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Colorimetric detection of cyanide with phenyl thiourea derivatives

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ABSTRACT

Three structurally simple thiourea derivatives **1–3** were prepared, and their chromogenic behaviors toward various anions were investigated in aqueous solution. Among them **1** showed good sensitivity and selectivity for cyanide ion and also can distinguish it from other anions by different color changes. Besides that, the receptor **1** has a sensitive detection limit (1.27 μ M) for cyanide ion accordingly it can be used as a colorimetric sensor for the determination of cyanide ion. The use of the test strip of sensor **1** to detect cyanide ion was also reported.

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1. Introduction

Anion recognition is an area of growing interest in supramolecular chemistry due to its important role in a wide range of environmental, chemical and biological applications. Recently, considerable research attention has been focused on the design of host molecules that can selectively recognize and sense anion species through visible, electrochemical and optical response [1–3]. Among the important anions, cyanide is of particular interest because it is a detrimental anion causing poisoning in biology and environment [4–6]. Despite its toxicity, its application in various areas as raw materials for synthetic fibers, resins, herbicides, and the gold-extraction process is inevitable [7], which releases cyanide into the environment as a toxic contaminant. Therefore, it is highly desirable to develop selective, sensitive and convenient assays for cyanide anion.

In recent years, many efforts have been devoted to design various chemosensors specific for cyanide detection [8–26]. The most attractive approach focuses on the research of novel colorimetric cyanide anion sensors, which allow naked eyes detection of the color change without resorting to the use of expensive instruments. Moreover, simple and easily synthesized colorimetric sensors that are cable of recognizing cyanide ion in aqueous environment may still a great challenge.

To date, many of the reported cyanide anion receptors have relied on hydrogen-bonding motifs and, as a consequence, have displayed poor selectivities in aqueous media [27–29]. To overcome this limitation, reaction-based receptors have been developed recently [30–41]. This reaction-based recognition mode takes

advantage of the particular feature of the cyanide ion: its good nucleophilic character, and little competition from the aqueous media. Based on this idea, nucleophilic addition of cyanide to oxazine [9,10], pyrylim [30], squarane [13], trifluoroacetophenone [31,32], acyltrazene [33], acridinium [34], salicylaldehyde [35,36], caboxamide [37,38], benzamide [39], fluorescein aldehyde [40], and benzyl [41] have been reported in recent few years. However, many receptors for cyanide reported so far have several limitations such as poor selectivity over F⁻ or AcO⁻, or utilization of expensive instruments, complicated synthesis, and many of receptors are reported to work only in organic media.

With these considerations in mind, we report herein three simple yet effective colorimetric sensors **1–3**. They utilize either a nitronaphthyl or a nitrophenyl or a trifluoromethylphenyl diazenylphenyl as a chromophore and a thiourea group as an electrophile. It is well known that cyanide is a strong nucleophililic reagent, and the nucleophilic attack to the carbon atom of an electron-deficient thiocarbonyl (C=S) group can achieve the so-called 'naked eye' detection of cyanide anion in aqueous medium.

2. Experimental

2.1. Reagents

Anions including F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, CN⁻, SCN⁻, AcO⁻ and $H_2PO_4^-$ are in the form of tetrabutylammonium salts. These anions were purchased from Sigma–Aldrich chemical company and stored in desiccators under vacuum containing self-indicating silica. Solvents were purified prior to use and stored under nitrogen. Dimethyl sulfoxide was dried with calcium hydride and distilled in reduced pressure. Unless stated otherwise, commercial grade chemicals were used without further purification.

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Scheme 1. The synthetic procedure for the receptors 1-3.

2.2. General methods

Unless otherwise specified, all of the UV–Vis titration experiments were carried out at 298 K. The ¹H NMR spectra were recorded on a Bruker 400 MHz and VARIAN INOVA 600 MHz spectrometer. UV–Vis spectra were performed on a Cary 300 spectrophotometer.

2.3. UV-Vis titration studies

The binding ability of the receptor **1** for anions (as tetrabutylammonium salts) was investigated by UV–Vis spectroscopy in DMSO/H₂O (6/4, v/v) solution using a constant host concentration $(1.0 \times 10^{-4} \text{ M})$ and increasing concentrations of anions. The change in absorbance at 506 nm for receptor was plotted against anion concentration and fitted by the equation as described by Connors [42].

