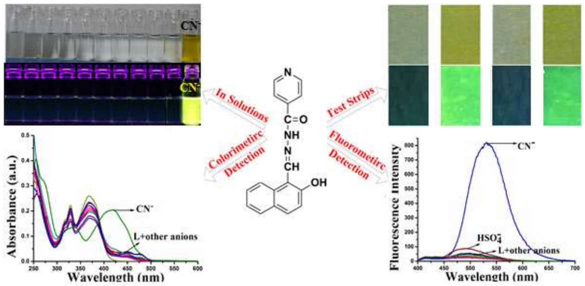
Volume 1 | Number 1 | Jan 2013 | Pages 1–100
NJC
New Journal of Chemistry
www.rsc.org/njc
A journal for new directions in chemistry
ROYAL SOCIETY OF CHEMISTRY
cnrs

Graphical Abstract

Selective colorimetric and "turn-on" fluorimetric detection of cyanide using an acylhydrazone sensor in aqueous media

Jing-Han Hu[*], Jian-Bin Li, Jing Qi, You Sun



Graphical abstract: A simple cyanide highly selective and sensitive fluorescent enhanced chemosensor **L** based on acylhydrazone group as binding site and naphthalene group as the fluorescence signal group had been designed and synthesized.

NJC

New Journal of Chemistry

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

PAPER

Selective colorimetric and “turn-on” fluorimetric detection of cyanide using an acylhydrazone sensor in aqueous media

JingHan Hu[*], JianBin Li, Jing Qi, You Sun

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A simple cyanide selective colorimetric and fluorimetric chemosensor **L** was designed and synthesized, which showed both a colorimetric and a fluorescence turn-on response for cyanide ions in aqueous solution with specific selectivity and high sensitivity. The probe shows an immediate visible change in color from colorless to yellow only after the addition of CN^- in aqueous solution; these color changes can be readily observed visually. Moreover, the detection limit on fluorescence response of the sensor to CN^- is down to 1.20×10^{-9} M, which is far lower than the maximum level for cyanide of 1.9×10^{-6} M in drinking water from WHO guidelines. Test strips based on **L** were fabricated, which could act as a convenient and efficient CN^- test kit to detect CN^- in aqueous solution for “in-the-field” measurement.

1. Introduction

The cyanide anion (CN^-) is known to be an extremely toxic anion and can directly lead to the death of human beings in several minutes because it strongly binds cytochrome-c, thereby disrupting the mitochondrial electron-transport chain and causing a decreased oxidative metabolism and oxygen utilization [1-2]. The cyanide ion also detrimentally affects vascular, visual, central nervous, cardiac, endocrine, and metabolic functions. However, cyanide toxicity, large quantities of cyanide salts are still widely used in industrial production such as metallurgy (1.5 million tons per year), electroplating, and the synthesis of fine chemicals [3]. As a result, the purposeful design and synthesis of efficient chemosensors to selectively detect CN^- ion at the environmental and biological fields have been in recent years attracted much attention. Although a wide variety of chemical and physical sensors for the detection of CN^- have been reported [4-5], most of physical methods require expensive and sophisticated equipment or involve time-consuming and laborious procedures that can be carried out only by well-trained professionals, which seriously stumbling block to the practical application of these CN^- sensors [6]. For purposes of simplicity, convenience, easily prepared and high sensitivity [7] CN^- colorimetric and fluorimetric chemodosimeter have become particularly attractive.

Several organic molecules and transition metal complexes able to signal the presence of cyanide based on supramolecular approaches according to the hydrogen-bonding motifs with dramatically changes in their absorption and emission properties have been already identified [8-14]. Some of these chemosensors can even detect micromolar amounts of cyanide [15-19]. However, some of them suffer the severely interference from coexisting anions such as F^- [11], AcO^- [13], and $H_2PO_4^-$ [15]. In addition, many of them are reported to work only in organic media [20-22], but relatively few of them result in spectral changes in both absorption and emission spectra. Therefore, it is still worthwhile to exploit new colorimetric and “Turn-on” fluorimetric sensors for selective recognition of toxic anions (CN^-) in the organo-aqueous media and then in pure water solution for environment system or biological applications.

Our research group has a longstanding interest in molecular recognition [23]. Herein, we have designed and synthesized a compound (**L**), **L** as probe for cyanide comprising 2-hydroxy-1-napthaldehyde and isoniazid functionalities. Receptor **L** possesses a hydroxyl and it is well-established that the OH group due to strong acid is readily deprotonated when basic ions appear. The naphthalene group is introduced as fluorophore to achieve fluorescent recognition. Sensor **L** showed fluorescent and UV-vis selectivity for CN^- in $DMSO/H_2O$ (6:4, v/v) binary solution over other anions. The detection limit on fluorescence response of the sensor to CN^- is down to 1.22×10^{-9} M, which indicates that this sensor could potentially be useful as a probe for monitoring CN^- levels. The mechanism of this process has been investigated by ^1H NMR and UV spectrum and ESI-mass spectrometry.

