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Chromogenic Chemodosimeter for Highly Selective Detection of Cyanide in Water and Blood Plasma Based on Si–O Cleavage in the Micellar System

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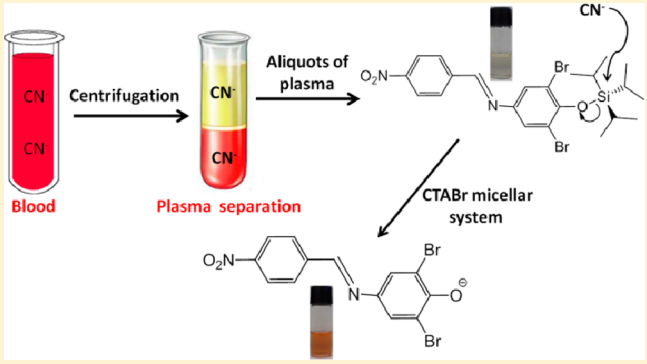
Supporting Information

ABSTRACT: A novel silylated imine was designed to act efficiently in a chemodosimeter approach for the selective detection of cyanide in an aqueous micellar CTABr solution. This simple system allows the detection of cyanide, with high sensitivity and specific selectivity, in water and in human blood plasma.



The recognition and detection of anionic analytes is a field which is attracting increasing interest due to the importance of these species in biological, industrial, and chemical processes.[1−12] A notable example of such anions is cyanide (CN^-), given its widespread use in various industrial activities, such as metallurgy, mining, and the fabrication of polymers.[13] CN^- is lethal in very small concentrations because it binds strongly to the active site of cytochrome-oxidase, causing a decrease in the oxidative metabolism.[14] This anion is delivered through hydrolysis from some fruit seeds, and roots,[15−17] and some neurotoxic compounds used in warfare release CN^- through hydrolysis.[18] Thus, many chromogenic and fluorogenic chemosensors have been designed for CN^-.[19−25] The fact that CN^- is commonly present in aqueous systems leads to the need to develop strategies to allow the naked-eye and quantitative detection of this anion in water.

Among the strategies applied to the detection of anions,[26,27] the chemodosimeter approach, based on the strong affinity between F^- and silicon, has been investigated by many research groups.[28,29] Many studies in aqueous solvents have been developed for detection of F^-,[29−38] but long detection time is required, due to the fact that the nucleophilicity of F^- is reduced in the presence of water due to its high hydration energy.[39] Tang et al. have developed a fluorogenic chemodosimeter for the highly selective detection of F^- in aqueous solution and living cells, which is based on probes having a quaternary ammonium moiety on their molecular structure.[30] In addition, no reports are found in the literature regarding the use of the cleavage of the Si–O bond to design chemodosimeters for the detection of CN^- in organic and aqueous solutions. Thus, we considered the possibility of developing chemodosimeters based on Si–O group with a good leaving group in their molecular structure, since this could be of importance in obtaining systems able to react with CN^-. In addition, the solubilization of these systems in water could be improved, in principle, with the use of surfactants.[40,41] Few studies in which surfactants were employed to solubilize optical detection systems in order to use them in water for the detection of anionic species are reported in the literature.[42−49]

Herein, we report a simple, efficient, and low cost strategy for the detection of CN^-, which is based on the use of 3,5-dibromo-*N*-(4-nitrobenzylidene)-4-[(triisopropylsilyl)oxy]aniline (compound **1**) in an aqueous cetyltrimethylammonium bromide (CTABr) solution, in order to provide an anionic detection device exhibiting as the main properties high sensitivity and specific selectivity for CN^- in water.

