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ARTICLE

Colorimetric probes designed to provide high sensitivity and single selectivity for CN^- in aqueous solution

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The specific colorimetric detection of CN^- in the context of interference from coexisting anions, such as F^-, AcO^-, and $H_2PO_4^-$, in aqueous solutions is still a challenge. Therefore, easily-made CN^- colorimetric probes **L1**-**L4** bearing hydrazone moieties as the binding sites and nitrophenylfuran moieties as the signal groups were designed and synthesized. The probe **L1** showed excellent colorimetric single selectivity and sensitivity for CN^- in DMSO/H_2O solutions. When CN^- was added to the solution of **L1**, a dramatic color change from yellow to violet was observed, while the anions F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- and ClO_4^- did not interfere with the recognition process for CN^-. The detection limits of CN^- were 8×10^{-5} and 5×10^{-6}mol/L according to the visual color changes and UV-vis changes, respectively.

1. Introduction

The cyanide anion (CN^-) is extremely hazardous to living organisms,[1-3] which can strongly binds the active site of cytochrome-c and inhibit the mitochondrial electron-transport chain, leading to decreased oxidative metabolism and oxygen utilization.[1-4] The industrial use of cyanide salts, however, remains widespread, particularly in gold mining, electroplating, and metallurgy.[4] Therefore, there is a strong need for efficient probes that can selectively recognize CN^- in supramolecular chemistry. A variety of molecular probes showing chemical and physical methods of responding to CN^- have been proposed.[5-9] Many of these receptors, however, suffer from several problems: they (i) act only in pure organic solvents or solutions containing a large amount of organic solvents; (ii) show poor selectivity to CN^-; and, (iii) show high detection limit.[5,6,10,11] As a result, the design of CN^- probes with high selectivity and sensitivity is currently the focus of attention. Furthermore, cyanide probe interactions widely occur in the aqueous solution in both environmental and life sciences, therefore, much attention has been paid to developing CN^- probes that work in the aqueous phase.[12-17]

To date, many strategies have been proposed for the detection of CN^- in aqueous solutions, including metal ion complexation,[15-19] adduct formation,[20,21] hydrogen-bonding interaction,[22,23] nucleophilic addition reaction[24,25] and so on. For example, a series of reaction-based probes can identify cyanide with specific selectivity and high sensitivity. Nevertheless, such probes also suffer from some disadvantages, such as complicated organic synthesis, environmentally harmful systems, or poor solubility in water. From the viewpoint of practical applications, an excellent probe should be not only highly sensitive and selective but also simple and economical to operate. Thus, the development of new, efficient optical probes for detecting CN^- in the aqueous solution is essential.

In view of this requirement and as part of our research effort devoted to ion recognition,[26-29] an attempt was made to obtain efficient colorimetric probes which can identify cyanide with specific selectivity and high sensitivity in aqueous solutions. This paper details the design and synthesis of a series of CN^- colorimetric probes **L1**-**L4** bearing hydrazone and nitrophenylfuran groups (Scheme 1). The strategies for the design of these probes were as follows. Firstly, the hydrazone group (–CH=N–NH–) was introduced, which can act as CN^- binding sites. Secondly, owing to the excellent photophysical properties of 5-Aryl furfural derivatives,[30,31] we introduced nitrophenylfuran groups as the signal groups to achieve "naked-eye" colorimetric recognition. Finally, the probe was designed to be easy to synthesize. Additionally, in order to establish the contribution of signal groups to the probes' colorimetric sensing abilities for CN^-, similar compounds **L2**-**L4** were also synthesized.

2. Experimental

2.1. Materials and instruments

^1H NMR spectra were recorded with a Mercury-400BB spectrometer at 400 MHz. ^1H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with the solvent resonances as internal standards). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped

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with ESI interface and ion trap analyzer. Low-resolution mass spectra were recorded on a Bruker Esquire 6000 MS instrument. Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer.

The tetrabutylammonium salts were purchased from Alfa Aesar Chemical Reagent Co. (Tianjin, China) and stored in a vacuum desiccator. All solvents and other reagents were of analytical grade, commercially purchased and were used without further purification.

2.2. General procedure for UV-vis spectroscopy

All the UV-vis experiments were carried out in DMSO/H_2O solution on a Shimadzu UV-2550 spectrometer. Any changes in the UV-vis spectra of the synthesized compound were recorded on the addition of tetrabutylammonium salts while the concentration was kept constant in all experiments.