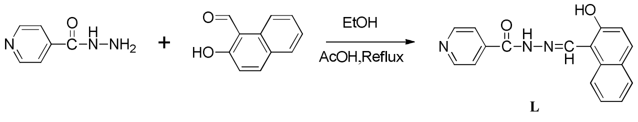
2. Experimental section

2.1. Materials and physical methods

Fresh double distilled water was used throughout the experiment. The tetrabutylammonium salts and N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid (HEPES) were purchased from Alfa Aesar Chemical Reagent Co. (Tianjin, China). All reagents and solvents were commercially available at analytical grade and were used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Mercury-400BB spectrometer at 400 MHz and 100 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards) UV-vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Shimadzu RF-5301 fluorescence spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus was purchased from Beijing Tech Instrument Co. (uncorrected). Infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer.

2.2. Synthesis of sensor L

The synthesis route of receptor molecule **L** is demonstrated in Scheme 1. To an ethanol solution (25 mL) of 2-hydroxy-1-naphthaldehyde (0.86g, 5 mmol) and isoniazid (0.54g, 5 mmol) to the solution. Then, the reaction of mixture solution was stirred and refluxed 6h. After cooling to room temperature, quietly placed, produced a large number of yellow precipitation, filtered and washed with distilled ethanol three times, then recrystallized with absolute ethanol to get yellow crystal of **L** in 89% yield (m.p. 273-275 □), ^1H NMR (400 MHz, DMSO) δ: 12.54 (s, 1H), 12.42 (s, 1H), 9.49 (s, 1H), 8.85 (d, J = 4.3 Hz, 2H), 8.33 (d, J = 8.5 Hz, 1H), 8.08-7.74 (m, 4H), 7.64 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.3 Hz, 1H), 7.26 (d, J = 8.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ: 160.96, 158.12, 150.39, 147.94, 139.74, 133.03, 131.56, 128.90, 127.80, 123.53, 121.35, 120.83, 118.75, 108.46. IR (KBr) v: 3447.66 cm^{-1} (−OH), 3218.90 cm^{-1} (−NH), 3038.39 cm^{-1}, 1576.92 cm^{-1} (C=N−H), 1680.77 cm^{-1} (−C=O). ESI-MS calcd for $C_{17}H_{13}N_3O2$+H 292.10, found 292.02.



Scheme 1. Synthetic procedures for receptor **L**.

2.3. General procedure

All UV-vis spectroscopy and all fluorescence spectroscopy was carried out just after the addition of tetrabutylammonium anion salt (0.01 M) in $DMSO/H_2O$ (6:4, v/v) solution, while keeping the ligand concentration constant (2.0×10^{-5} M) on a Shimadzu UV-2550 spectrometer and a Shimadzu RF-5301spectrometer. The solution of anions were prepared from the tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, SCN^-, but CN^- was prepared in NaCN. The excitation wavelength was 368 nm.

For ^1H NMR titrations, the sensor of stock solutions was prepared in DMSO-d_6, the cyanide anion was prepared in distilled water. Aliquots of the two solutions were mixed directly in NMR tubes.

Test strips were prepared by immersing filter papers into a $DMSO/H_2O$ (6:4, v/v) binary solution of **L** (0.01 M) followed by exposure to air until complete drying. The test strips containing this sensor **L** were utilized to detect CN^- and other cations.

3. Results and Discussion

Receptor was found to have limited solubility in water, and this compelled us to use these sensor in mixed solvent, such as $H_2O/DMSO$ (4:6, v/v), for recognition studies of **L**. UV-vis absorption spectral response of chemosensor **L** was tested with aqueous solutions of the tetrabutylammonium salts of all common anionic analytes such as (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^- and SCN^-) as well as CN^-. The solution of **L** resulted in an immediate change in color from colorless to yellow (Fig. 1). In the corresponding UV-vis spectrum, two strong absorption band at 328 nm and 368 nm disappeared, while a new band developed at 420 nm after addition of CN^- (Fig. 2). All examined anions including the more basic and nucleophilic ones such as F^- and SCN^- did not cause any obvious color and spectral changes. These results suggested that sensor **L** displayed an excellent selectivity for CN^- over all other anions tested.

