

Reaction-Based Colorimetric Cyanide Chemosensors: Rapid Naked-Eye Detection and High Selectivity

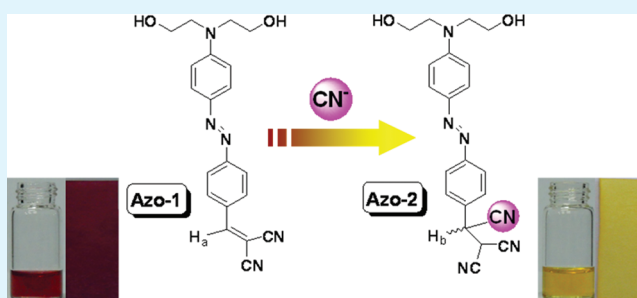
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Supporting Information

ABSTRACT: Taking advantages of both the well-known azobenzene structure and the special nucleophilicity of cyanide toward the acceptor moiety, a new ratiometric colorimetric chemodosimeter (**Azo-1**) toward cyanide anion was designed and synthesized by using intramolecular charge transfer (ICT) as a signaling mechanism. Upon the addition of CN^- anion, the probe displayed apparent color changes from deep red to light yellow, which could be observed by naked eyes. With the aid of the UV-vis spectrometer, the detection limit could be as low as $1.1 \mu\text{M}$. The probe possessed high selectivity for cyanide with respect to other common anions. In addition, **Azo-1** could serve as practical colorimetric probe for “in-the-field” measurements that would not require any additional equipment by virtue of “dip-sticks” approach.

KEYWORDS: chemodosimeter, cyanide, reaction-based, intramolecular charge transfer, colorimetric, high selectivity



INTRODUCTION

Currently, the development of molecular probes for anions such as cyanide has been a subject of intense research interest, because anions play important roles in biological systems and also constitute some pollutants in our environment.¹ Cyanide is an extremely toxic anion and can affect many functions in the human body, including the vascular, visual, central nervous, cardiac, endocrine, and metabolic systems.² Nevertheless, cyanide is widely used in many chemical processes, such as electroplating, plastics manufacturing, gold and silver extraction, tanning, and metallurgy.³ Cyanide containing salts are widespread chemicals found in surface water originating not only from industrial waste but also from biological sources.⁴ Therefore, easy and affordable detection methods are in great demand for various situations. In this regard, optical sensors for cyanide, in which a change in color and/or fluorescence intensity (or emission wavelength) is monitored, have been studied actively over the past ten years due to their simple, inexpensive, and rapid implementation.⁵ Especially, colorimetric sensors are especially promising because the color change can easily be observed by naked-eyes, thus requiring less labor and no equipment.⁶ On the other hand, ratiometric colorimetric probes can enable the measurement of absorption intensities at two different wavelengths, providing a built-in correction for environmental effects and increasing the dynamic range of absorption measurement. This was considered as a good approach to overcome the major limitation of intensity-based probes, in which variations in the environmental sample and probe distribution were problematic for quantitative

measurements. However, so far, the ratiometric colorimetric probes for cyanide were still very scarce.

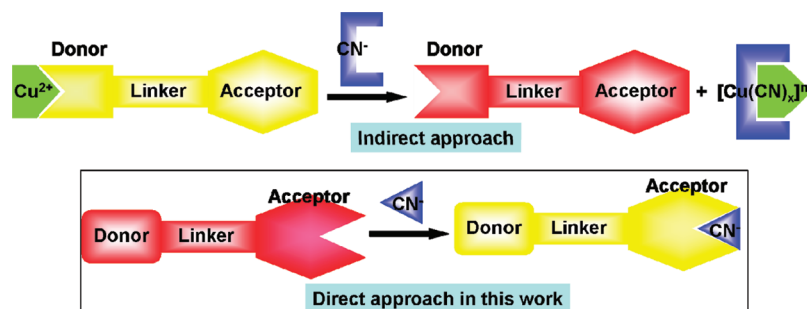
Over the past four years, we developed an indirect strategy to detect cyanide utilizing the affinity of this anion toward copper (Scheme 1).⁷ One of the most important advantages of sensors based on this displacement approach was that they could be operable in aqueous solutions. For example,^{7,7e} copper ions could coordinate with the electron donor moiety of the sensor molecule (see Chart S1 in the Supporting Information), which reduced the ability of the donor to participate the ICT process and then gave rise to large changes in the absorption spectra (from red to yellow). However, the added cyanide could preferentially react with copper ions in the above coordination to form stable $[\text{Cu}(\text{CN})_x]^{n-}$ species. As a result, the liberated donor moiety of the sensor molecular recovered its electron-donating ability to participate the ICT process with color changes from yellow to red. Differently from the indirect approach, here, we considered whether direct detection of the cyanide anions could be achieved by regulating the acceptor moiety of the sensor molecule to affect the ICT efficiency and induce naked-eye color changes. After checking the literature carefully, we found that chemodosimetric sensors relied on the special nucleophilicity of cyanide was promising owing to their highly selectivity. Actually, as a potential sensing system, specific nucleophilic reactions between the sensor molecule and cyanide accompanying with some spectroscopic change have

