



A Highly Selective Colorimetric Chemosensor for Instant Detection of Cyanide in Aqueous Solution

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An easy-to-make colourimetric chemosensor (L) for detection of cyanide anion was designed and synthesized. The chemosensor (L) showed the excellent colourimetric specific selectivity and high sensitivity in the recognition for CN^- and can be distinguished by naked-eyes and UV-visible spectra changes in aqueous solutions (DMSO/ H_2O , 5:5, v/v). The detection limits were 5×10^{-5} and $1.6 \times 10^{-7} \text{ mol L}^{-1}$ for CN^- using the visual colour changes and UV-visible spectra changes respectively. The colourimetric test strips detected CN^- easily and rapidly.

Keywords: Cyanide anion, Colorimetric, Azosalicylic aldehyde, Nucleophilic addition, test kit.

INTRODUCTION

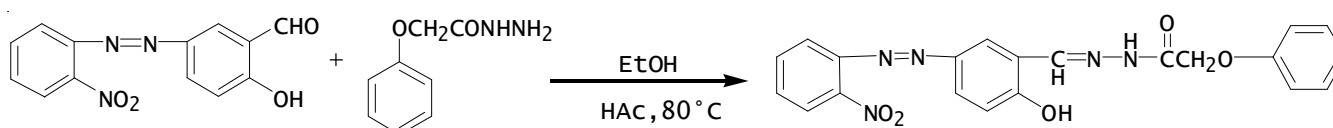
Development of anion sensors is a great interest in supramolecular chemistry due to their chemical¹ and biological importance^{2,3}. Among various anions, cyanide is known to be extremely toxic to living organisms, which can affect many functions in the human body, including the vascular, visual, central nervous, cardiac, endocrine and metabolic systems^{4,5}. However, cyanide anions are widely used in industry, such as in the synthesis of nitriles, nylon, acrylic plastics, fertilizers, precious metal mining and metal plating. According to the World Health Organization, the maximum acceptable level of cyanide in drinking water is $1.9 \mu\text{M}$ ⁶. Thus, cyanide sensing has drawn ever increasing interests in the field of chemical and environmental sciences.

In recent years, the powerful Michael addition reaction has been successfully used in the design of the colorimetric and fluorescent chemosensors for cyanide⁷⁻⁹. In spite of this, the number of colorimetric cyanide sensors is still rather limited compared with other anion sensors. Moreover, most of these methods require expensive equipment and involve time consuming and laborious procedures¹⁰.

In view of this requirement and the research effort devoted to anion recognition^{7-9,11-13}, an attempt was made to obtain efficient colorimetric sensors which could sense CN^- with specific selectivity and high sensitivity in aqueous solution (**Scheme-I**). Thus, the design of receptor as the chemosensor was mainly based on the fact that: (i) the receptor contains both phenol -OH and -NH groups as the binding sites; (ii) in order to achieve "naked-eye" recognition, the nitrophenylazobenzol group as the chromophore was designed. Finally, the sensor was designed to be easy to synthesize.

EXPERIMENTAL

Melting points were measured on X-4 digital melting-point apparatus and were uncorrected. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. Mass spectra were measured with a Bruker Daltonics Esquire 6000. Fluorescence spectra were recorded on a Shimadzu RF-5301 fluorescence spectrometer. ¹H NMR spectra were recorded on a Varian Mercury plus-400 MHz spectrometer with DMSO as solvent and analytical grade TMS as an internal reference.



Scheme-I: Synthetic procedure for receptor L

L

All the UV-visible experiments were carried out in DMSO or H₂O/DMSO binary solutions on a Shimadzu UV-2550 spectrometer. Any changes in the UV-visible spectra of sensor L were recorded upon the addition of TBA salts while keeping the concentration of sensor L constant in all experiments.