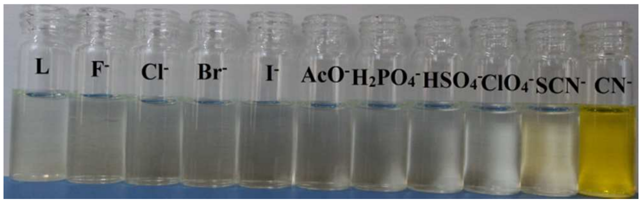


Fig. 1. Color changes observed upon the addition of various anions (50 equiv.) to solutions of sensor **L** (2×10^{-5} M) in DMSO/H_2O (6:4, v/v) solutions.

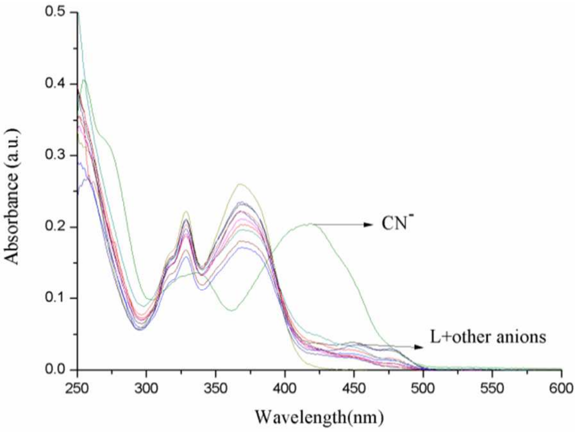


Fig. 2. UV-vis spectra changes of **L** (2×10^{-5} M) and in the presence of 50 equiv. of various anions in H_2O/DMSO (4:6, v/v) binary solution at room temperature.

Compound **L** alone displays a weak, single fluorescence emission band at 494 nm when excited at 368 nm in aqueous media H_2O/DMSO (4:6, v/v), which exhibits a low quantum yield (Φ_R = 0.14). Changes in spectral pattern were observed only in the presence of added 50 equivalent of CN^-, chemosensor **L** produced a strong fluorescence response band and shifted toward 530 nm, with a increasement quantum yield (Φ_R = 0.42), and responded with a dramatic color change, from pale colorless to yellow. No change in spectral pattern for receptor **L** in the presence of other anions suggests either a very weak or no interaction between these anions and the compound (Figs. 3 and 4).

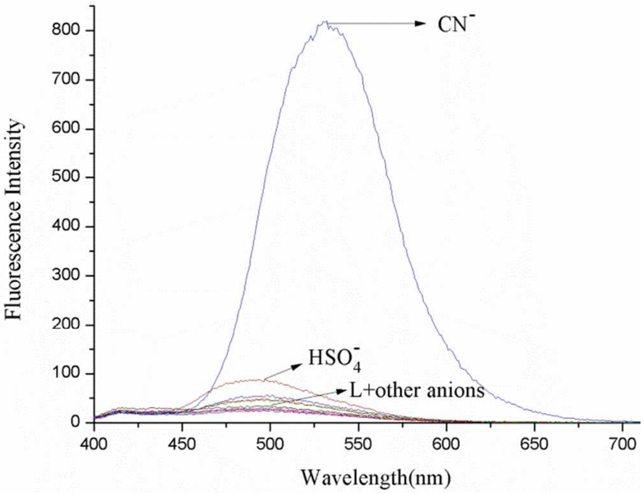


Fig. 3. Fluorescence spectra of **L** (2×10^{-5} M) and in the presence of 50 equiv. of various anions in H_2O/DMSO (4:6, v/v) binary solution at room temperature.

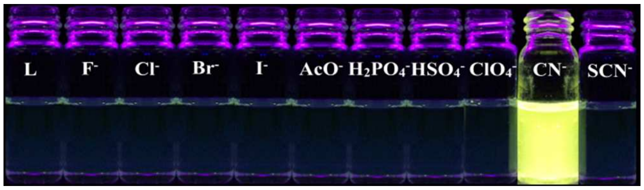


Fig. 4. Color changes observed upon the addition of various anions (50 equiv.) to solutions of sensor **L** (2×10^{-5} M) in DMSO/H_2O (6:4, v/v) solutions, which was taken under a UV-lamp (365 nm).

To validate the selectivity of sensor **L**, various anions including F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^- and SCN^- contacting with **L** were investigated by UV-vis absorption and fluorescence spectra. Among various anions, only the addition of cyanide displayed noticeable color changes from colorless to yellow. Fluorescence spectra showed that **L** had a high selectivity for cyanide ion, other anions almost caused no change in fluorescence. This highly selective detection of cyanide could be demonstrated even in the presence of other anions (Figs. 5 and 6). The selectivity of cyanide over other anions, especially F^-, AcO^-, and $H_2PO_4^-$ is important because many reported cyanide sensors suffer from deleterious interference of these anions.