2.4. ¹H NMR titrations

¹H NMR titration experiments were carried out in the DMSO- d_6 or DMSO- d_6/D_2O solution. A 10 mM solution of the receptor **1** in DMSO- d_6 or DMSO- d_6/D_2O was prepared. Then, the increased amount of cyanide anion was added to the above-mentioned solution and ¹H NMR of the host-guest system was tested.

2.5. Synthesis

2.5.1. Synthesis of N-(4-nitronaphthyl)-N'-phenylthiourea (1)

To a stirred solution of aniline (0.17 g, 1.77 mmol) in CH₂Cl₂ (50 mL), 4-nitronaphthyl isothiocyanate (0.41 g, 1.77 mmol) in CH₂Cl₂ (30 mL) was added at room temperature. The resulting mixture was stirred at room temperature for 18 h. The solution was then concentrated in vacuum. The solid product was recrystallized from ethanol to give **1** (0.45 g, 78%) as a yellow solid. Mp: 185–186 °C. $\lambda_{max}/nm (\varepsilon/M^{-1} cm^{-1}) 372 (5000)$. ¹H NMR (600 MHz, DMSO-*d*₆): δ 7.16 (t, 1H, *J*=7.8 Hz), 7.53 (t, 2H, *J*=7.2 Hz), 7.54 (d, 2H, *J*=7.8 Hz), 7.75-7.85 (m, 3H), 8.22 (d, 1H, *J*=8.4 Hz), 8.35 (d, 1H, *J*=8.4 Hz), 8.44 (d, 1H, *J*=9.0 Hz), 10.11 (s, 1H), 10.20 (s, 1H). ¹³C NMR (DMSO-*d*₆): 122.6, 122.8, 124.0, 124.1, 124.4, 125.9, 125.3, 127.4, 128.5, 129.6, 139.2, 141.5, 143.5, 181.0. FAB MS *m*/*z* = 323.0796 [M]⁺, calc. for C₁₇H₁₃O₂N₃S = 323.0808.

2.5.2. Synthesis of N-(4-nitrophthyl)-N'-phenylthiourea (2)

The preparation of **2** followed the above-mentioned procedure using aniline and 4-nitrophenyl isothiocyanate in the same molar ratios; yield: 0.39 g (80%); Mp: 145–146 °C. ¹H NMR (400 MHz,DMSO- d_6): δ 7.16 (t, 1H, *J*=7.2 Hz), 7.36 (t, 2H, *J*=7.6 Hz),

7.48 (d, 2H, J = 8.0 Hz), 7.82 (d, 2H, J = 8.8 Hz), 8.20 (d, 2H, J = 8.8 Hz), 10.28 (s, 1H), 10.38 (s, 1H). ¹³C NMR (DMSO- d_6):122.0, 124.2, 124.9, 125.5, 129.1, 139.5, 142.7, 146.7, 179.8. FAB MS m/z = 274.0648 [M+H]⁺, calc. for C₁₃H₁₂O₂N₃S = 274.0650.

2.5.3. Synthesis of N-(4-(4-trifluoromethyl)phenyldiazenyl phenyl)-N'-phenyl-thiourea (**3**)

The preparation of **3** followed the above-mentioned procedure using aniline and 4-trifluoromethylphenyldiazenylphenyl isothiocyanate in the same molar ratios; yield: 0.17g (24%); Mp: 184.5-185.2° C. ¹H NMR (400 MHz,DMSO-*d*₆): δ 7.14 (dd, 1H, *J* = 7.6, 7.2 Hz), 7.35 (dd, 2H, *J* = 7.6, 8.0 Hz), 7.50 (d, 2H, *J* = 8.0 Hz), 7.81 (d, 2H, *J* = 8.8 Hz), 7.93 (d, 2H, *J* = 8.8 Hz), 7.94 (d, 2H, *J* = 8.4 Hz), 8.02 (d, 2H, *J* = 8.4 Hz), 10.13 (s, 1H), 10.24 (s, 1H). ¹³C NMR (DMSO-*d*₆): 123.8, 124.2, 124.9, 126.0, 126.6, 127.9, 129.8, 131.5, 131.8, 140.4, 145.0, 149.0, 155.5, 180.5. FAB MS *m*/*z* = 401.1056 [M+H]⁺, calc. for C₂₀H₁₆N₄F₃S = 401.1045.