2.3. General procedure for ^{1}H NMR titrations

For ^{1}H NMR titrations, the solution of **L1** was prepared in DMSO-d_6 and the appropriate concentrated solution of the guest was prepared in double distilled water. Aliquots of the two solutions were mixed directly in NMR tubes.

2.4. Synthesis and characterization of probes L1-L4

Synthesis of 5-(4-nitro)phenyl-2-furaldehyde. 5-(4-Nitro)phenyl-2-furaldehyde was synthesized according to literature methods, yield 67%, mp 241-242 ℃.[32]

The synthetic route and molecular structures of probes **L1**-**L4** are shown in Scheme 1. 5-(4-Nitro)phenyl-2-furaldehyde (2 mmol), 2,4-dinitrophenyl hydrazine (2 mmol) and glacial acetic acid (0.1 mL, as a catalyst) were added to ethanol (20 mL). Then the reaction mixture was stirred under refluxed conditions for 2 hours. After removing the solvent, the precipitate of **L1** yielded and then it was recrystallized with DMF-EtOH to get solid of probe **L1**. The other compounds **L2**-**L4** were prepared by similar procedure.

L1: Yield: 84.3%. m.p. ＞290 ℃. IR (KBr, cm^{-1}) *v*: 1331 (-NO_2), 1512 (C＝C), 1618 (C＝N), 3271 (Ph), 3444 (N-H). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.47 (s 1H, NH), 8.33-7.99 (m, 8H, Ph), 7.48 (s, 1H, -CH=N), 7.20-7.08 (m, 2H, Furan). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 153.60, 151.24, 147.09, 144.82, 138.85, 137.92, 134.44, 130.60, 126.03, 125.04, 123.78, 117.91, 117.28, 113.19. ESI-MS calcd for $[C_{17}H_{11}N_5O_7 + H]^+$ = 398.0658, found 398.0730.

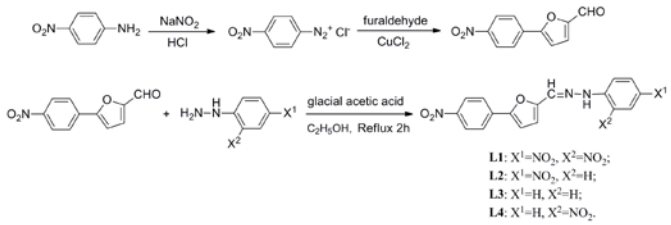
L2: Yield: 77.2%. m.p. 244-246 ℃. IR (KBr, cm^{-1}) *v*: 1325 (-NO_2), 1499 (C＝C), 1590 (C＝N), 3281 (Ph), 3448 (N-H). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.81 (s 1H, NH), 8.87-8.32 (m, 8H, Ph), 8.07 (s, 1H, -CH=N), 7.54-7.23 (m, 2H, Furan). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 167.63, 156.72, 155.27, 151.35, 150.75, 144.05, 140.52, 136.37, 131.34, 129.58, 119.60, 117.83, 116.79. ESI-MS calcd for $[C_{17}H_{12}N_4O_5 + H]^+$ = 353.0808, found 353.0717.

L3: Yield: 71.7%. m.p. 204-207 ℃. IR (KBr, cm^{-1}) *v*: 1325 (-NO_2), 1494 (C＝C), 1601 (C＝N), 3294 (N-H). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.63 (s 1H, NH), 8.30-7.42 (m, 8H, Ph), 7.26 (s, 1H, -CH=N), 7.10-6.80 (m, 2H, Furan). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 152.61, 150.50, 145.64, 144.59, 135.55, 129.08, 126.15, 124.43, 123.67, 119.10, 112.62, 112.13, 111.41. ESI-MS calcd for $[C_{17}H_{13}N_3O_3 + H]^+$ = 308.0957, found 308.1030.

L4: Yield: 76.8%. m.p. 253-255 ℃. IR (KBr, cm^{-1}) *v*: 1327 (-NO_2), 1494 (C＝C), 1614 (C＝N), 3292 (Ph), 3421 (N-H). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.35 (s 1H, NH), 8.50 (s, 1H, -CH=N), 8.33-7.95 (m, 8H, Ph), 7.70-6.97 (m, 2H, Furan). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 152.41, 151.96, 146.87, 146.20, 141.55, 136.97, 136.75, 135.57, 131.44, 126.14, 124.94, 118.96, 116.67, 115.49, 112.99. ESI-MS calcd for $[C_{17}H_{12}N_4O_5 + H]^+$ = 353.0808, found 353.0883.