The synthesis of compound **1** is described in Scheme 1. First, 4-nitrophenol was brominated using *N*-bromosuccinimide (NBS) and 4-toluenesulfonic acid (TsOH) in aqueous KBr solution. Compound **2** was generated, which was reduced in the presence of tin(II) chloride to yield 4-amino-2,6-dibromophenol (**3**). The silylation of the latter with triisopropylsilyl chloride (TIPS-Cl) and imidazole in DMF yielded 3,5-dibromo-4-[(triisopropylsilyl)oxy]aniline (compound **4**), which was reacted with 4-nitrobenzaldehyde to form the imine **1**. 2,6-Dibromo-4-[(4-nitrobenzylidene)amino]-phenol (compound **5a**) was also synthesized through the condensation of compound **3** with 4-nitrobenzaldehyde. The

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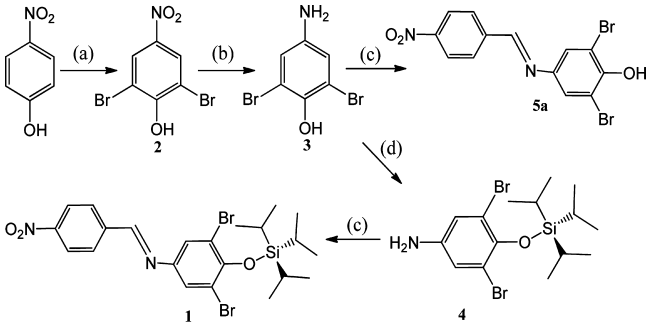
Scheme 1. Synthetic Route to Obtaining the Chemodosimeter 1[a]



[a](a) KBr, *p*-TsOH, NBS, H_2O, 40 °C; (b) $SnCl_2$, EtOH, reflux, 8 h; (c) 4-nitrobenzaldehyde, AcOH (one drop), EtOH; (d) imidazole, DMF, TIPS-Cl, 36 °C, 8 h.

novel compounds **1**, **4**, and **5a** were fully characterized (see the Supporting Information).

Figure 1A shows the solutions of compound **1** in an aqueous solution of CTABr at pH 8.0 in the absence and presence of

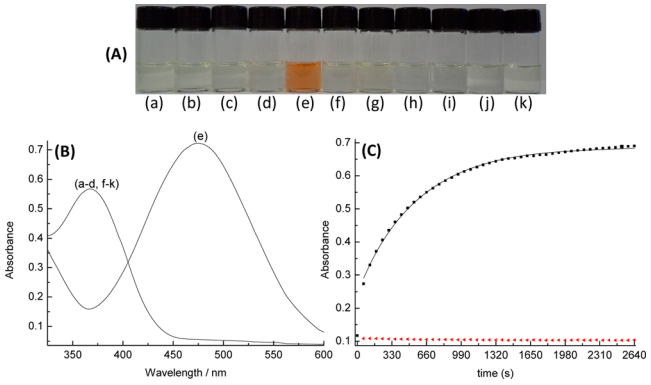
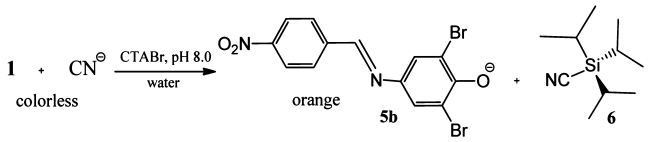


Figure 1. (A) Solutions and (B) UV–vis spectra of **1** in an aqueous CTABr micellar system in the absence (a) and in the presence of HSO_4^- (b), $H_2PO_4^-$ (c), NO_3^- (d), CN^- (e), CH_3COO^- (f), F^- (g), Cl^- (h), Br^- (i), I^- (j), and sulfide (k). All spectra were made after 20 min from the addition of the anions. (C) Absorbance values of **1** as a function of the time at 25 °C in the presence of CN^- (red ▲; 428 nm) in water and (■; 474 nm) in aqueous CTABr micellar system. *c* (**1**) = 4.0×10^{-5} mol L^{-1}; *c* (CTABr) = 2.0×10^{-3} mol L^{-1}; *c* (anion) = 1.0×10^{-3} mol L^{-1}; pH = 8.0.