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Scheme 1. Approach in This Work for Direct Detection of Cyanide



Scheme 2. Structure of Azo-1 and the Sensing Mechanism



recently attracted the attention of many scientists, i.e., the dicyano-vinyl group,⁸ cyanohydrin reaction,⁹ chromogenic oxazines,¹⁰ pyrylium or acridinium compounds,¹¹ and squaraine, croconium, or triarylmethane dyes.¹²

With these considerations in mind and based on our previous work, herein, we developed a ratiometric colorimetric chemodosimeter for cyanide anion, namely, compound **Azo-1**. The design of this chemodosimeter took advantages of both the well-known azobenzene structure and a dicyano-vinyl group as a putative cyanide-dependent reactive subunit. As shown in Scheme 2, it was expected that cyanide could serve as the only nucleophiles to attack the α -position of the dicyano-vinyl group, namely, the acceptor moiety in compound **Azo-1**, to generate stabilized anionic species **Azo-2**. Then, the extent of effective conjugation in the sensor molecular would be broken, which could affect the intramolecular charge transfer (ICT) efficiency and optical properties of the sensing system. Receptor **Azo-1** is deep-red in color with the maximum absorption wavelength centered at about 515 nm, thus, nucleophilic addition of cyanide to the α -position of the vinyl group would produce a spectral change and loss in color or at least in perceived brightness consequently. Fortunately, the mechanism did work, and the detection limit of cyanide could be as low as 1.1 μM , with high selectivity. Here, we describe the

synthesis and the spectroscopic evaluation of the new ratiometric colorimetric chemodosimeter in detail.

MATERIALS AND INSTRUMENTATIONS

Ethanol was dried over and distilled from Na under an atmosphere of dry nitrogen. Triethylamine (Et_3N) was distilled under normal pressure and kept over potassium hydroxide. All other reagents were of analytical reagent grade and used without further purification. Doubly distilled water was used in all experiments. The ^1H and ^{13}C NMR spectra were measured on Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The ESI mass spectra were measured on a Finnigan LCQ advantage mass spectrometer. Elemental analyses were performed by a CARLOERBA-1106 microelemental analyzer. UV-vis spectra were obtained using a Shimadzu UV-2550 spectrometer. **Azo-0** was prepared according to the literature procedure.¹³

Synthesis of 2-(4-(4-(Bis(2-hydroxyethyl)amino)phenyl)diazenyl)benzylidene)malononitrile (Azo-1**).** Under an atmosphere of dry argon, compound **Azo-0** (125.2 mg, 0.4 mmol) and malononitrile (53 mg, 0.8 mmol) in absolute ethanol (5 mL) were refluxing overnight with trace Et_3N as catalyst. Then, the resultant mixture was cooled to room temperature and the solvent was removed under reduced pressure. The resultant residue was purified by silica gel column chromatography using ethyl acetate as eluent to afford compound **Azo-1** as a deep red solid (105 mg, 73%). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm): 8.51 (s, 1H, $-\text{CH}=\text{C}-$), 8.04–8.07 (d, 2H, $J = 9.0$ Hz, ArH), 7.86–7.89 (d, 2H, $J = 9.0$ Hz, ArH), 7.75–7.78