3. Results and discussion

The synthesis of probes **L1**-**L4** is shown in Scheme 1. They have been characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and ESI mass specrometry. The structure of probe **L2** was further confirmed by single-crystal X-ray diffraction (Fig. 1).



Scheme 1 The synthetic route and molecular structures of probes **L1**-**L4**.

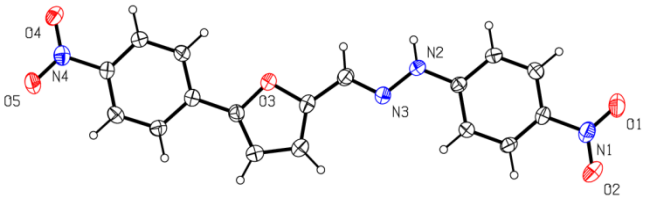


Fig. 1 Single-crystal X-ray structure of probe **L2**.

The sensing ability of **L1** toward various anions, such as F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^- and CN^- were investigated by UV–vis spectroscopy. With the aim of excluding the possible influence of pH fluctuation, we carried out experiments in DMSO/H_2O (85/15, v/v; pH 7.20). Upon adding 50 equiv. of CN^- to the solution, the max absorption at 447 nm shifted to 560 nm, and the intensity of absorption bands at 560 nm increased. The apparent color change from yellow to violet could be distinguished by the naked eye. When adding the anions F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, or ClO_4^- to DMSO/H_2O (v/v, 85/15) solutions of probe **L1**, no significant color or spectrum changes were observed. It was confirmed that **L1** showed single colorimetric selectivity to CN^- in DMSO/H_2O binary solution (Fig. 2).

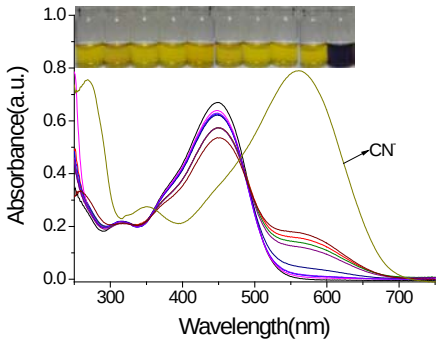


Fig. 2 UV–vis spectra of probe **L1** (2×10^{-5} mol/L) with various anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^- and CN^-) in DMSO/H_2O (85/15, v/v; pH = 7.20) solution. Inset: color changes of **L1** with various anions.

The selectivity of **L1** to CN^- was also examined over a wide range of pH values. No apparent changes of the absorbance spectra were observed, and the detection of CN^- can work well in the range of pH 3.0-13.0 (Figure S1).

To validate the selectivity of probe **L2**, in this case, when water solution of CN^- was added to the DMSO/H_2O (9/1, v/v) solutions of **L2** (ESI,† Fig. S2), the colors of the solutions changed from yellow to green. In corresponding UV-vis spectra, the absorption peak at 460 nm shifted to 637 nm, while other anions couldn't cause such color and spectra changes. Therefore, the **L2** could also colorimetric detect CN^- selectively. The same tests were applied to **L3** and **L4** (ESI,† Fig. S3, S4). In this case, when various anions were added to the DMSO/H_2O (9/1, v/v) solutions of **L3** and **L4**, respectively, no obvious changes were observed. In corresponding absorption spectrum of **L3** and **L4**, there is no selectivity for the recognition of CN^-, which indicated that both **L3** and **L4** couldn't naked and selectively sense CN^- under these conditions. Therefore, according to these results we can find that, the para position of the phenyl groups of **L1** and **L2** are substituted by nitro group, which lead to the better charge separation on **L1** and **L2** and finally resulted in color changes from yellow to violet and green, respectively. In contrast, the probe **L4** possesses nitro group in ortho position which has less influence on the charge separation and didn't cause any color change. The charge separation does not occur in sensor **L3** due to the absence of nitro group in the phenyl unit. As a result no color change has been observed to response for cyanide anion.