various anions as sodium or potassium salts, after a period time of 20 min. It was observed that the solutions turned orange only in the presence of CN^-. Experiments were performed to verify the influence of the pH on the rate of the reaction of **1** with CN^- (see the Supporting Information) and the best results were obtained at pH 8.0. This is due to the fact that at pH values below 8.0, CN^- is in its protonated form, since the pK_a of HCN in water is 9.21.[50] On the other hand, the rate constants are reduced at pH values above 8.0 due to the increase in the $c(OH^-)$ with the pH increase, and the interaction of hydroxide with the cationic groups in the CTABr[51] makes difficult the nucleophilic action of CN^- on the Si–O center. Figure 1B shows the UV–vis spectra for compound **1** and the product of the reaction of **1** with CN^- under the same experimental conditions. It was observed that the band of **1**, with a maximum at 368 nm, disappears with the addition of the anion, and another band at λ_{max} = 474 nm appears. Compound **5a** was solubilized under the same experimental conditions, and it was observed that the color and UV–vis spectrum of its solution were the same as those of the product of the reaction of compound **1** with CN^-. The pK_a of compound **5a** was estimated to be 7.37 (see the Supporting Information), indicating that under the experimental conditions of the assay the deprotonated form of **5a** (**5b**) is present and this is responsible for the color of the solution. In addition, the pK_a of **5a** was determined in an aqueous solution of CTABr. The value of 4.03 obtained shows that, as expected, the micellar system is responsible for a considerable increase in the acidity of **5b** and thus the compound is fully deprotonated under the experimental conditions applied.

According to the representation shown in Scheme 2, CN^- nucleophilically attacks the silicon center in the chemo-

Scheme 2. Proposed Reaction of the Chemodosimeter 1 with CN^-



dosimeter, releasing the colored **5b** species as the leaving group. The hydrolysis of the Si–CN bond in the product **6** could deliver CN^- and the anion could act as a catalyst reacting with more molecules of **1**. However, a ^1H NMR study demonstrated that **6** species is stable until 20 min in the conditions of the experiment. In addition, some experiments were performed using $c(CN^-)$ below the concentration of **1**, and in these experimental conditions only a fraction of the chemodosimeter undergoes reaction. Thus, these observations discard a possible catalytic action of the anion. The nucleophilic attack of CN^- on the C=N bond of imines represents the basis of some optical detection strategies for this anion.[52−54] Data obtained from UV–vis and ^1H NMR spectra discarded this possibility. It was also observed that the final UV–vis spectra of the reaction of **1** with CN^- after 20 min coincided with the UV–vis spectrum of **5b** at the same experimental conditions, discarding the hydrolysis of the C=N bond of compound **1**.

Figure 1C shows the behavior of compound **1** in the presence of CN^- at pH 8.0 in water and in the aqueous micellar medium. While the system did not react in water, a rapid reaction occurred in the micellar medium (k_{obs} = 1.78×10^{-3} s^{-1}; $t_{1/2}$ = 389 s). We observed in the course of the studies that compound **5b** is a solvatochromic probe (Figure 2A), i.e., it has a band in the visible region, and its position changes depending on the polarity of the medium.[55] UV–vis spectra were made of dye **5b** in various solvents (Figure 2B). In dimethyl sulfoxide (DMSO), the solvatochromic band of **5b** has a maximum at 540 nm, which is hypsochromically shifted to 472 nm in ethanol and to 428 nm in water (Table 1). The UV–vis spectrum for **5b** in the aqueous CTABr micellar system shows that the compound has a maximum at 474 nm, suggesting that the microenvironment of the dye is similar to that in ethanol, very different from water. These data show that the reaction of CN^- with **1** is made possible in micellar medium due to the fact that the compound is protected from water in the interior of the CTABr micelles, enabling the anion to act efficiently as a nucleophile.