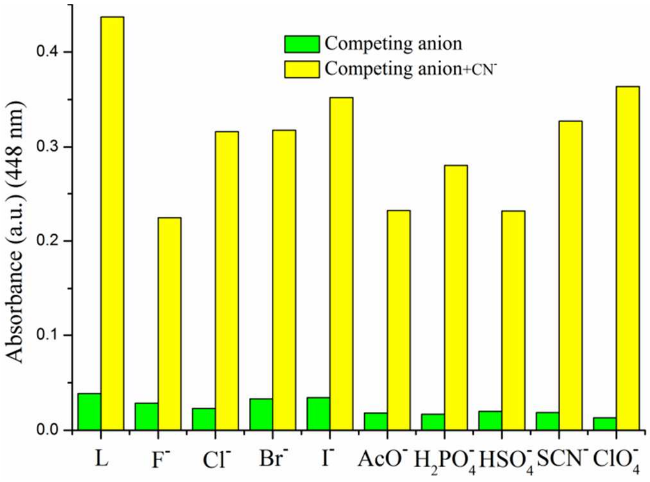


Fig. 5. Absorbance spectra of **L** (2×10^{-5} M) in the presence of various anions (50 equiv.) in DMSO/H_2O (6:4, v/v) in response to CN^- (50 equiv.).

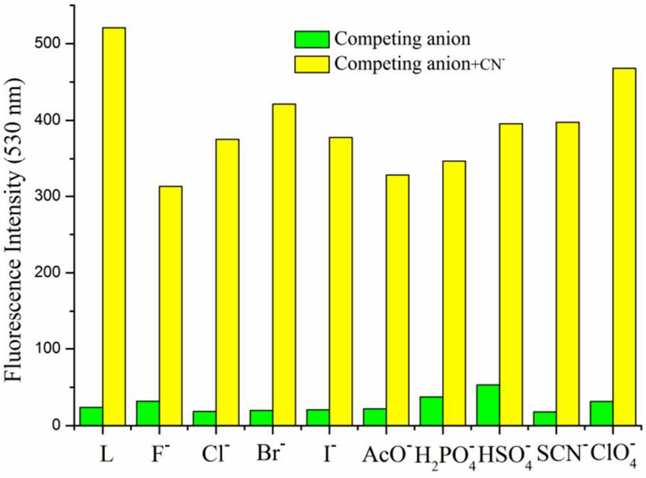


Fig. 6. Fluorescence spectra of **L** (2×10^{-5} M) in the presence of various anions (50 equiv.) in DMSO/H_2O (6:4, v/v) in response to CN^- (50 equiv.).

The detection limit is one of the most important parameters in ion sensing. For many practical purposes, it is very important to detect the analytes at low concentrations. The fluorimetric detection limits of sensor **L** for CN^- were also determined. The detection limit of the fluorescence measurements, as calculated on the basis of $3S_B/S$ [24] (where S_B is the standard deviation of the blank solution and S is the slope of the calibration curve), Fig. 7 showed the detection limit of 1.20×10^{-9} M for CN^-, which is far lower than the maximum level for cyanide of 1.9×10^{-6} M in drinking water from WHO guidelines.

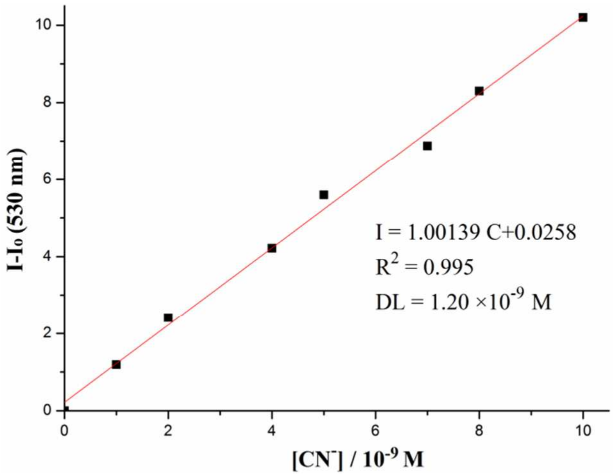


Fig. 7. Fluorescence detection limit spectra of **L** (2×10^{-5} M) in (H_2O/DMSO, 4:6, v/v) solution upon adding of an concentration of CN^- (1×10^{-4} M).

