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A Fluorescence Turn-on Detection of Cyanide in Aqueous Solution Based on the Aggregation-Induced Emission

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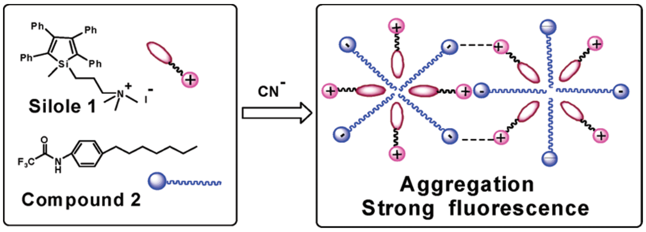
ABSTRACT



The nucleophilic addition of cyanide to the trifluoroacetylamino group in 2 yields an amphiphilic species which would induce the aggregation of silole 1, and as a result, the fluorescence of the ensemble increases largely. Accordingly, a fluorescence turn-on detection of cyanide in aqueous solution can be established with the ensemble of silole 1 and compound 2. Also, this ensemble displays good selectivity toward cyanide over other common inorganic anions.

Cyanide binds to the ferric form of cytochrome-c and inhibits the mitochondrial electron-transport chain.[1] For this reason, cyanide is one of the most toxic anions and harmful to human health and the environment. A large proportion of fatalities among fire victims is due to cyanide poisoning, as blood cyanide concentrations reach a level of 23−26 μM.[2] Furthermore, cyanide concentrations in drinking water have been required to be lower than 1.9 μM.[3] However, the use of cyanide salts remains widespread, particularly in gold mining, electroplating, and metallurgy.[4] Also, cyanide salts have been widely applied in the production of organic chemicals and polymers including nitriles, nylon, and acrylic plastics.[5] Despite the increasing level of monitoring and strict control, accidental releases of cyanide into the environment do occur. Therefore, it is highly desirable to develop sensitive and selective chemical sensors for cyanide. By making use of the coordination ability and nucleophilic reactivity of cyanide, a number of chemical sensors for cyanide were developed.[6] For instance, Sessler et al. have recently described a selective cyanide indicator based on the benzyl cyanide reaction.[7] However, drawbacks exist for these cyanide sensors. These

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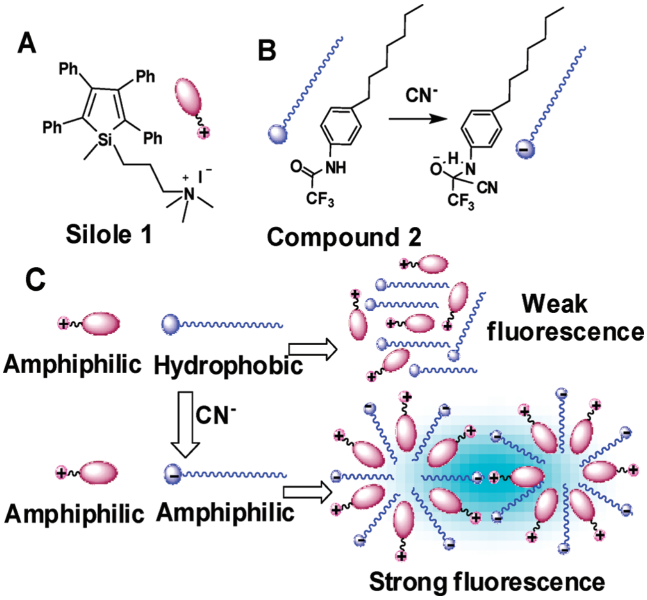
include poor selectivity,[8] particularly in the presence of fluoride or acetate, and the fact that the detection of cyanide cannot be performed in aqueous solution in some cases. Fluorescent probes for cyanide were reported,[9] but fluorescence turn-on detection still remains rare. Thus, there remains a need for improved sensing ensembles for cyanide. In this paper, we will report a fluorescence turn-on sensing ensemble for cyanide in aqueous solution by making use of the aggregation-induced-emission (AIE) feature of silole (silacyclopentadiene) compounds.