(d, 2H, $J = 9.0$ Hz, ArH), 6.84–6.87 (d, 2H, $J = 9.0$ Hz, ArH), 4.83 (br, 2H, –OH), 3.56 (m, 8H, –CH₂CH₂–). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm): 160.8, 156.3, 152.8, 143.4, 132.7, 131.9, 126.6, 123.1, 112.3, 81.1, 58.8, 54.0. MS (ESI), m/z [M+H]⁺: 362.4, calcd, 362.2. C₂₀H₁₉N₃O₂ (EA) (% found/calcd): C, 66.70/66.47; H, 5.132/5.30; N, 19.75/19.38.

Preparation of Solutions of Anions. One millimole of inorganic salt (NaOAc·3H₂O, NaNO₂, NaNO₃, Na₂SO₃, NaF, Na₂CO₃, Na₂SO₄, Na₃PO₄, NaCl, NaIO₃, KClO₃, KBr, Na₂HPO₄·12H₂O, NaHSO₃, NaHSO₄, Na₂S₂O₃·5H₂O, Na₂S, KI, KH₂PO₄, KSCN, KOH, and NaCN) was dissolved in distilled water (10 mL) to afford 1 × 10⁻¹ mol/L aqueous solution. The stock solutions were diluted to desired concentrations with water when needed.

UV Absorption Changes of Azo-1 by CN⁻. A solution of Azo-1 (1 × 10⁻⁵ mol/L) was prepared in CH₃CN. Then 3.0 mL of the solution of Azo-1 was placed in a quartz cell (10.0 mm width) and the UV–vis absorption spectrum was recorded. The NaCN aqueous solution was introduced in portions and the absorption changes were recorded at room temperature each time.

UV Absorption Changes of Azo-1 by Other Anions. A solution of Azo-1 (1 × 10⁻⁵ mol/L) was prepared in CH₃CN. Then 3.0 mL of the solution of Azo-1 was placed in a quartz cell (10.0 mm width) and the UV–vis absorption spectrum was recorded. Different anion solutions were introduced and the changes of the absorption changes were recorded at room temperature each time.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization. The synthetic route to compound Azo-1 was depicted in Scheme 1. It was easily seen that the target compound was prepared conveniently through the general Knoevenagel condensation reaction between Azo-0 and malononitrile, according to the reported literature.¹⁴ The whole synthetic route was simple and the purification was easy.

Compound Azo-1 exhibited good solubility in common organic solvents, such as acetone, DMF, DMSO, CH₃CN, THF, etc. Its structure was characterized by spectroscopic methods, and all gave satisfactory spectral data (see Experimental Section). Compound Azo-0 was light red in color with the maximum absorption wavelength centered at about 455 nm.¹⁵ After the condensation reaction with malononitrile, the maximum absorption wavelength of the resultant compound Azo-1 shifted to 515 nm. This was easily understood. The electronic property of azo compounds changed before and after the condensation reaction, directly leading to the different absorption behaviors and obvious color changes.

Sensing Properties. Because the optical signal changes relied on the chemical reaction between compound Azo-1 and CN⁻, thus, the reaction rate might affect the experimental results. From this point, we investigated the influence of the reaction time on the probing results, and the obtained results were demonstrated in Figure 1. When the concentration of CN⁻ was lower than 1.0 × 10⁻⁵ M, there were gradual changes in the absorption intensity from 0 to 10 min; however, after 10 min, the changes became smaller than before. When the concentration of CN⁻ was 1.5 × 10⁻⁵ M, a plateau of absorption intensity changes could be achieved after 15 min. With the increasing of the concentration of cyanide, such as 10 × 10⁻⁵ M, less than 3 min were needed to achieve a plateau. That was to say, in high concentrations, the reaction almost completed within 15 min, whereas in low concentrations, the reaction time was longer, because of the different reaction efficiencies of different amounts of CN⁻.