The photophysical and photochemical phenomena of **L** (0.01 M) in the presence of cyanide were assumed to undergo the deprotonation of hydroxyl and amino groups by CN^- (0.5 M). NMR spectra showed a strong evidence to support this assumption (Fig. 8). According to ^{1}H NMR spectra of **L** and CN^-, the protons signal of –OH and –NH at 12.54 (s, 1H) and 12.42 (s, 1H) ppm had completely disappeared, which stated clearly the –OH and –NH had deprotonation and the other aromatic proton chemical upfield shifts from 9.49-7.26 to 9.02-6.79 ppm. This indicated that the aromatic protons were shielded by the negative charge of the deprotonated hydoxyl group.

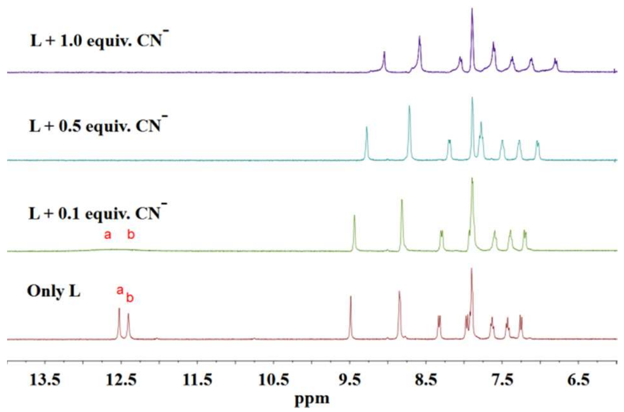
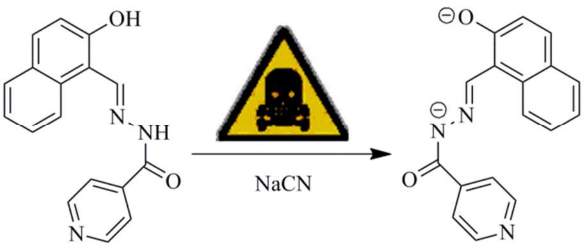


Fig. 8. Partial ^{1}H NMR spectra of **L** (0.01 M) and in the presence of varying amounts of CN^- (0.5 M).

This deprotonation caused a high charge separation between acceptor and donor unit in **L**, and consequently excellent electron delocalization to isoniazid unit. The excited states in the complexes were stabilized upon the binding of CN^-, resulting in a bathochromic shift in the absorption band with $\Delta\lambda$=81 nm for **L**. Moreover, a new emission band at 530 nm for **L** and CN^- was observed. It possibly caused by a large charge separation between isoniazid unit and the naphthalene rings resulting in a strong intramolecular charge transfer (ICT). Consequently, the observed fluorescence enhancement is most likely caused by the ICT. A schematic illustration is shown in Scheme 2. Therefore, it can be clearly seen the chemosensors **L** selectively response of cyanide over other anions such as F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^- and SCN^- in aqueous media (H_2O/DMSO, 4:6, v/v).



Scheme 2. Possible sensing mechanism.

The selective detecting properties of **L** towards CN^- can be described by the basicity of anions. The charge transfer process could not occur in the case of fluoride ion due to its high hydration enthalpy and low basicity (ΔH^0_{hyd}=-504 kJ/mol, pK_a=3.18) in an aqueous system [25]. Furthermore, the recognition properties of receptor **L** towards CN^- was carried out by UV-vis and fluorometric titrations. The absorption spectral changes of **L** on addition of cyanide (0.01 M) in DMSO/H_2O (6:4, v/v) solutions are shown in Fig. 9. The absorption band at 368 nm decreased, while a new band at 420 nm appeared. A clear isosbestic point of 395 nm indicated an interconversion into single discrete chemical species during the titration process. Fig. 10 shows the emission spectrum for compound **L** on addition of CN^- (0.1 M). When excited at 352 nm, the emission intensity at 533 nm remarkably increased on changing the concentration of CN^- from 0 to 3.8 μM.