3. Results and discussion

Preparation of receptors **1–3** is depicted in Scheme 1. Reaction of aniline with 4-nitronaphthyl isothiocyanate or 4-nitrophenyl isothiocyanate or 4-trifluoromethylphenyldiazenylphenyl isothiocyanate afforded the corresponding receptors **1–3**, respectively. All of these compounds were characterized by ¹H NMR, ¹³C NMR and HRMS.

3.1. Anion binding studies

In order to gain systematic knowledge on the effect of water on the binding affinity and selectivity for cyanide, we chose DMSO/H₂O mixtures as solvents (9/1, 7/3, and 6/4 of DMSO/H₂O (v/v), respectively). The anions of interest, namely, F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, SCN⁻, AcO⁻, H₂PO₄⁻ and CN⁻ as their tetrabutylammonium salts were added to the solution of 1, respectively. The corresponding UV-Vis absorption spectra upon addition of different anions in DMSO/H₂O mixtures are shown in Fig. 1. In 9/1 DMSO/H₂O mixture, receptor 1 displayed an absorption band at 521 nm, and CN⁻, F⁻ and AcO⁻ showed significant effect to the band, whereas less basic anions such as Cl⁻, Br⁻, I⁻, NO₃⁻, SCN⁻, and H₂PO₄⁻ showed less or no effect to the band (Fig. 1a). In 7/3 DMSO/H₂O mixture, though only CN⁻, F⁻ and AcO⁻ showed obvious interaction with the receptor **1** (Fig. 1b), but the selectivity for CN⁻ was still affected by the interference of F⁻ and AcO⁻. While in 6/4 DMSO/H₂O mixture, a remarkably higher selectivity for CN⁻ over the other anions were obtained, and other anions did not cause any significant changes in the absorption intensity (Fig. 1c). These results indicate that



Fig. 1. UV-Vis spectra of 1 (0.1 mM) on addition of various anions in different DMSO/H₂O (v/v). (a) 9:1 DMSO/H₂O, 1.0 equiv of anions; (b) 7:3 DMSO/H₂O, 1.0 equiv of anions; (c) 6:4 DMSO/H₂O, 1.0 equiv of anions.

the selectivity for CN^- is greatly influenced by water. Anions such as F^- and AcO^- could interact with the water through Hydrogenbonding, and this leads to a large decrease in their nucleophilicity. In contrast, cyanide has much weaker Hydrogen-bonding ability in comparison with F^- and AcO^- and has stronger thiocarbonyl carbon affinity, which results in the addition reaction of CN^- to thiocarbonyl carbon. Subsequent proton transfer of thiourea hydrogen to the developing alksulfide anion of **1** produces an active state (its anionic state) of **1**, which enhanced the charge-transfer interactions between the electron-rich and electron-deficient moieties, resulting in a visible color change (Scheme 2). In order to investigate the interaction mechanism between the receptor **1** and cyanide, ¹H NMR titration experiments were carried out by addition of cyanide to either the deuterated DMSO solution or the mixture of deuterated DMSO/D₂O (6/4, v/v). Upon addition of 0.2 equiv of the cyanide, there was significant line broadening of both the NH peaks of the thiourea. This indicates interaction of the cyanide with both the NH protons (N–H_a and N–H_b). When more of the CN⁻ anion was added, all the N–H peaks disappeared completely (Fig. SI-1). This evidence supports that the cyanide anion participates in the deprotonation of the NH in the deuterated DMSO system. However, with the increasing addition of cyanide in the



Scheme 2. The proposed sensing mechanism of 1 for cyanide.



Fig. 3. Family of spectra taken in the course of the titration of $1 (1.0 \times 10^{-4} \text{ M})$ in aqueous solution (DMSO/H₂O = 6/4, v/v) with cyanide anion at 25° C. Titration profiles (insert) indicate the formation of a 1:1 stoichiometry.

mixture of deuterated DMSO/D₂O (6/4, v/v), not only the disappearance of N–H peaks but also the existence of upfield shift of the aromatic protons (H₂–H₄, H₇, and H₈) to different extent (Fig. 2). These upfield shifts may due to the fact that after the addition reaction of CN[–] to thiocarbonyl carbon and subsequent proton transfer

of thiourea hydrogen to the developing alksulfide anion of **1**. Thus, the electron density in the aromatic ring increases, which results in an upfield shift of the protons. While the phenyl proton H_1 and the naphthyl protons (H_6 and H_9) exhibited downfield shifts to different extent. These downfield shifts may caused by the elec-



Fig. 4. The corresponding color changes when receptor 1 (0.5 mM) was treated with various anions (1.0 eqiv.) in DMSO/H₂O (6/4, v/v).