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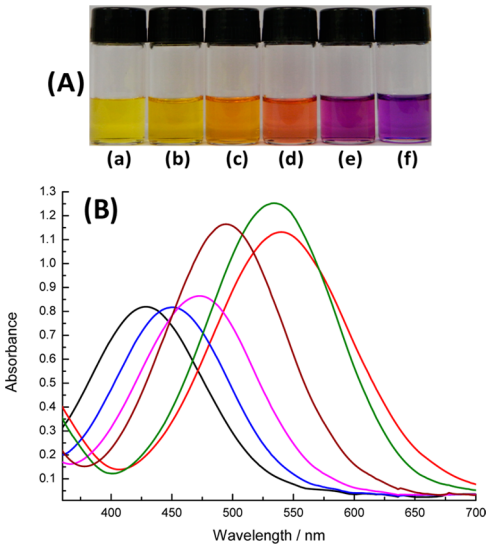

Figure 2. (A) Solutions of **5b** in water (a), methanol (b), ethanol (c), propan-2-ol (d), tetrahydrofuran (e), and DMSO (f). (B) UV–vis spectra of **5b**, measured in water (black), methanol (blue), ethanol (pink), propan-2-ol (brown), tetrahydrofuran (green), and DMSO (red).

Table 1. Maximum Wavelength Values of 5b in Six Pure Solvents at 25 °C

solvent	λ_{max}/nm
water	428
methanol	452
ethanol	472
propan-2-ol	494
tetrahydrofuran	534
DMSO	540

Figure 3 shows the influence of the time on the reactivity of compound **1** in aqueous CTABr micellar medium in the

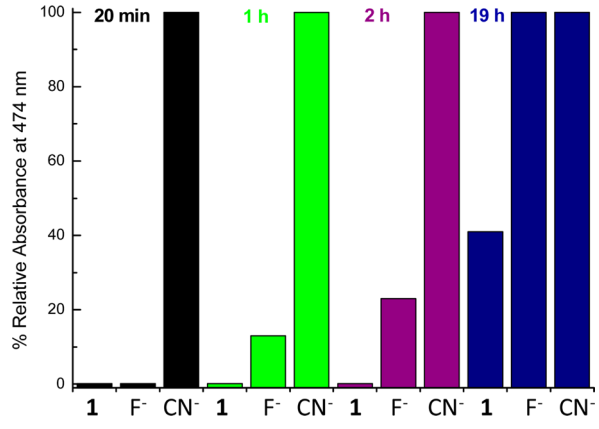

Figure 3. Relative absorbance at 474 nm for **1** in the absence and in the presence of F^- and CN^- after 20 min (black), 1 h (green), 2 h (purple), and 19 h (blue) of reaction.

absence and in the presence of NaF and KCN. Data show that after 20 min of reaction, **1** reacted completely with CN^- while the system with F^- did not show any alteration. Compound **1** reacts very slowly with F^-: after 1 and 2 h, 13 and 23% of the total amount of the chemodosimeter reacted, while 100% of reaction occurred after 19 h. However, the formation of **5b** receives contribution of the hydrolysis reaction: after 2 h compound **1** slowly undergoes hydrolysis and 47% of the total amount of **1** reacted after 19 h.

Figure 4A shows the UV–vis spectra for the addition of increasing amounts of CN^- to the solution of **1** in aqueous

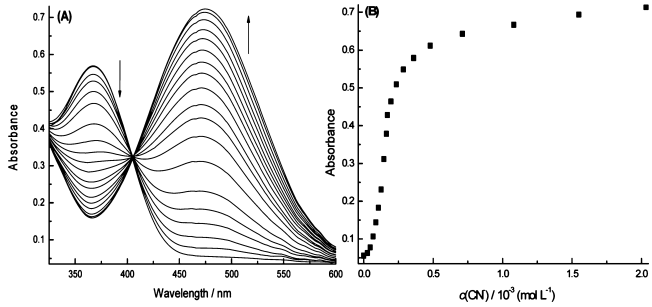

Figure 4. (A) Influence of addition of increasing amounts of CN^- on the UV–vis spectra of **1** (4.0×10^{-5} mol L^{-1}) in aqueous CTABr (2.0×10^{-3} mol L^{-1}) micellar system at pH 8.0 and 25 °C. (B) Curve of the variation in the absorbance at 474 nm of **1** with the addition of increasing amounts of CN^-. The final concentration of CN^- was 2.0×10^{-3} mol L^{-1}.