An important feature of the probe is its specific selectivity toward the analyte over other competitive species. The variations of UV-vis absorbance and visual color changes of probe **L1** in DMSO/H_2O binary solutions caused by the anions F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^- and CN^- , were recorded in Fig. 3. It is noticeable that the miscellaneous competitive anions did not lead to any significant interference. In the presence of these ions, the CN^- still produced similar color and optical spectral changes. These results showed that the selectivity of probe **L1** toward CN^- was not affected by the presence of other anions.

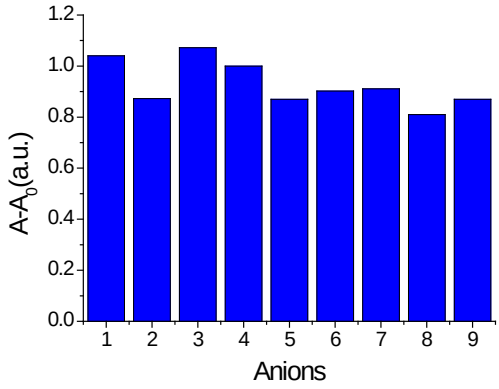


Fig. 3 Selectivity of **L1**. The blue bars represent the absorbance intensity at 560 nm of A-A_0. A and A_0 are the absorbance intensity of **L1** in the presence of other anions (50 equiv.) and addition of 50 equiv. of CN^- to the above solution. From 1 to 9: none, F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- , ClO_4^-.

As **L1** showed single selectivity for CN^-, a series of experiments was carried out to investigate the recognition capability and mechanism of **L1**. The interacting of the probe **L1** and CN^- were further studied by UV–vis titration experiments (Fig. 4). In a DMSO/H_2O solution of **L1**, the intensity of absorption bands at 560 nm increased, while the absorption bands at 447 nm decreased until it reached a limiting value. Moreover, the presence of three isosbestic points at 486, 354, and 327 nm indicated that probe **L1** reacts with cyanide anions to form a stable complex.

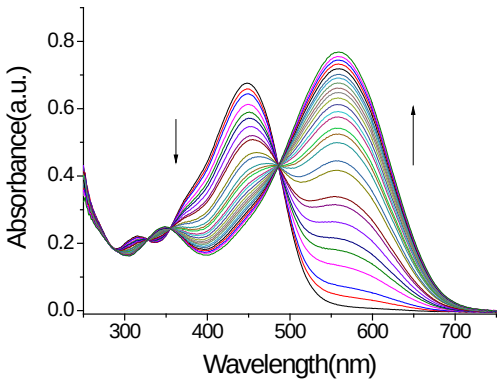


Fig. 4 UV-vis titration of probe **L1** (2×10^{-5} mol/L) with CN^- (0.1 mol/L) in DMSO/H_2O solution.

The colorimetric and UV-vis limits of probe **L1** for CN^- anion were also tested and are presented in Fig. 5. The detection limit using visual color changes was at concentration of 8×10^{-5} mol/L of CN^- anion in 2×10^{-6} mol/L solution of probe **L1**, while the detection limit of the UV-vis changes calculated on the basis of $3S_B/S^{33}$ is 5×10^{-6} mol/L for CN^- anion, which can point to the high detection sensitivity.

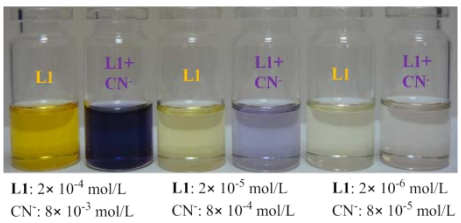


Fig. 5 Color changes observed upon the addition of various concentrations of CN^- water solution to the solutions of probe **L1** (from left to right, 2×10^{-4} mol/L, 2×10^{-5} mol/L, 2×10^{-6} mol/L) in DMSO/H_2O (v/v, 85/15).

The reversibility of probe **L1** has been measured by alternating addition of a few microliters of TFA (0.25 mol/L) to the deprotonated **L1**, which containing CN^- in a mixed solvent of DMSO and H_2O 85:15 (v/v). To our delight, the violet color disappeared after adding acid, while the max absorption was also restored to its initial state. This cycle could be repeated more than several times without considerable loss of sensing ability of the probe.