It is known that silole derivatives are weakly fluorescent in solution but become highly fluorescent after aggregation. This intriguing phenomenon was referred to as aggregation-induced enhanced emission (AIE) first reported by Tang, Zhu, and their co-workers in 2001.[10] Chemo-/biosensors have been reported on the basis of the AIE features of silole and relevant compounds.[11] We have recently established a fluorescence turn-on detection of heparin in serum,[12] DNA and label-free fluorescence nuclease assay,[13] and continuous on-site label-free ATP fluorometric assay[14] by taking advantage of the AIE feature of silole compounds. The present sensing ensemble toward cyanide contains silole **1** and compound **2** with a trifluoroacetylamino group. The design rationale is illustrated in Scheme 1 and is explained as follows: (1) silole **1** with a positive ammonium group shows weak fluorescence in aqueous solution but in the presence of an amphiphilic compound with a negatively charged group aggregation would occur due to the intermolecular electrostatic and hydrophobic interactions schematically shown in Scheme 1;[15] (2) cyanide can easily react with the trifluoroacetylamino group[16] in compound **2**, leading to formation of an amphiphilic compound with a negative headgroup. As a result, it is anticipated that coaggregation of silole **1** and compound **2** would occur in aqueous solution after addition of cyanide, and accordingly, the fluorescence of silole **1** would increase. The results show that a fluorescence turn-on detection of cyanide in aqueous solution can be established with the ensemble of silole **1** and compound **2**.

Scheme 1. (A) Chemical Structure of Silole **1** with an Ammonium Group; (B) Chemical Structure of Compound **2** and the Reaction with Cyanide; (C) Illustration of the Design Rationale for the Fluorescence Turn-on Detection of Cyanide by Making Use of the AIE Feature of Silole Compounds



Silole **1** was prepared according to a previous report.[13,17] Compound **2** was obtained simply by the reaction of 4-hexylanine with trifluoroacetic anhydride (see the Supporting Information). Silole **1** can be dissolved in pure water, and the solution exhibits rather weak fluorescence as expected. Compound **2** is not soluble in water, but it can be dissolved in DMSO. A clear solution of **1** (7.5×10^{-5} M) and **2** (4.0×10^{-4} M) in a mixture of DMSO and water

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(15) The critical micelle concentration (CMC) of **2** after reaction with ca. 1.0 equiv of CN$^-$ was estimated to be 0.35 mM. For the fluorescence measurements, the concentration of **2** was 0.4 mM. Therefore, it is probable that the reaction adduct of **2** with CN$^-$ forms micelles in aqueous solution and the hydrophobic part of **1** may enter into the hydrophobic core of the micelles. Moreover, such micelles may be further interconnected due to the electrostatic interactions between the ammonium group in **1** and anionic part of the reaction adduct.

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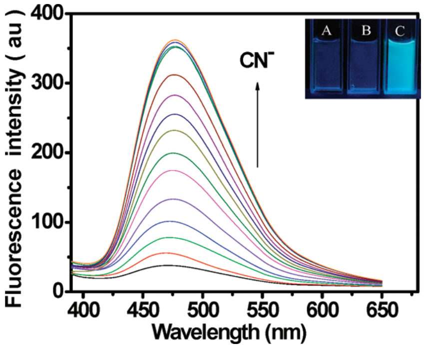

Figure 1. Fluorescence spectra ($\lambda_{ex} = 370$ nm) of the ensemble of silole **1** (7.5×10^{-5} M) and compound **2** (4.0×10^{-4} M) in DMSO/H_2O (1/75, v/v) in the presence of different concentrations of sodium cyanide (from 0 to 1.4×10^{-4} M) at room temperature. The solution was detected immediately when sodium cyanide was added at room temperature; the pH value was changed from 6.7 to 8.7 after addition of cyanide (1.2×10^{-4} M). Inset: photos of the solutions of silole **1** (A), mixture of silole **1** (7.5×10^{-5} M) and compound **2** (4.0×10^{-4} M) (B), and the mixed solution of silole **1** and compound **2** in the presence of 2.0 equiv of NaCN (C) under UV light (365 nm) illumination.

