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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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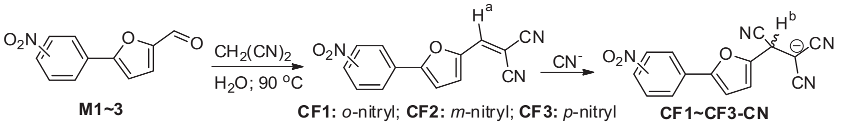

Scheme 1. The green synthesis of **CF1**–**CF3** and the CN^- sensing mechanism.

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.

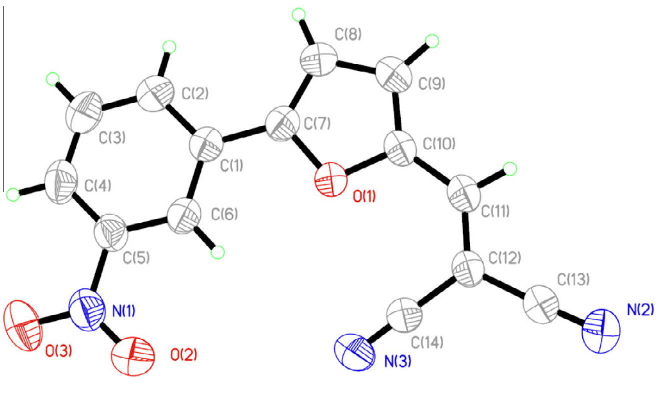

Figure 1. Single crystal structure of **CF2**.

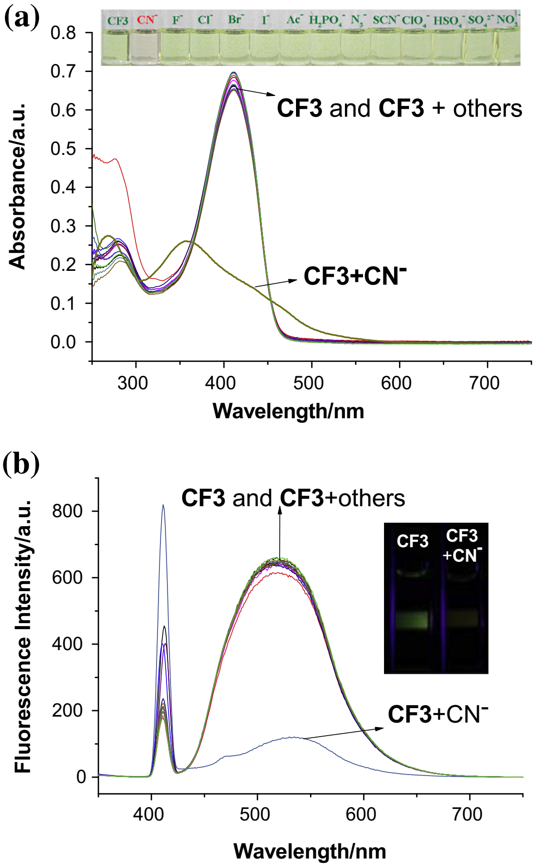

Figure 2. (a) UV–vis spectra of **CF3** with various anions in DMSO/H_2O (7/3, v/v; pH = 7.0) solutions. Inset: color changes of **CF3** with various anions; (b) fluorescence responses of **CF3** with various anions in DMSO/H_2O solution (λ_{ex} = 437 nm). Inset: Fluorescent photograph of **CF3** and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