Synthesis and characterize: Compound L was prepared by mixing azosalicylic aldehyde (270 mg, 0.1 mol) and 2-phenoxyacetohydrazide (166 mg, 0.1 mol) in absolute alcohol (40 mL) under stir in room temperature for 8 h with 0.2 mL HAc as catalyst, then the crude product was purified by recrystallisation from ethanol to give compound L.

Compound L was obtained as a yellowish solid. Sensor L: (Yield: 78 %), m.p.: 203-205 °C. ¹H NMR (DMSO-*d*₆, 400 MHz ppm) δ: 11.94 (s, 1H, OH), 11.68 (s, 1H, NH), 8.71 (s, 1H, N=CH), 8.39-8.08 (m, 4H, Ar-CH), 7.89-7.67 (m, 3H, Ar-CH), 7.35-7 (m, 5H, Ar-CH), 5.15 (s, 1H, CH), 4.7 (s, 1H, CH); IR (KBr, ν_{max}, cm⁻¹): 3428 (-OH), 3162 (N-H), 1672 (C=N-H); MS/(EI): *m/z* 420.2 (M + H)⁺. Anal. Calc. for C₂₁H₁₇N₅O₅: C, 59.97; H, 4.05; N, 16.66. Found: C, 59.88; H, 4.12; N, 16.45.

RESULTS AND DISCUSSION

The sensing abilities of L toward various anions, such as F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻ and CN⁻ were investigated by UV-visible spectra. When 50 equivalent (equiv.) of CN⁻ was added to the solution of L (2 × 10⁻⁵ M), the sensor responded with dramatic colour changes from colourless to yellow. In the corresponding UV-visible spectra, two new and strong absorption peaks appeared at 375-475 nm. Whereas when adding the anions F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻ into the DMSO/H₂O (5:5, v/v) solutions of sensor L, no significant colour or spectra changes were observed (Fig. 1 (a)). With the aim of excluding the possibility of these results being due to pH changes, we carried out experiments in DMSO/H₂O (5:5, v/v), HEPES (10 mM) buffered solutions at pH = 7.04 for sensor L. To validate the selectivity of L, the same tests were applied to other anions; no obvious changes were observed. Therefore, in DMSO/H₂O (5:5, v/v) solutions, L showed specific colorimetric selectivity to CN⁻ (Fig. 1 (b)).

In order to investigate the CN⁻ recognition capability and mechanism of L, a series of experiments were carried out, hoping gain an insight into the stoichiometry of the L-CN⁻ adduct. The method of continuous variations (Job's method) was used (Fig. 2). When the molar fraction of sensor L was 0.45, the absorbance value approached a maximum, which demonstrated the formation of a 1:1 adduct between the sensor L and CN⁻.

The association sensor L and CN⁻ were investigated by UV-visible titration (Fig. 3). The absorption change of the sensor L was monitored in DMSO/H₂O (5:5, v/v) solutions. The intensity of the UV-visible spectra gradually changed as the concentration of CN⁻ anions increased. With the increasing concentration of CN⁻, an isosbestic point was clearly observed at 370 nm. This suggested that sensor L reacted with CN⁻ and formed a stable adduct. By nonlinear least squares fitting at λ_{max} = 475 nm for sensor L, the association constant K_a of the sensor L towards CN⁻ was obtained as 9.68 × 10⁴ M⁻¹ (R = 0.999).