Fig. 5. UV–Vis absorption responses of **1** $(1.0 \times 10^{-4} \text{ M})$ to various anions $(2.0 \times 10^{-4} \text{ M})$ in aqueous solution (DMSO/H₂O = 6/4, v/v). Bars represent the intensity ratios of absorption at 506 nm. A_0 represents the responses of **1** + CN⁻, A represents either the responses of **1** + X⁻ or the responses of **1** + (CN⁻ + X⁻).

trostatic through-space effect [42]. These results are compatible with the proposed mechanism shown in Scheme 2. The formation of cyanide adduct was further confirmed by mass spectroscopy. The electrospray ionization mass spectrum of the cyanide adduct showed a molecular mass of 350.8, which corresponds to the formula of [1 + CN + H] (calculated m/z 350.1, see Fig. SI-2). The above results clearly demonstrated that a highly selective sensing system for CN⁻ can be developed on the basis of the specific chemical reaction.

To quantitatively study the cyanide-sensing ability of **1** in 6/4 DMSO/H₂O mixture, UV–Vis monitoring was performed by using 0.1 mM solution of **1**. Upon addition of cyanide anions, the intensity of the absorption peak at 372 nm was gradually decreased, while the intensity of the peak at 506 nm evolved and after the addition of 2.0 equiv. of CN⁻ anion, reached to their limiting values (Fig. 3a). The isosbestic point at 395 nm indicated a clean conversion throughout the titration process. Interestingly, the color of the solution changed from its initial orange color to red color (Fig. 4). The signaling was completed within 2 min (Fig. SI-3). By plotting the changes of **1** in the absorbance at 506 nm as a function of CN⁻ anion concentration, a sigmoidal curve was obtained and is shown in the inset of Fig. 3b. To corroborate 1:1 ratio between **1** and CN⁻, Job's plot analysis was also executed. The measured absorbance variation ($\Delta A = A_{abs} - A_i$)

reaches to a maximum when the molar fraction of ([1]/[CN⁻]+[1]) is 0.5, confirming the 1:1 stoichiometry (Fig. 3c) [43].

The selectivity of the system for cyanide was then examined by competition experiments. Fig. 5 shows UV-Vis absorption intensity changes upon addition of cyanide when 2 equiv. of F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, AcO⁻, SCN⁻, and H₂PO₄⁻ are also present. It is noticeable that the absorption intensity was almost identical to that obtained in the absence of anions. The miscellaneous competitive anions did not lead to any significant spectral and color changes. The colorimetric detection limit of **1** for CN⁻ ion was also tested. A plot of $(A - A_0)$ versus the cyanide concentration in DMSO/H₂O (6/4, v/v) solution gave a linear relationship (Fig. 6). The detection limit was calculated on the basis of $3\sigma/K$ [44] is 1.27 µM, which makes receptor **1** as a powerful tool for the detection of cyanide ion. (The WHO suggested that the maximum allowed cyanide concentration in drinking water is 1.90 µM). In order to investigate how the different substituent group on the thiourea moiety can influence the binding affinity and selectivity for cyanide, the 4-nitronaphthyl group was replaced by 4-nitrophenyl group or 4-trifluoromethyl-phenyldiazenylphenyl group; receptors 2 and 3 were examined. We repeated these measurements using receptors 2 and 3 in 6/4 DMSO/H₂O and 7/3 DMSO/H₂O (due to its solubility problem), respectively. In fact, **2** shows different titration profiles to **1** upon CN⁻ ion introduction. The intensity of the absorption peak at 350 nm was gradually decreased, while the intensity of the shoulder peak at 425 nm evolved (Fig. 7a). The Job's plot analysis indicates 1:1 stoichiometry between 2 and CN⁻ ions (Fig. SI-4b). The color of the solution changes from colorless to gold color in the presence of CN⁻ ions (Fig. 7b). The high selectivity for cyanide was also observed for receptor 2 (Fig. 7a). However, the detection limit of 2 toward cyanide was determined to be 6.84 µM (Fig. SI-5). It seems that the nitrophenyl group has less effect on the charge-transfer interaction compare with the nitronaphthyl group in receptor **1**. From ¹H NMR titration experiment, it was found that except H₃ all the other aromatic protons underwent upfield shifts after the increasing concentration of CN⁻ anion was added (Fig. SI-6). These results are compatible with the above proposed mechanism. The



Fig. 6. (a) Photograph of 1 in aqueous solution (DMSO/H₂O = 6/4, v/v) in the presence of the CN⁻ ion. (b) Absorption intensity of 1 versus CN⁻ concentrations. [1] = 0.1 mM.