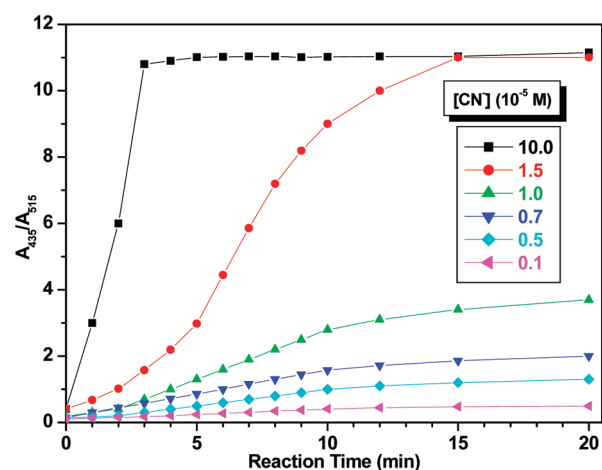


Figure 1. Reaction-time profile of probe Azo-1 (10 μM, in CH₃CN) in the presence of different concentrations of CN⁻.

As shown in Scheme 2 and Figure 2, compound Azo-1 was deep red in color with the maximum absorption wavelength

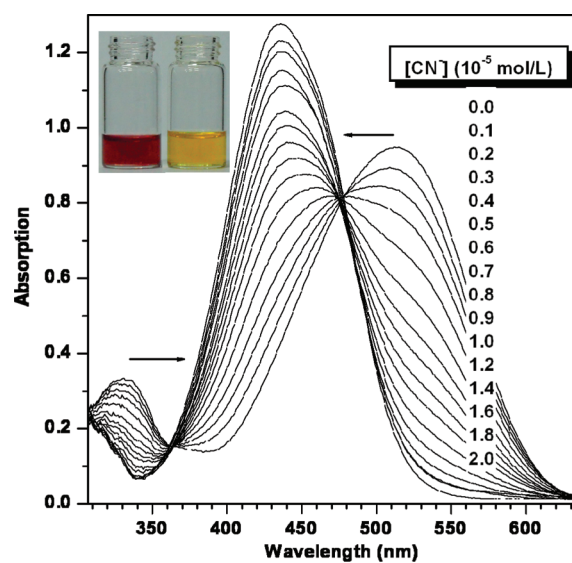


Figure 2. UV–vis spectra of Azo-1 (10 μM, in CH₃CN) in the presence of different concentrations of CN⁻. The arrow showed the shift of the maximum absorption wavelength.

centered at about 515 nm in its UV–vis spectrum, corresponding to its intramolecular charge transfer character due to the push–pull effect. Then, it was expected that the nucleophiles such as cyanide could attack the α -position of the dicyano-vinyl group in compound Azo-1 to generate the stabilized anionic specie of Azo-2. As a result, the extent of effective conjugation in the sensor molecule should be broken, which would affect the electronic structure and optical properties. Chemodosimeter Azo-1 was deep-red in color, thus, nucleophilic addition of CN⁻ to the α -position of the vinyl group was expected to produce the blue-shifted spectrum and loss in color or at least in perceived brightness consequently. If cyanide anion was the only nucleophile capable of inducing these changes, it seemed that compound Azo-1 could act as a cyanide-selective colorimetric chemodosimeter.

Then, we added cyanide anion into the diluted solution of compound **Azo-1** and investigated its response toward CN^- in CH_3CN in detail. As shown in Figure 2, the absorption maximum of **Azo-1** shifted from 515 to 435 nm, with an isosbestic point at about 475 nm, indicating the formation of new species. Meanwhile, the absorption intensity centered at about 330 nm decreased with an isosbestic point at about 360 nm. With the increasing of the concentrations of CN^- , we could see that the new band at 435 nm demonstrated a larger molar absorption coefficient than the original one. We compared the intensities at different wavelengths of 435 and 515 nm, with the results summarized in Figure 3. It was easily