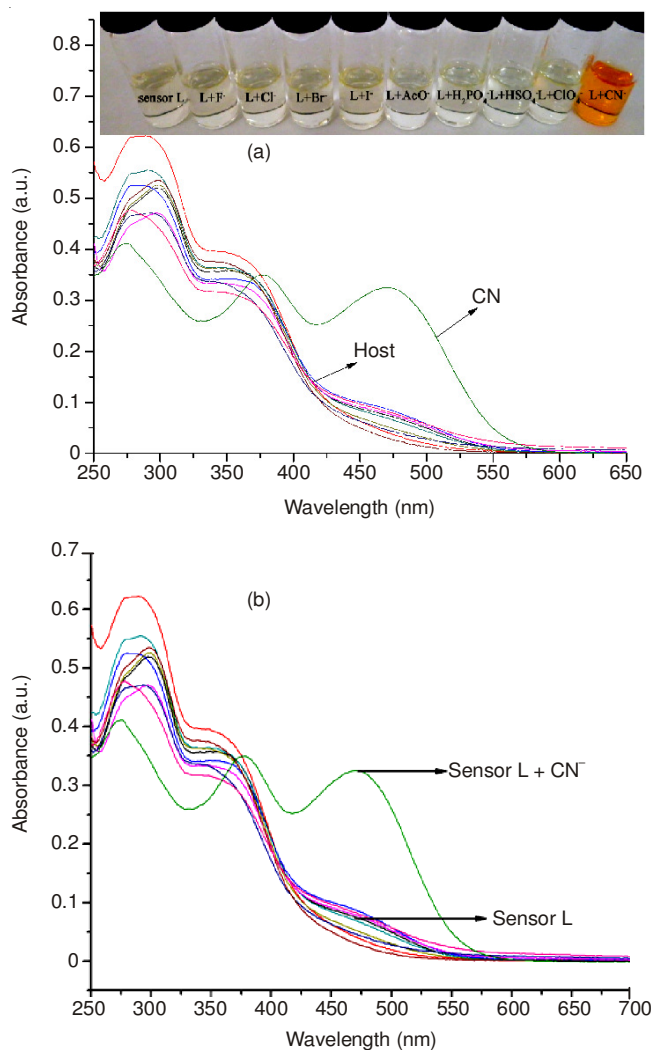


Fig. 1. (a) UV-visible absorption changes of sensor L (20 μM) with various anions (50 equiv.) in (DMSO/H₂O, 5:5, v/v). Inset: The color changes of sensor L with various anions. (b) UV-visible absorption changes of sensor L (20 μM) with various anions (50 equiv.) in (DMSO/H₂O, 5:5, v/v) HEPES buffered solution at pH = 7.04

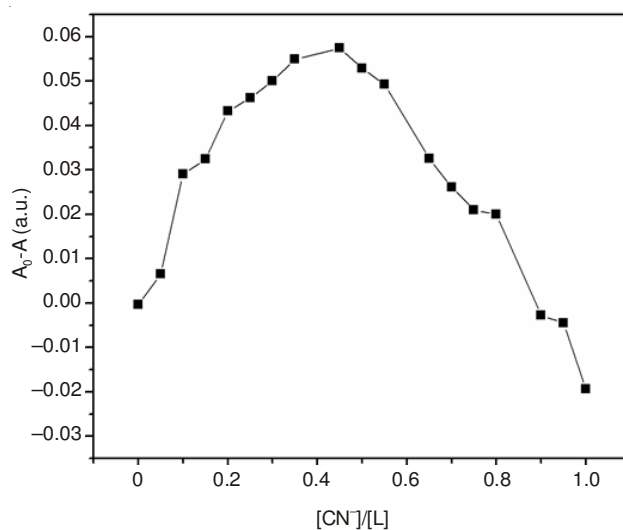


Fig. 2. Job plot of L and CN⁻ at a total concentration of 2 × 10⁻⁵ M, [CN⁻] + [L] = 20 μM at 298.2 ± 0.2 K. A and A₀ stand for the absorbance of the whole system of sensor L + CN⁻ and the absorbance of free sensor L, respectively