(1/75, v/v) was prepared for the following studies. The mixed solution of silole **1** and compound **2** shows negligible emission (see Figure 1). However, the fluorescence intensity of the solution increased gradually after addition of different amounts of NaCN as shown in Figure 1. For instance, the fluorescence intensity of the solution at 476 nm was enhanced 8 times after the concentration of cyanide in the solution reached 1.2×10^{-4} M. Indeed, such fluorescence enhancement after introducing cyanide to the solution can be distinguished by the naked eye as shown in the inset of Figure 1, where the photos of the aqueous solutions with and without addition of cyanide under UV light (365 nm) illumination are shown.

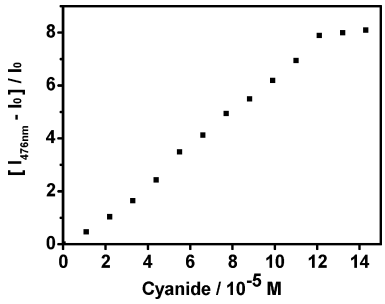

Figure 2. Plot of ($[I_{476} - I_0]/I_0$), where I_{476} and I_0 refer to the fluorescence intensity of the ensemble of silole **1** and compound **2** at 476 nm in the presence and absence of cyanide, respectively, vs the concentration of cyanide.

Figure 2 shows the plot of $[I_{476} - I_0]/I_0$, where I_0 refers to the fluorescence intensity at 476 nm before addition of cyanide vs the concentration of cyanide. Of interest, there is a nearly linear relation between $[I_{476} - I_0]/I_0$ and the concentration of cyanide ($y = 0.66283x - 0.28899$, $r = 0.99822$, $n = 12$). The detection limit of cyanide with the ensemble of silole **1** and compound **2** under these conditions was estimated to be 7.74 μM, which is lower than concentrations of cyanide in the blood of fire victims.

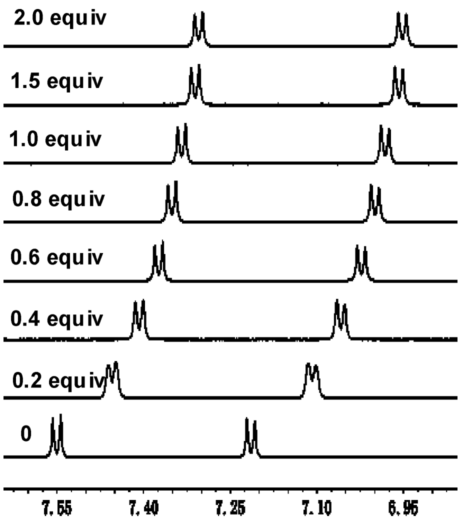

Figure 3. Partial ^1H NMR spectra of compound **2** (4.0×10^{-3} M) in DMSO-d_6/D_2O (5/1, v/v) in the presence of different amounts of NaCN.

The fluorescence enhancement after addition of cyanide to the mixture of silole **1** and compound **2** can be understood as follows: (1) addition of cyanide to the trifluoroacetylamino group in compound **2** leads to the formation of an amphiphilic compound with a negative headgroup (see Scheme 1); (2) coaggregation of silole **1** and the new amphiphilic compound generated from compound **2** would occur in aqueous solution[18] as schematically shown in Scheme 1, and as a result the fluorescence of silole **1** would be enhanced. Both ^1H NMR and dynamic light scattering (DLS) experiments support these assumptions. Figure 3 shows the partial ^1H NMR spectra of compound **2** in the presence of different amounts of cyanide. Clearly, the signals due to the aromatic protons were upfield shifted. The signals at 7.55 and 7.22 ppm were shifted to 7.34 and 6.98 ppm, respectively, when 1.0 equiv of cyanide was added. This is likely due to the transformation of the trifluoroacetylamino group in compound **2** into an anionic group in the presence of cyanide. But, the ^1H NMR signals kept almost unchanged if more than 1.0 equiv of cyanide was introduced to the solution. This implies the 1:1 reaction stoichiometry between compound **2** and cyanide, which is in agreement with the previous reports.[19] ^{13}C NMR, ^{19}F NMR, and mass spectroscopic data

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also supported the reaction of **2** with CN^- (see the Supporting Information).