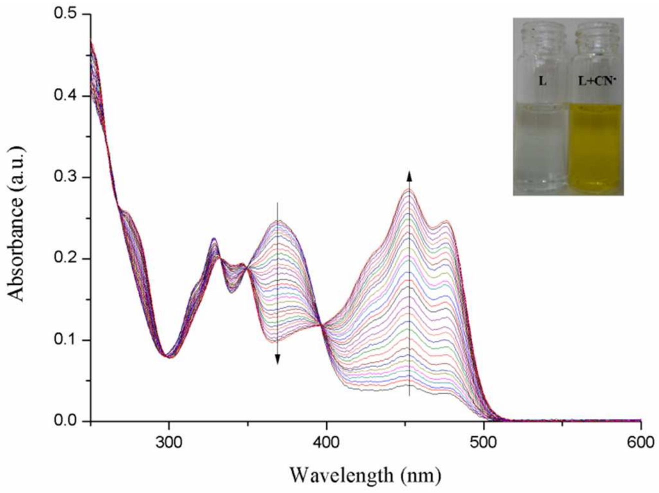


Fig. 9. UV-vis spectra of **L** (2×10^{-5} M) in DMSO/H_2O (6:4, v/v) upon adding of an increasing concentration of CN^- (0.01 M).

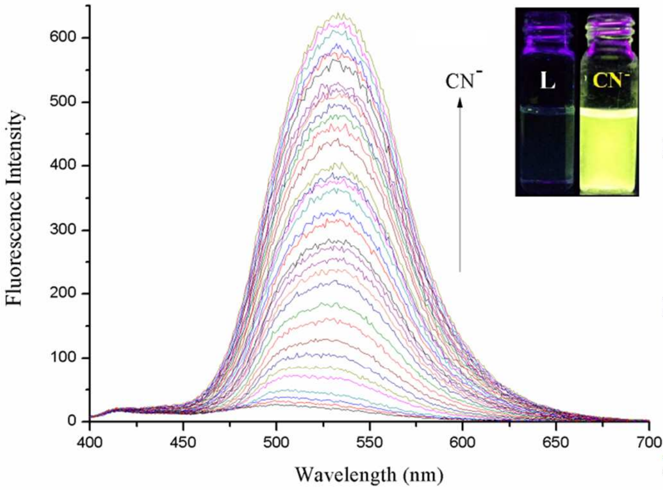


Fig. 10. Fluorescence titration spectra (λ_{ex}=368 nm) of **L** (2×10^{-5} M) in (H_2O/DMSO, 4:6, v/v) solution upon adding of an increasing concentration of CN^- (0.1 M). The inset shows fluorescence change of **L** observed upon excitation at 365 nm after the addition of CN^- anions (0-3.8 μM).

To further investigate the interaction between sensor **L** and CN^-, the infrared spectra were performed and displayed in Fig. 11. The sensor **L** of the stretching vibration absorption peaks at 3447.66 cm^{-1} (−OH), 3218.90 cm^{-1} (−NH), 3038.29 cm^{-1},1576.92 cm^{-1} (C=N−H), 1680.77 cm^{-1} (−C=O), compared with the **L**+CN^- compound the N−H peak at 3218.90 cm^{-1} disappeared, at the same time, the peak of (−C=O) and (C=N−H) at 1680.77 cm^{-1}, 1576.92 cm^{-1} moved to 1605.52 cm^{-1} and 1536.29 cm^{-1}, respectively, which demonstrated receptor **L** reacted with CN^-. Moreover, the mass spectrum obtained and confirmed the sensor **L** ion peak was detected at m/z 292.02, which are corresponding to $[\mathbf{L}+H]^+$ (Fig. S2). The probe with NaCN confirmed the revival of m/z 313.97 also demonstrated the presence of compound $[\mathbf{L}\text{-}2H+Na^++H]^+$ (Fig. S3). Conclusion, the IR and mass spectrum experiments suggested that the sensing mode of chemosensor **L** and cyanide.

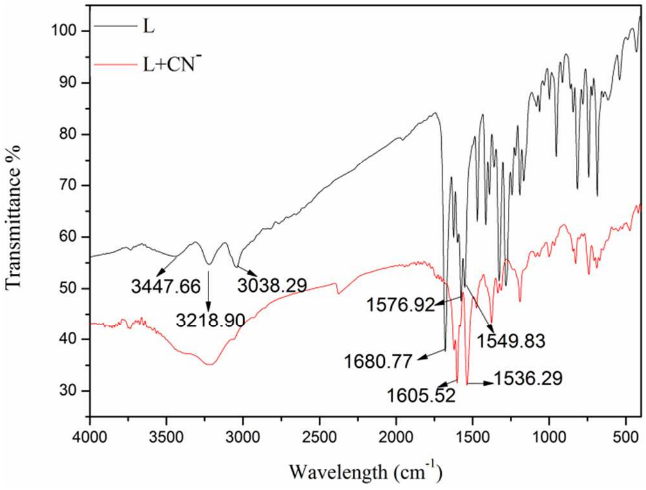


Fig. 11. Infrared spectra of **L** (black line) and its complex **L**+CN^- (red line).

