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

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A simple, selective colorimetric and fluorimetric cyanide chemosensor **L** was designed and synthesized, which showed both colorimetric and fluorescence turn-on responses 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 $1.20 \times 10^{-9}$ M, which is far lower than the maximum level of $1.9 \times 10^{-6}$ M for cyanide in drinking water according to WHO guidelines. Test strips based on **L** were fabricated, which could be used 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 death of human beings in several minutes because it strongly binds to 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, despite cyanide toxicity, large quantities of cyanide salts are still widely used in industrial applications such as metallurgy (1.5 million tons per year), electroplating, and the synthesis of fine chemicals.[3] As a result, in recent years, the purposeful design and synthesis of efficient chemosensors to selectively detect $CN^-$ ions in the environmental and biological fields have attracted much attention. Although a wide variety of chemical and physical sensors for the detection of $CN^-$ have been reported,[4,5] most of the 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 are serious stumbling blocks to the practical application of these $CN^-$ sensors.[6] For purposes of simplicity, convenience, easy preparation and high sensitivity,[7] colorimetric and fluorimetric chemodosimeters for $CN^-$ have become particularly attractive.

Several organic molecules and transition metal complexes able to detect the presence of cyanide based on supramolecular approaches using hydrogen-bonding motifs with dramatic changes in their absorption and emission properties have already been identified.[8–14] Some of these chemosensors can even detect micromolar amounts of cyanide.[15–19] However, some of them suffer severe 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 exhibit 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 applications in environmental or biological systems.

Our research group has a longstanding interest in molecular recognition.[23] Herein, we have designed and synthesized a compound (**L**), **L** as a probe for cyanide comprising 2-hydroxy-1-napthaldehyde and isoniazid functionalities. Receptor **L** possesses a hydroxyl group 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 a fluorophore to achieve fluorescence recognition. Sensor **L** showed fluorescence 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 $1.22 \times 10^{-9}$ M, which indicates that this sensor could potentially be used as a probe for monitoring $CN^-$ levels. The mechanism of this process has been investigated by $^1H$ NMR, UV and ESI-mass spectrometry.

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# 2. Experimental section

## 2.1. Materials and physical methods

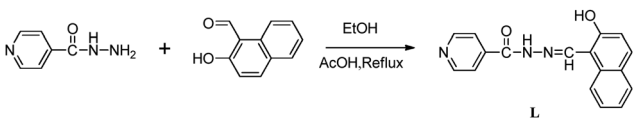
Fresh double distilled water was used throughout the experiment. The tetrabutylammonium salts and *N*-2-hydroxyethylpiperazine-*N*′-2-ethanesulfonic acid (HEPES) were purchased from Alfa Aesar Chemical Reagent Co. (Tianjin, China). All reagents and solvents were commercially available and were of analytical grade and were used without further purification. $^{1}$H NMR and $^{13}$C NMR spectra were recorded on a Mercury-400BB spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, $\delta$ scale with solvent resonances as internal standards) UV-vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were recorded on a Shimadzu RF-5301 fluorescence spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus purchased from Beijing Tech Instrument Co. (uncorrected). Infrared spectra were recorded 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 (0.86 g, 5 mmol), isoniazid (0.54 g, 5 mmol) was added. Then the reaction mixture solution was stirred and refluxed for 6 h. After cooling to room temperature, quietly placed, a large amount of yellow precipitate was formed, which was filtered and washed with distilled ethanol three times, then recrystallized with absolute ethanol to get yellow crystals of **L** in 89% yield (m.p. 273–275 °C), $^{1}$H NMR (400 MHz, DMSO) $\delta$: 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) $\delta$: 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) $\nu$: 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 $C_{17}H_{13}N_3O_2$ + H 292.10, found 292.02.

## 2.3. General procedure

Both UV-vis spectroscopy and fluorescence spectroscopy were 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 ($2.0 \times 10^{-5}$ M) on a Shimadzu UV-2550 spectrometer and a Shimadzu RF-5301 spectrometer, respectively. The anion solutions were prepared from the tetrabutylammonium salts of $F^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $H_2PO_4^-$, $HSO_4^-$, $ClO_4^-$ and $SCN^-$, but $CN^-$ was prepared in NaCN. The excitation wavelength was 368 nm.