Fig. 7. UV-Vis spectra (a) and color changes (b) of $2(1.0 \times 10^{-4} \text{ M})$ in the presence of various anions (1.0 equiv) in DMSO/H₂O (6/4, v/v).

formation of cyanide adduct was also confirmed by mass spectroscopy. The electrospray ionization mass spectrum showed a molecular mass of 299.3, which corresponds to the formula [2+CN] (calculated m/z 299.1, see Fig. SI-7).

Subsequently, the titration experiments were repeated for receptor **3** in the 7/3 DMSO/H₂O system. Receptor **3** shows similar titration profiles to **2** upon CN⁻ ion introduction. An intense band for the $\Pi - \Pi^*$ transition of the 4-trifluoromethyl-



Fig. 8. (a) UV–Vis spectra of **3** $(5.0 \times 10^{-5} \text{ M})$ in the presence of the CN⁻ $(2.5 \times 10^{-4} \text{ M})$ and miscellaneous anions (X) including F⁻, Cl⁻, Br⁻, I⁻, SCN⁻, AcO⁻, NO₃⁻ and H₂PO₄⁻, respectively. (b) Color changes of **3** $(5.0 \times 10^{-4} \text{ M})$ upon addition of tetrabutylammonium salt of X in aquesous solution (DMSO/H₂O = 7/3, v/v).



Fig. 9. (a) Photographs of the test kit with **1** for detecting CN⁻ anion in aqueous solution (DMSO/H₂O = 6/4, v/v) with different concentrations. Left to right: 0, 5.0×10^{-5} M and 1.0×10^{-4} M. (b) Photographs of the test kits with **1** for detecting miscellaneous anions including F⁻, Cl⁻, Br⁻, I⁻, SCN⁻, AcO⁻, NO₃⁻, H₂PO₄⁻ and CN⁻ (1.0×10^{-4} M) in aqueous solution (DMSO/H₂O = 6/4, v/v).

phenyldiazenylphenyl chromophore appears at 380 nm. The intensity of this absorption peak was gradually decreased, while the intensity of the shoulder peak at 475 nm evolved (Fig. SI-8a). The Job's plot analysis indicates 1:1 stoichiometry between **3** and CN⁻ ions (Fig. SI-8c). The color of the solution changes from yellow to red color in the presence of CN⁻ ions is shown in Fig. 8. The detection limit of **3** for CN⁻ ions is also determined to be 3.41 μ M (Fig. SI-9). However, the selectivity of **3** for cyanide was interfered by F⁻, AcO⁻, and H₂PO₄⁻ (Fig. SI-10). Apparently, the receptor **1** has the best detect limit and the least interference among these three receptors.

To explore potential and analytical applications of the receptor 1 for CN⁻ anion tested, the test strips were carried out. They were prepared by immersing filter papers into a DMSO/H₂O (6/4, v/v) solution of 1 (0.1 M) and then drying in vacuum (oven temperature 100–110° C, 70 mmHg). The test strips containing 1 were utilized to sense different anions (Fig. 9). To these anion solutions, different test kits were immersed. An immediate obvious color change was observed only with CN⁻ solution. Also, these test strips were applied for sensing different CN⁻ concentrations, exhibiting colorimetric changes differentiable by naked eyes. As depicted in Fig. 9a, the color changes of the test strips changing from 0 to 5.0×10^{-5} and 1.0×10^{-4} M show that the discernible concentration of CN⁻ can be as low 1.0×10^{-4} M.

4. Conclusion

In conclusion, three colorimetric anion receptors **1–3** were synthesized. Among them, receptor **1** shows high selectivity toward CN⁻ ion over miscellaneous competitive anions and also distinguishes CN⁻ from other anions by color changes. In DMSO/H₂O (6/4, v/v) solution, the receptor **1** can selectively detect cyanide ion with a detection limit of 1.27 μ M. While the test strip containing **1** also exhibits a good selectivity and sensitivity (ca. 1.0×10^{-4} M) to

 CN^- . Therefore, the colorimetric sensor **1** can be used practically to determine CN^- ion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.04.087.

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