CTABr solution (pH = 8.0). On the addition of the anion, the intensity of the band corresponding to **1**, with a maximum at 368 nm, decreases simultaneously with the appearance of another band with maximum at 474 nm, related to product **5b**. An isosbestic point was also observed at 405 nm, suggesting equilibrium between the two species in solution. The absorbance values for each anion addition were collected at 474.0 nm, resulting in the titration curve presented in Figure 4B. The addition of CN^- caused a fast Si–O bond cleavage in compound **1** until a plateau was reached. A comparison of the final spectrum for the titration with the UV–vis spectrum for compound **5b** at the same concentration as that of **1** and under the same experimental conditions reveals that the reaction yield is 100%. The detection and quantification limits were calculated as 1.48×10^{-5} and 4.93×10^{-5} mol L^{-1}, respectively.

The lethal dose of CN^- in human blood plasma varies between 9×10^{-5} and 1.15×10^{-4} mol L^{-1},[56–58] which suggests that the system presented here could be used for the detection of CN^- in human blood plasma. It is important to emphasize that few studies can be found in the literature involving the use of optical chemosensors for the detection of CN^- in blood plasma[59–61] and whole blood.[62,63] Thus, an experiment was performed to verify the potential of **1** for application to address this issue. First, CN^- was added to human blood (see the Supporting Information), which was then centrifuged to separate the plasma. Subsequently, a solution of **1** in the aqueous CTABr micellar solution was added to the plasma. Figure 5A shows the UV–vis spectra for **1** in the absence and in the presence of blood plasma, without CN^- added, and it can be observed that no changes occurred. However, for the systems with CN^- added, the UV–vis spectra showed the appearance of a visible band with a maximum at 474 nm, indicating that the CN^- was in a concentration sufficient to react with **1**, generating **5b**. The absorbances were read at 474 nm, and the data used to construct the titration curve in Figure 4B indicated concentrations of CN^- in the blood plasma of 9.71×10^{-5}, 1.69×10^{-4}, and 2.89×10^{-4} mol L^{-1} (Figure 5B).

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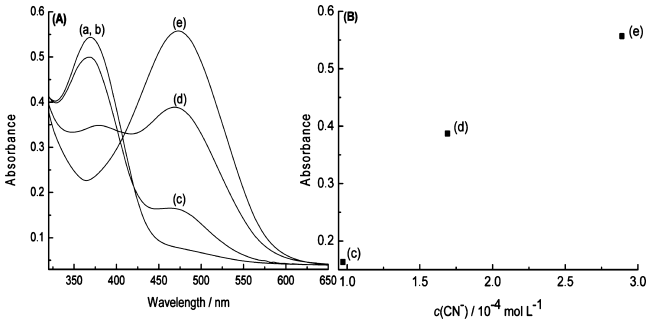

Figure 5. (A) UV–vis spectra of **1** (4.0×10^{-5} mol L^{-1}) in the absence (a) and in the presence of blood plasma without CN^- (b) and with CN^- at concentrations of (c) 9.71×10^{-5} mol L^{-1}, (d) 1.69×10^{-4} mol L^{-1}, and (e) 2.89×10^{-4} mol L^{-1}. (B) Absorbance values at 474 nm of **1** versus different detected concentrations of CN^- in plasma aliquots. All solutions were prepared in an aqueous CTABr (2.0×10^{-3} mol L^{-1}) micellar system at pH 8.0, and the spectra were obtained at 25 °C after 20 min of reaction.

In conclusion, a simple strategy was developed in this study, based on the chemodosimeter approach, for the highly selective detection of CN^- in aqueous solution. Compound **1** represents the first example of a chemodosimeter based on the oxygen–silicon bond breakage with CN^- as the nucleophile. The results reported herein open the way for the development of novel optical detection systems operating in water for the detection of CN^- and even for less nucleophilic anions, for instance, with the use of fluorescent probes in the synthesis of the chemodosimeter and/or improving the nature of the leaving group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, procedures, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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