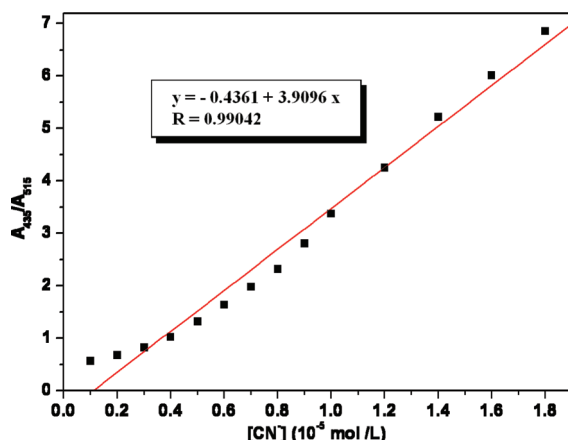


Figure 3. Ratiometric calibration curve A_{435}/A_{515} of **Azo-1** ($10 \mu\text{M}$, in CH_3CN) as a function of the concentration of CN^- .

seen that the intensity change was almost linear to the concentrations of the cyanide anion. Accordingly, the detection limit could be determined to be $1.1 \mu\text{M}$,¹⁶ which was lower than the maximum contaminant level (MCL) for cyanide in drinking water. of ($2.7 \mu\text{M}$) set by the World Health Organization (WHO).¹⁷ Taking advantage of the nucleophilic addition of cyanide, Tong and Wang et al. prepared a reaction-based conjugated polymer chemosensor toward cyanide. Thanks to the molecular wire effect of the conjugated polymer, the detection limit could be as low as $0.5 \times 10^{-6} \text{ M}$.¹⁸ In addition, Liu and He et al. designed a dicyanovinyl-substituted benzofurazan derivative as an efficient ratiometric chemosensor for cyanide anion. It showed remarkable dual changes in absorption and emission bands and the fluorescence detection limit was estimated to be $1.47 \times 10^{-6} \text{ M}$.¹⁹ Compared with these reported work, it was clear that the performance of **Azo-1** was among the best results of the cyanide chemosensors with the same sensing approach. More importantly, the colorimetric difference for the solution of **Azo-1** (from deep-red to light yellow) before and after the addition of cyanide could be distinguished by the naked eyes (the inset pictures of Figure 2), validating our design of ratiometric colorimetric chemodosimeter toward cyanide, based on the nucleophilic addition reaction of CN^- to the dicyano-vinyl group.

As motioned above, the ultimate goal of this research was to develop “naked eye” colorimetric sensors. **Azo-1** had good sensitivity and high selectivity, thus, potentially, it could be used for direct naked eye sensing toward CN^- . The pictures in Figure 4 showed that although not so sensitive as measured by the UV-vis spectrometer, we could easily distinguish the color change at concentrations as low as $60 \mu\text{M}$ of CN^- (Figure 4D).

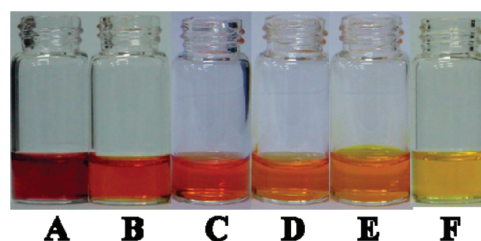


Figure 4. Photograph of **Azo-1** to various concentration of CN^- ($\times 10^{-5} \text{ mol/L}$): (A) 0, (B) 2, (C) 4, (D) 6, (E) 9, (F) 15.

We further studied the influence of trace water on the sensing process (see Figure S1 in the Supporting Information). The absorption of **Azo-1** changed at a very limited degree even after $100 \mu\text{L}$ of H_2O was introduced, indicating that the water in the cyanide solutions did not affect the results of the titration experiment. Thus, the above results indicated that upon the addition of cyanide, the nucleophilic addition reaction between **Azo-1** and CN^- really occurred as expected, and the apparent color change was observed.

To assess the specificity of our chemodosimetric sensor toward CN^- , various anions were examined in parallel under the same conditions. As shown in Figure 5 and Figure S2 in the

