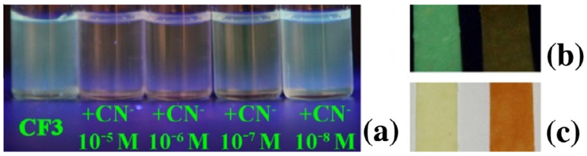

Figure 5. (a) Color changes observed upon the addition of various concentrations of CN^- water solution to the solutions of **CF3** in DMSO/H_2O (v/v, 7/3); (b) photographs of test strips of **CF3** and **CF3** + CN^- under an UV lamp at 360 nm; (c) under nature light.

To investigate the practical application of chemosensor **CF3**, test strips were prepared by immersing filter papers into a DMSO solution of **CF3** (0.1 M) and then drying in the air. The test strips containing **CF3** were utilized to sense different anions. As shown in Figure 5b and c, the obvious color and fluorescence changes were observed only with CN^- water solution when different anion solutions were added to the test kits respectively. Therefore, the test strips could conveniently detect CN^- in water solutions.

The further **CF3**–CN^- reaction mechanism was observed from ^1H NMR titration experiments (Fig. S4 in the Supplementary data) in DMSO-d_6/D_2O. It was obvious that the resonance signal corresponding to the vinyl proton (H^a) at 8.39 ppm completely disappeared, whereas a new signal grew at 6.30 ppm corresponding to the α-proton (H^b). Meanwhile, the furan protons and aromatic protons displayed upfield shift compared to those of **CF3** due to the breaking of the conjugation. These observations obviously indicated that the cyanide anion was added to the vinyl group.

The results of EI-MS experiments also support this presumption. In the EI-MS spectra of **CF3**, the $[\mathbf{CF3} + H]^+$ peak appeared at 266.2 (m/z_{calcd} = 266.1). However, when 1 equiv of CN^- was added to the solution of **CF3**, the $[\mathbf{CF3} + H]^+$ peak at 266.2 disappeared and a new peak appeared at 291.2, coinciding well with that for the species $[\mathbf{CF3} + CN^-]$ (m/z_{calcd} = 291.1) and indicating the formation of the stabilized anionic species **CF3**–CN^-.

In summary, an easy-to-make CN^- sensor **CF3** was designed and synthesized via a green chemistry method. This sensor could dual-channel instantly detects CN^- in water solutions at room temperature. The investigation of the recognition mechanism indicated that the sensor **CF3** recognized CN^- by a nucleophilic addition reaction. The coexistence of other anions did not interfere with the CN^- recognition process. Moreover, the detection limit of the sensor **CF3** toward CN^- was 1.0×10^{-8} M (10 nM), which indicated that the sensor **CF3** may be useful as a chemosensor for monitoring CN^- levels in physiological and environmental systems. In addition, test strips based on **CF3** were fabricated, which also exhibit a good selectivity to CN^- as in solution. We believe the test strips could act as a convenient and efficient CN^- test kit.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.07.022. These data include MOL files and InChiKeys of the most important compounds described in this article.

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11. General procedure for the synthesis of **CF1**–**CF3**: 5-(4-nitrophenyl)furan-2-carbaldehydes (2.17 g, 10 mmol) (M3) and malononitrile (0.66 g, 10 mmol) were combined in 30 mL pure water. The solution was stirred under 90 °C for 2 h, after cooling to room temperature, the yellow precipitate was filtrated, washed with 75% ethanol three times, then recrystallized in ethanol to get yellow powdery product **CF3** (2.35 g, 8.9 mmol) 89% yield. The other compounds **CF1** and **CF2** were prepared by the similar procedure.
    CF1: yield: 75%; mp 155–156 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 8.32 (d, J = 2 Hz, 1H, HC = N), 8.07–8.10 (m, 1H, Ph), 7.95–7.98 (m, 1H, Ph), 7.86–7.91 (m, 1H, Ph), 7.75–7.80 (m, 1H, Ph), 7.56–7.58 (m, 1H, Furan), 7.22–7.23 (m, 1H, Furan); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C 155.26, 149.12, 147.81, 144.12, 133.90, 132.11, 130.77, 127.85, 125.47, 122.12, 114.98, 114.68, 113.73, 76.18; IR (KBr, cm^{-1}) ν: 2222 (CN); Anal. Calcd for $C_{14}H_7N_3O_3$: C, 63.40; H, 2.66; N, 15.84. Found: C, 63.45; H, 2.62; N, 15.78. ESI-MS: Calcd for $C_{14}H_8N_3O_3$ $[M+H]^+$ 266.1; Found 266.2.
    CF2: yield: 87%; mp 240–241 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 8.67 (d, J = 2.0 Hz, 1H, Ph), 8.33 (d, J = 1.6 Hz, 1H, HC = N), 8.27–8.29 (m, 2H, Ph), 7.81–7.85 (m, 1H, Ph), 7.71–7.72 (m, 1H, Furan), 7.56–7.57 (m, 1H, Furan); ^{13}C NMR (DMSO-d_6, 100 MHz) δC 157.73, 149.02, 148.64, 143.96, 131.50, 131.43, 130.02, 128.53, 124.94, 120.02, 115.13, 114.48, 113.08, 75.61; IR (KBr, cm^{-1}) ν: 2222 (CN); Anal. Calcd for $C_{14}H_7N_3O_3$: C, 63.40; H, 2.66; N, 15.84. Found: C, 63.44; H, 2.69; N, 15.90. ESI-MS: calcd for $C_{14}H_8N_3O_3$ $[M+H]^+$ 266.1; Found 266.2.
    CF3: yield: 89.5%; mp 219–221 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 8.42 (d, J = 2.8 Hz, 1H, Ph), 8.39 (d, J = 2.0 Hz, 1H, HC = N), 8.37 (d, J = 2.8 Hz, 1H, Ph), 8.12–8.16 (m, 2H, Ph), 7.74–7.75 (m, 1H, Furan), 7.59–7.61 (m, 1H, Furan); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C 157.64, 149.26, 148.23, 144.06, 134.12, 128.46, 126.46, 125.16, 115.03, 114.38, 76.23; IR (KBr, cm^{-1}) ν: 2220 (CN); Anal. Calcd for $C_{14}H_7N_3O_3$: C, 63.40; H, 2.66; N, 15.84. Found: C, 63.47; H, 2.62; N, 15.81. ESI-MS: Calcd for $C_{14}H_8N_3O_3$ $[M+H]^+$ 266.1; Found 266.2.
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