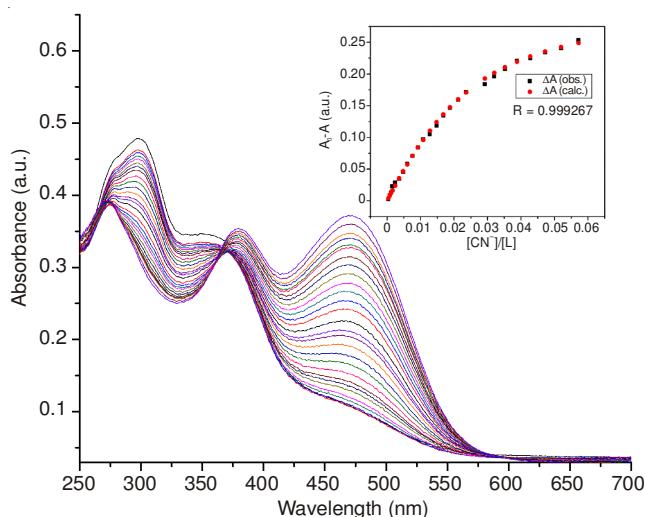


Fig. 3. UV-visible titration of 2×10^{-5} M solution of L with a standard solutions of CN^- in DMSO/ H_2O (5:5, v/v); Inset: The best fitting curves by a 1:1 addition model of L and CN^- . A and A_0 stand for the absorbance of the whole system of sensor L + CN^- and the absorbance of free sensor L, respectively

To further elucidate the binding mode of the sensor L with CN^- , ^1H NMR-titration experiments were carried out by gradually adding CN^- into DMSO- d_6 solution of L. As shown in Fig. 4, before the addition of CN^- , the original signals of $-\text{OH}^a$ and $-\text{NH}^b$ protons appearing at 11.94 and 11.68 ppm. After adding 0.1 equiv. of CN^- , the signals of $-\text{OH}^a$ and $-\text{NH}^b$

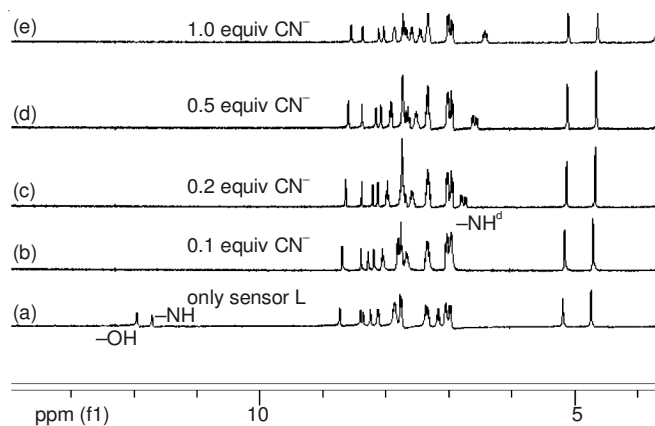


Fig. 4. ^1H NMR spectra of sensor L and the presence of CN^- in DMSO- d_6 : (a) sensor L only, (b) sensor L + 0.1 equiv. of CN^- , (c) sensor L + 0.2 equiv. of CN^- , (d) sensor L + 0.5 equiv. of CN^- and (e) sensor L + 1 equiv. of CN^-