The pH dependence of the sensor **L** in HEPES buffer system was also checked by UV-vis and fluorescent spectroscopy. cyanide ion was added to the buffered solution of **L** at different pH values. No apparent changes of the spectral were observed, the results indicated that the binding of **L** with the CN^- can not work well in the range of pH 1.0-12.0 (Fig. S5).

The realization of quick response to cyanide is quite meaningful for the sensor in its practical application in portable sensing devices. To facilitate the use of **L** for the detection of cyanide, test strips were prepared by immersing filter papers into a DMSO/H_2O (6:4, v/v) binary solution of **L** (0.01 M) following by exposing it to air to dry it. Intriguingly, the fluorescence color can be changed immediately from blue to mazarine once the test paper was immersed into an aqueous solution (5 μM) of cyanide under UV irradiation (Fig. 12). Thereby chemosensor **L** exhibits excellent UV visual and fluorescence sensing performance, which will be very useful for the fabrication of sensing devices with fast and convenient detection for cyanide and ions.

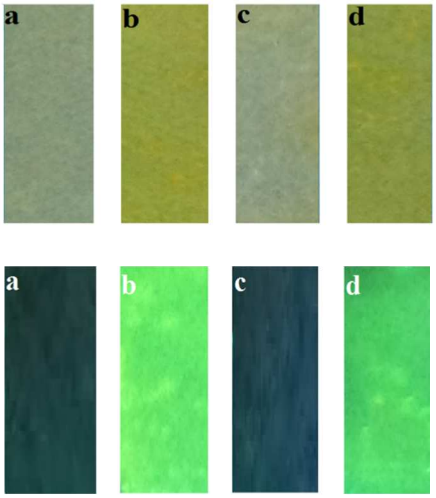


Fig. 12. Photographs of **L** (0.01 M) on test strips (a) only **L**, (b) after immersion into water solutions with CN$^-$, (c) after immersion into water solutions with other anions, (d) after immersion into water solutions with CN$^-$ and other anions under at room temperature and irradiation with UV light at 365 nm, respectively.

4. Conclusions

In conclusion, we have presented a facile, rapid and efficient chemosensor **L**, which showed specially selectivity and highly sensitivity UV-vis absorption and fluorescence recognition for CN$^-$ in DMSO/H$_2$O (6:4, v/v) solutions. Moreover, the sensor demonstrates the detection limit on fluorescence response of the sensor to CN$^-$ is down to 1.20×10^{-9} M, which is far lower than the maximum level for cyanide of 1.9×10^{-6} M in drinking water from WHO guidelines. In addition, test strips based on **L** were fabricated, which could serve as a practical colorimetric and fluorimetric sensor to detect CN$^-$ in field measurements or in test kits. We believe that these characteristics of **L** make it attractive for further molecular modifications and underlying applications as colorimetric and fluorimetric sensor for CN$^-$.

“This work was supported by the the support of the Nature Science Foundation of China (No. 21467012), the Science and Technology Bureau of Lanzhou, Gansu Province of China (No. 2013-4-63).”

Notes and references

College of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu, 730070, P. R. China. E-mail: hujinghan62@163.com

† Electronic Supplementary Information (ESI) available: [Complete experimental procedures and some of the spectroscopic]. See DOI: 10.1039/b000000x/

1 a) M. A. Holland, L. M. Kozlowski, Clin. Pharm. 1986, **5**, 737-741. b) R. Koenig, Science. 2000, **287**, 1737-1738.

2 a) C. Young, L. Tidwell, C. Anderson, Warrendale, 2001. b) F. J. Baud, Hum. Exp. Toxicol. 2007, **26**, 191-201.

3 Q. Lin, X. Liu, T. B. Wei, and Y. M. Zhang, Chem. Asian J. 2013, **8**, 3015-3021.

4 a) L. S. Bark, H. G. Higson, Analyst, 1963, **88**, 751-760. b) D. E. Barnes, P. J. Wright, S. M. Graham, E. A. Jones-Watson, Geostand. Geoanal. Res. 2000, **24**, 183-195.

5 a) Z. C. Xu, X. Q. Chen, H. N. Kim, J. Yoon, Chem. Soc. Rev. 2010, **39**, 127-137. b) J. J. Du, M. M. Hu, J. L. Fan, X. J. Peng, Chem. Soc. Rev. 2012, **41**, 4511-4535. c) Y. Yang, Q. Zhao, W. Feng, F. Li, Chem. Rev. 2013, **113**, 192-270. d) F. Wang, L. Wang, X. Q. Chen and J. Yoon, Chem. Soc. Rev. 2014, **43**, 4312-4324.