A DLS signal corresponding to particles with sizes around 10 nm was detected for the solution of silole **1** and compound **2** in DMSO/H_2O (1/75, v/v). This is likely due to the self-aggregation of compound **2** because of its hydrophobic feature. However, the DLS measurement (see Figure S2, Supporting Information) indicated that aggregates with sizes around 100 nm were formed for the solution of silole **1** and compound **2** after addition of cyanide. As discussed above, the intermolecular hydrophobic and electrostatic interaction between silole **1** and the amphiphilic compound generated from compound **2** may induce the formation of such molecular aggregates.

In order to demonstrate the selectivity of the ensemble of silole **1** and compound **2** toward cyanide, fluorescence spectra of the ensemble in the presence of excess amounts of NaOAc, NaBr, NaCl, NaF, NaH_2PO_4, $NaHSO_4$, NaN_3, and $NaNO_3$ were recorded respectively (see Figure S1, Supporting Information). As shown in Figure 4, where the respective fluorescence intensities at 476 nm of the ensemble in the presence of 10.0 equiv NaCN and 1. equiv other salts are shown, significant fluorescence enhancement was detected only in the presence of cyanide. Therefore, it can be concluded that the ensemble of silole **1** and compound **2** can function as a selective chemosensor for cyanide. This may be understandable by considering the fact that cyanide is more nucleophilic reactive than other anions such as fluoride and acetate in aqueous solution.

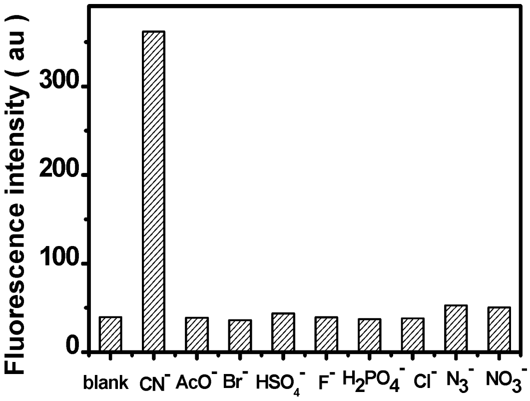

Figure 4. Variation of the fluorescence intensity at 476 nm for the ensemble of silole **1** (7.5×10^{-5} M) and compound **2** (4.0×10^{-4} M) in DMSO/H_2O (1/75, v/v) after addition of 1.0 equiv of cyanide and 10 equiv of $CN^-/AcO^-/Br^-/Cl^-/F^-/ H_2PO_4^-/HSO_4^-/N_3^-/NO_3^-$.

In summary, we have successfully established a selective and relatively sensitive chemosensor for cyanide by making use of the AIE feature of silole compounds and high nucleophilic reactivity of cyanide in aqueous solution. It should be noted that the present sensing ensemble for cyanide has the following advantages: (1) it is a fluorescence turn-on sensor; (2) the detection can be carried out in aqueous solution; (3) silole **1** and compound **2** are easily accessible. The present investigation provides a good avenue for sensing cyanide, and further optimization of the ensemble, in particular the structure of compound **2**, is in progress with the aim of improving the sensitivity toward cyanide.

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Supporting Information Available: Synthesis and characterization data of compound **2**; DLS data for the ensemble of **1** and **2** in the absence and presence of cyanide; isothermal titration microcalorimetry (ITC), ESI-mass, and NMR spectral studies of **2** after reaction with CN^-. This material is available free of charge via the Internet at http://pubs.acs.org.

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