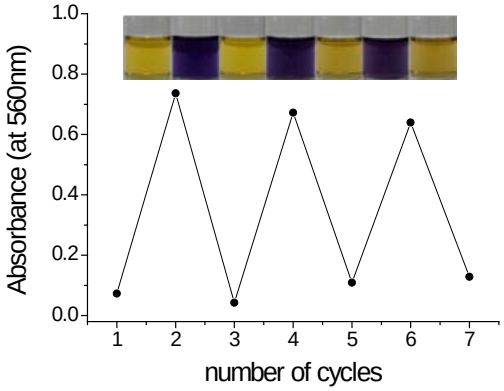


Fig. 6. UV-vis absorption switching cycles of **L1** (2×10^{-5} mol/L) was controlled by alternating addition of TFA and CN^- in DMSO/H_2O (v/v, 85/15). Above are the vials showing visual color change.

To investigate the practical application of probe **L1**, test strips were prepared by immersing filter papers into a DMSO solution of **L1** (0.1 M) and then drying in the air. The test strips containing **L1** were utilized to sense CN^-. As shown in Fig. 7, the obvious color changes were observed when CN^- water solution was added to the test kits. Therefore, convenient colorimetric CN^- test kits were made.

Fig. 7 Photographs of the **L1** based test strips colorimetric detecting CN^- (from left to right: free test strip, test strip + CN^-).

To further elucidate the binding mode of the probe **L1** with CN^-, ^1H NMR-titration spectra were undertaken, which illustrated the characteristic structural changes that occurred upon interaction with CN^- in DMSO-d_6/D_2O. As shown in Fig. 8, Probe **L1** was dissolved in DMSO-d_6 and CN^- was dissolved in D_2O. Before adding CN^-, the ^1H NMR chemical shift of –N–H on the hydrazone moiety is at 11.49 ppm, because there is an intramolecular hydrogen bond between hydrazone –N–H and ortho nitro groups in the molecule of **L1** (Fig. 9). This hydrogen bond enhanced the acidity of the –N–H group. After the addition of 0.2 equiv. CN^-, the signal of the –N–H proton shifted downfield. With the continuous addition of CN^-, the –N–H signal completely disappeared; meanwhile, the proton signals on furanyl shifted upfield. These phenomena indicated that the –N–H group might undergo a deprotonation process (Fig. 9). The deprotonation process induced the color changes of the **L1** solution.

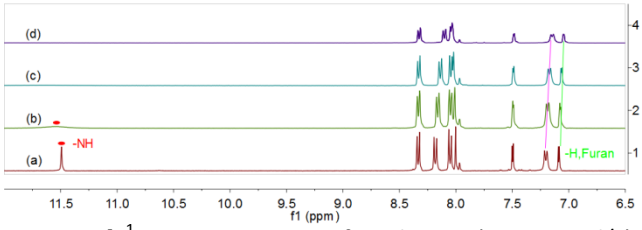


Fig. 8 CN^- ^1H NMR titration of probe **L1** (10.0 mmol/L) in DMSO-d_6: (a) **L1** only, (b) **L1** + 0.2 equiv. of CN^-, (c) **L1** + 0.5 equiv. of CN^-, (d) **L1** + 1.0 equiv. of CN^-.

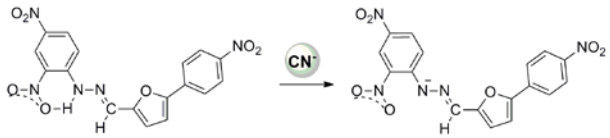


Fig. 9 A possible mechanism of **L1** response to CN^-.

4. Conclusion

Both **L1** and **L2** were developed as colorimetric probes for the selective and sensitive sensing of CN^- ion in aqueous solutions. The investigation of the recognition mechanism indicated that the probe **L1** recognized CN^- by deprotonating process, and the reversibility tested with the addition of TFA to the deprotonated species further confirmed this mechanism. The CN^- recognition process can hardly be influenced by the interference of coexisting anions. Moreover, the probe **L1** allows the detecting limit at 5×10^{-6} mol/L of CN^- by simple UV-vis analysis. Thus, **L1** can be used as a colorimetric probe for detecting CN^-. Furthermore, it exhibits a nice selectivity to CN^- in solution according to the fabricated test strips based on **L1**, showing that the test strips could act as convenient and efficient CN^- test kits.

Acknowledgement

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