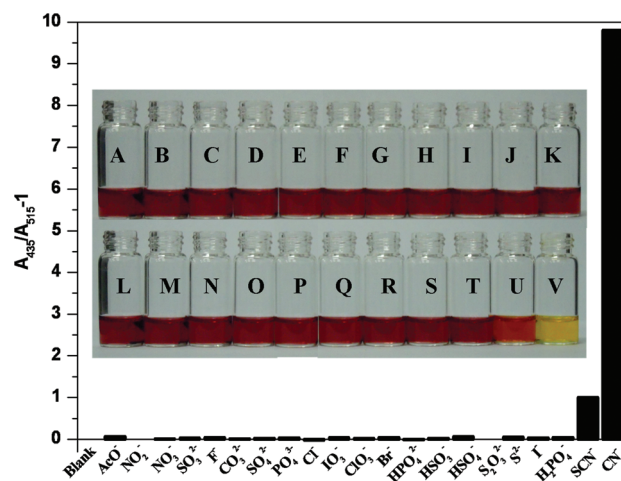


Figure 5. Ratiometric absorption of **Azo-1** ($10 \mu\text{M}$, in CH_3CN) in the presence of different anions (CN^- , $20 \mu\text{M}$; others, $40 \mu\text{M}$). Inset: Photograph of **Azo-1** to various anions ($40 \mu\text{M}$). (A) **Azo-1** ($10 \mu\text{M}$); (B–V) **Azo-1** + AcO^- , NO_2^- , NO_3^- , SO_3^{2-} , F^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , Cl^- , IO_3^- , ClO_3^- , Br^- , HPO_4^{2-} , HSO_3^- , HSO_4^- , $\text{S}_2\text{O}_3^{2-}$, S^{2-} , I^- , H_2PO_4^- , SCN^- , CN^- ($15 \mu\text{M}$).

Supporting Information, the reaction of **Azo-1** with CN^- gave strong absorbance changes; whereas other anions such as AcO^- , NO_2^- , NO_3^- , SO_3^{2-} , F^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , Cl^- , IO_3^- , ClO_3^- , Br^- , HPO_4^{2-} , HSO_3^- , HSO_4^- , $\text{S}_2\text{O}_3^{2-}$, S^{2-} , I^- , H_2PO_4^- , did not show any changes, except that SCN^- caused the negligible disturbance. Moreover, we measured the response of **Azo-1** to CN^- in the presence of other competitive anions. As shown in Figure S3 in the Supporting Information, the presence of other background anions did not show any obvious disturbance with the signal response induced by CN^- . These results further confirmed that only the addition of cyanide could induce the apparent color changes as shown in the inset pictures of Figure 5. Furthermore, the influence of OH^- anion on the sensing process was studied considering its nucleophilic property. With the addition of OH^- anion,

although it could induce the change in absorption of **Azo-1**, the sensitivity was not as high as that toward CN^- (see Figure S4 in the Supporting Information). Therefore, **Azo-1** has much higher selectivity for CN^- than other anions. This unique property enabled cyanide to be detected by the naked eyes directly over other species.

Motivated by the favorable features of this system in solution, we prepared test strips by immersing filter papers ($3 \times 1 \text{ cm}^2$) into the CH_3CN solution of **Azo-1** ($1 \times 10^{-3} \text{ mol/L}$) and then dried then in air to determine the suitability of a “dip-stick” method for the detection of CN^- , similar to that commonly used for the pH measurement. When the test strips coated with **Azo-1** were immersed into the aqueous solutions of CN^- with different concentrations, the obvious color change from deep-red to yellow was observed (Figure 6). The detection limit for

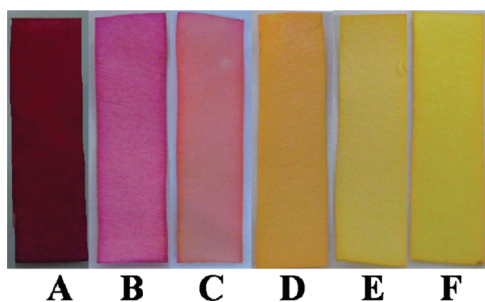


Figure 6. Photographs of test strips of **Azo-1** to various concentration of CN^- ($\times 10^{-5} \text{ mol/L}$): (A) 0, (B) 3, (C) 5, (D) 7, (E) 9, (F) 11.

these “dip-sticks” was relatively low ($3 \times 10^{-5} \text{ mol/L}$). The development of such a “dip-sticks” approach was extremely attractive for “in-the-field” measurements that did not require any additional equipment. However, as to the detection of CN^- in the practical water sample, the influence of the contaminants in water samples (such as metal ions) and the pH values could not be ignored. As we know, the presence of copper ions would snatch the added cyanide preferentially, which did disturb the sensing efficiency. It was still a pity, however, the disturbance could be inhibited by the necessary pretreatment, namely, the addition of chelating agent such as EDTA (ethylenediaminetetraacetic acid).