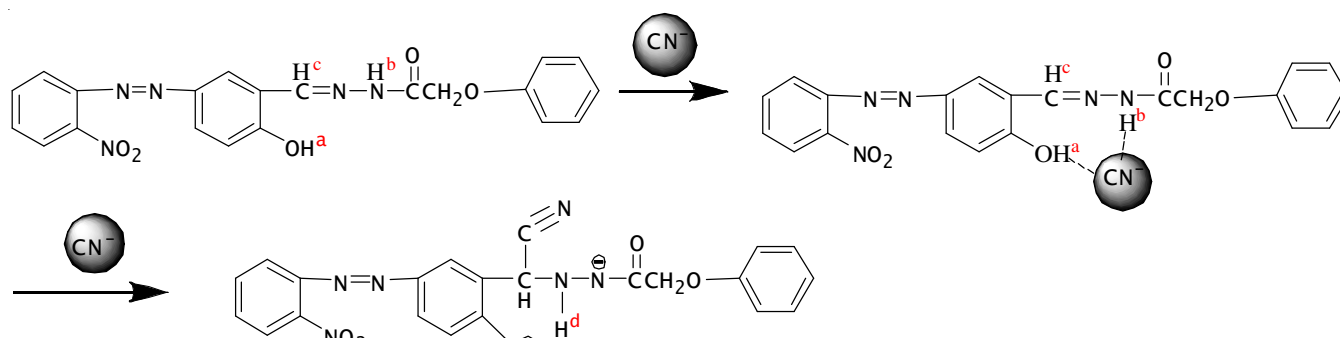


Fig. 5. Proposed binding mode of L with CN^- in aqueous solutions

protons obvious decreased, which suggested that CN^- is combined with sensor L by hydrogen bonding and the $-\text{OH}$ and $-\text{NH}$ groups participated in hydrogen bonding with CN^- . When 0.2 equiv. of CN^- was added, a new signal appeared at 6.81 ppm corresponding to the α -proton (H^d). With the addition of 0.5 equiv. of CN^- , the peak of α -proton (H^d) had an upfield shift. Meanwhile, the aromatic proton displayed a small upfield shift compared to those of L due to the breaking of the conjugation. These obviously indicated that the cyanide anion was added to the $-\text{C}=\text{N}$ group and combined in the ratio of 1:1 between L and CN^- anion.

Furthermore, this formation of L- CN^- adduct was also characterized by mass spectrometry analysis. It revealed that after the addition of CN^- into the solution of L, a relatively weak peak at about 442.2 appeared, coinciding well with that for the species $[\text{L} + \text{CN}]^-$ ($m/z_{\text{calcd}} = 443$), indicating the formation of the stabilized anionic species, in which the peak at m/z 420.2 corresponding to the species $[\text{L} + \text{H}]^+$ ($m/z_{\text{calcd}} = 420$) were clearly observed. From the UV-visible and ^1H NMR titration spectra, a possible binding model of sensor L with CN^- was proposed (Fig. 5). These results reveal that the binding process includes two stages: (i) hydrogen bonding interactions; (ii) CN^- was added to the $\text{C}=\text{N}$ group of sensor L.

For many practical purposes, the detection limit is one of the most important parameters in anion sensing. So the colorimetric and UV-visible limits of sensor L for CN^- were also tested and presented in Figs. 6 and 7. The detection limit using visual colour changes was a concentration of 5×10^{-5} M for CN^- in solution of sensor L, while the detection limit of the UV-visible changes calculated on the basis of $3S_B/S$ is 1.6×10^{-7} M (0.16 μM) for CN^- anions¹⁴. The result can also be calculated from the cyanide quantities added which made the initial changes of absorbance of sensor L during the process of UV-visible titration (DMSO/ H_2O , 5:5, v/v), pointing to the high detection sensitivity. It could be used to detect the WHO suggested maximum allowed cyanide concentration in drinking water (1.9 μM).

To investigate the practical application of sensor L, we prepared test strips by immersing filter papers into a solution of sensor L (1×10^{-3} M) in DMSO, then dried them in air to determine the suitability of a "dipstick" method for the detection of CN^- , similar to that commonly used for pH measurements. When the test strips coated with L were immersed into a solution of sodium cyanide in water, the obvious colour

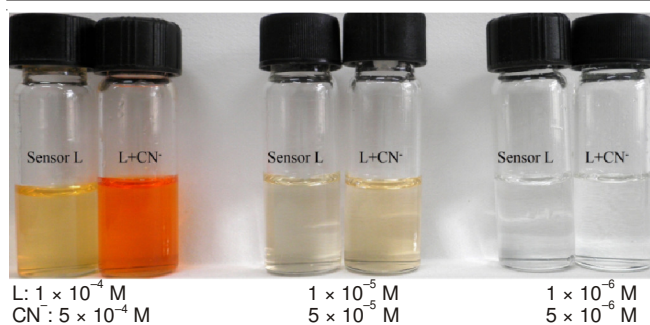


Fig. 6. Colour changes observed upon the addition of 50 equiv. of CN^- to the solutions of sensor L (from left to right, 1×10^{-4} M, 1×10^{-5} M, 1×10^{-6} M) in DMSO/ H_2O (5:5, v/v) solutions