6 a) S. Chattaraj, A. K. Das, Analyst. 1991, **116**, 739-741. b) S. Yen, C. T. Wang, J. S. Wang, Chem. Eng. Commun. 1991, **109**, 167-180.

7 a) Y. M. Zhang, Q. Lin, T. B. Wei, X. P. Qin, Y. Li, Chem. Commun. 2009, **45**, 6074-6083. b) B. B. Shi, P. Zhang, T. B. Wei, H. Yao, Q. Lin, Y. M. Zhang, Chem. Commun. 2013, **49**, 781-7814. c) Q. Lin, P Chen, J Liu, Y. P. Fu, Y. M. Zhang, T. B. Wei, Dye. Pigm. 2013, **98**, 100-106. d) T. B. Wei, P. Zhang, B. B. Shi, P. Chen, Q. Lin, J. Liu and Y. M. Zhang, Dye. Pigm. 2013, **97**, 297-303. e) H. B. Yu, Q. Zhao, Z. Jiang, J. G. Qin, Z. Li, Sensors and Actuators B. 2010, **148**, 110-116. f) Q. Zeng, P. Cai, Z. Li, J. G. Qin and B. Z. Tang, Chem. Commun. 2008, 1094-1096. g) X. D. Lou, D. X. Ou, Q. Q. Li and Z. Li, Chem. Commun. 2012, **48**, 8462-8477.

8 L. J. Tang, P. Zhou, K. L. Zhong, S. H. Hou, Sen. Actuators B. 2013, **182**, 439-445.

9 S. Goswami, A. Manna, S. Paul, A. K. Das, K. Aicha and P. K. Nandi, Chem. Commun., 2013, **49**, 2912-2914.

10 H. J. Kim, K. C. Ko, J. H. Lee, J. Y. Lee, J. S. Kim, Chem. Commun. 2011, **47**, 2886-2893.

11 V. Kumar, M. P. Kaushik, A. K. Srivastava, A. Pratap, V. Thiruvenkatam, T. N. Row, Anal. Chim. Acta, 2010, **663**, 77-84.

12 H. S. Jung, J. H. Han, Z. H. Kim, C. Kang, J. S. Kim, Org. Lett. 2011, **13**, 5056-5064.

13 M. O. Odago, D. M. Colabello, A. J. Lees, Tetrahedron, 2010, **66**, 7465-7471.

14 J. Jo, A. Olasz, C. H. Chen, and D. Lee, J. Am. Chem. Soc., 2013, **135**, 3620-3623.

15 J. Q. Li, T. B. Wei, Q. Lin, P. Li, Y. M. Zhang, Spectrochimica Acta Part A 2011, **83**, 187-193.

16 Y. K. Yang and J. S. Tae, Org. Lett. 2006, **8**, 5721-5723.

17 X. H. Huang, X. G. Gu, G. X. Zhang and D. Q. Zhang, Chem. Commun., 2012, **48**, 12195-12197.

18 Y. Kim, H. S. Huh, M. H. Lee, I. L. Lenov, H. Y. Zhao, Chem. Eur. J. 2011, **17**, 2057-2062.

19 T. F. Robbins, H. Qian, X. Su, R. P. Hughes, I. Aprahamian, Org. Lett., 2013, 15, 2386-2389.

20 G. J. Kim, H. J. Kim, Tetrahedron. Lett. 2010, **51**, 185-187.

21 A. O. El-Ballouli, Y. D. Zhang, S. Barlow, S. R. Marder, M. H. Al-Sayah, B. R. Kaafarani, Tetrahedron Lett. 2012, **53**, 661-665.

22 M. Kumar, R. Kumar, V. Bhalla, Tetrahedron. Lett. 2013, **54**, 1524-1527.

23 a) J. H. Hu, N. P. Yan and J. J. Chen, J. Chem. Res. 2012, **36**, 619-622. b) J. H. Hu, N. P. Yan, J. J. Chen, J. B. Li, Chem. J. Chinese U. 2013, **34**, 1368-1373. c) J. B. Li, J. H. Hu, J. J. Chen, J. Qi, Spectrochim. Acta A: Mol. Biomol. Spectrosc. 2014, **133**, 773-777. d) J. H. Hu, J. B. Li, J. Qi, J. J. Chen, N. J. Chem. 2015, **39**, 843-848. d) J. H. Hu, J. B. Li, J. Qi, Y. Sun, Sensors and Actuators B. 2015, **208**, 581-587.

24 Analytical Methods Committee, Analyst. 1987, **112**, 199-204.

25 T. W. Hudnall, F. P. Gabbai, J. Am. Chem. Soc. 2007, **129**, 11978-11986.