As a chemosensor with excellent performance, the application in practical samples was of great importance and further study was still in progress in our laboratory.

To explore the sensing mechanism of **Azo-1** to CN^- , the reaction mixture of **Azo-1** with excess CN^- was characterized by ^1H NMR spectra and ESI-MS spectrometry. The partial ^1H NMR spectra of the resultant complex of **Azo-1** and excess CN^- (as its tetra-butylammonium salts) was shown in Figure 7. It was obvious that the resonance signal corresponding to the vinylic proton (H_a) at 8.25 ppm completely disappeared, whereas a new signal grew in at 4.30 ppm corresponding to the α -proton (H_b). Meanwhile, the aromatic proton displayed small upfield shift compared to those of **Azo-1** due to the breaking of the conjugation. These observations obviously indicated that the cyanide anion was added to the vinyl group. In Figure S5 in the Supporting Information, it revealed that after the addition of excess CN^- into the solution of **Azo-1**, a relatively weak peak at about 389.7 appeared, coinciding well with that for the species $[\text{Azo-1} + \text{CN}^- + \text{H}]^+$ ($m/z_{\text{calcd}} = 389.2$), indicating the formation of the stabilized anionic species **Azo-2**.

CONCLUSIONS

In summary, a new “naked-eyes” ratiometric colorimetric chemodosimeter (**Azo-1**) was constructed by taking advantages of the special nucleophilicity of cyanide toward the acceptor moiety. **Azo-1** displayed high sensitivity and selectivity for CN^- with respect to other anions. In addition, the probe could serve as practical colorimetric sensors for “in-the-field” measurement, which did not require any additional equipment but just by virtue of “dip-sticks” approach.

ASSOCIATED CONTENT

Supporting Information

UV-vis spectra; ESI-mass spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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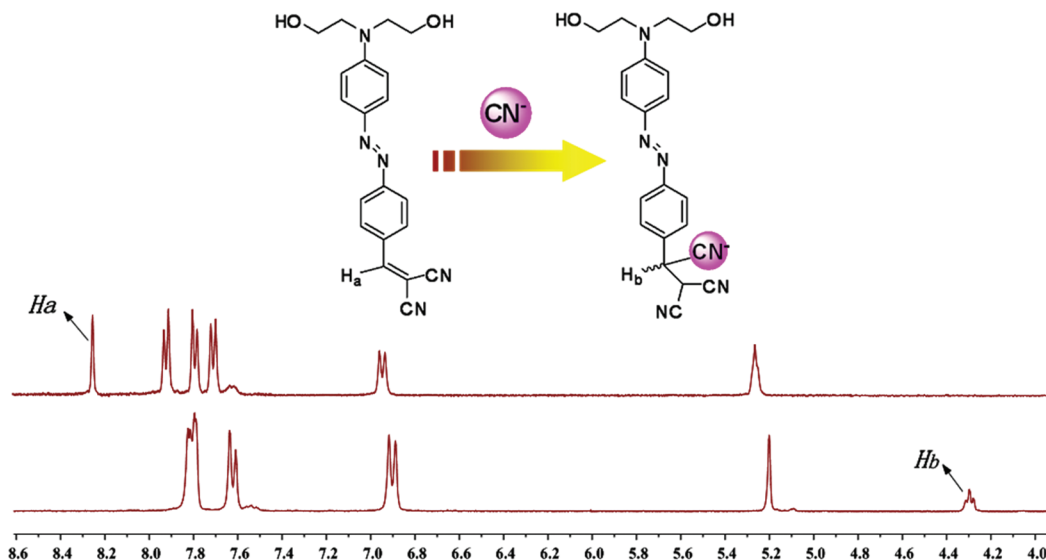


Figure 7. ^1H NMR spectra of **Azo-1** (top) and **Azo-1** + CN^- (bottom) as its tetra-butylammonium salts in $\text{DMSO}-d_6$.

Notes

The authors declare no competing financial interest.

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