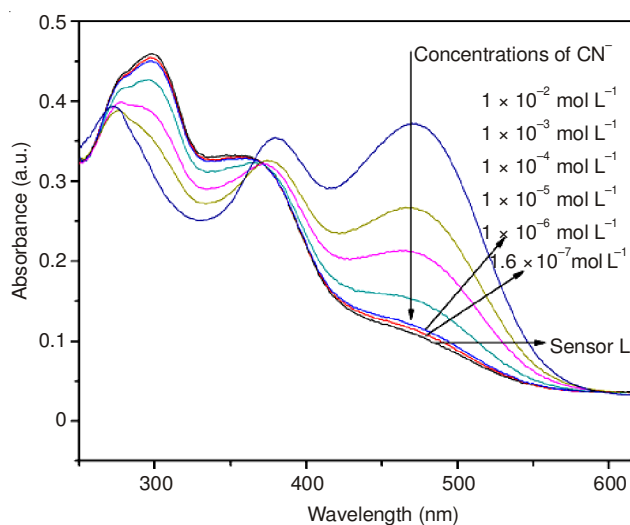


Fig. 7. Detection limitation of sensor L toward CN^- in DMSO/ H_2O (5:5, v/v) solutions

change from colourless to yellow was observed (Fig. 8) and no significant colour changes for other anions tested. Therefore the colorimetric test strips would have potential application to detect CN^- anion easily and rapidly.

Conclusion

In summary, an easy-to-make chemosensor L was designed and synthesized. It showed high selectivity and sensitivity to CN^- in DMSO/ H_2O binary solutions. UV-visible spectra showed that sensor L was a good sensor in single selective colorimetric recognition for CN^- over other anions such as F^- , Cl^- , Br^- , I^- , AcO^- , H_2PO_4^- , HSO_4^- and ClO_4^- in DMSO/ H_2O , (5:5, v/v). Naked eye detectable colour changes and single colorimetric recognition for CN^- anions made it possible to carry out practical application in detecting CN^- . The sensor behaved high selectivity to CN^- in DMSO/ H_2O binary solutions and was not influenced by miscellaneous anions. It showed remarkably high sensitivity toward CN^- down to 1.6×10^{-7} M. Which indicated

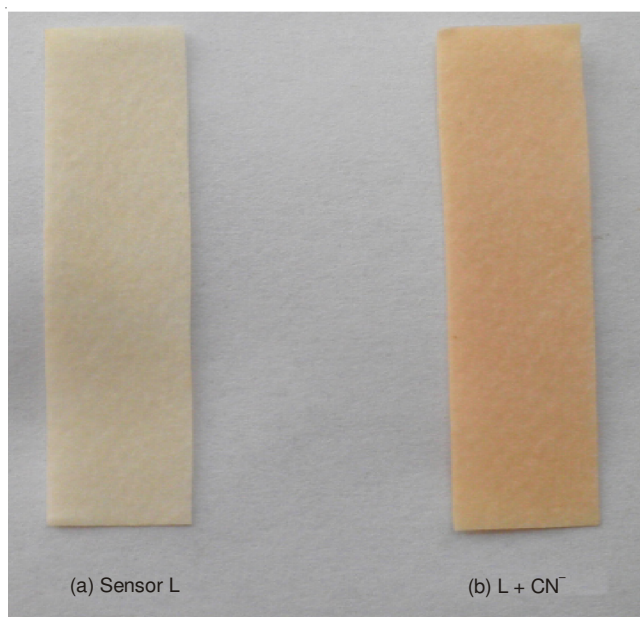


Fig. 8. Photographs of the colorimetric test kit with L for detecting CN^- anion in aqueous solutions. (a) Before the addition of CN^- anions and (b) after the addition of CN^- anions

that the sensor L potentially be useful as a chemosensor for monitoring CN^- levels in physiological and environmental systems.

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