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

For $^{1}$H NMR titrations, the sensor of stock solutions was prepared in DMSO-$d_6$, and 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 sensor **L** were utilized to detect $CN^-$ and other cations.

# 3. Results and discussion

The receptor was found to have limited solubility in water, and this compelled us to use this sensor in a 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 bands at 328 nm and 368 nm disappeared, while a new band appeared at 420 nm after the 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** shows excellent selectivity for $CN^-$ over all other anions tested.

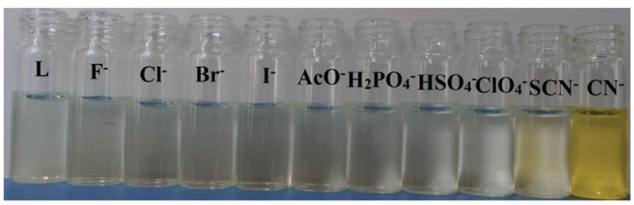



Fig. 1 Color changes observed upon the addition of various anions (50 equiv.) to solutions of sensor **L** ($2 \times 10^{-5}$ M) in DMSO/$H_2O$ (6 : 4, v/v).

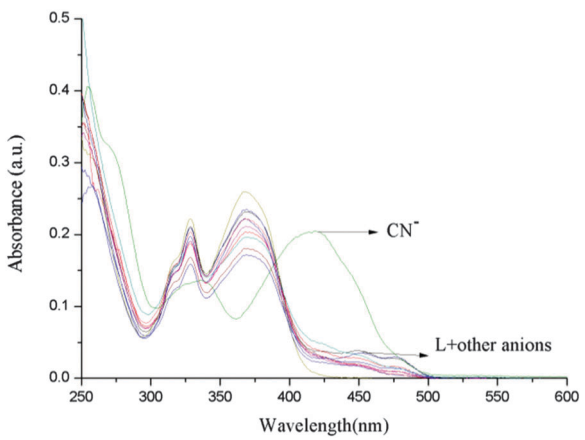



Fig. 2 UV-vis spectra of **L** ($2 \times 10^{-5}$ M) in the presence of 50 equiv. of various anions in $H_2O$/DMSO (4 : 6, v/v) binary solution at room temperature.

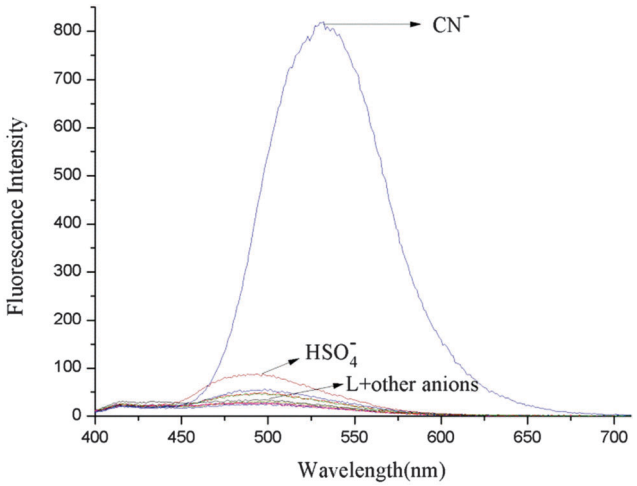



Fig. 3 Fluorescence spectra of **L** ($2 \times 10^{-5}$ M) in the presence of 50 equiv. of various anions in $H_2O$/DMSO (4 : 6, v/v) binary solution at room temperature.

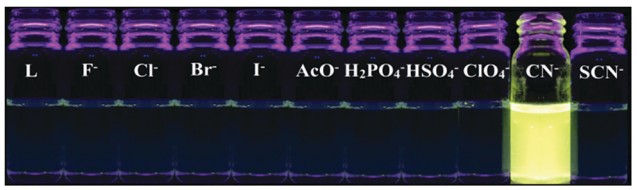



Fig. 4 Color changes observed upon the addition of various anions (50 equiv.) to solutions of sensor **L** ($2 \times 10^{-5}$ M) in DMSO/$H_2O$ (6 : 4, v/v), under a UV-lamp (365 nm).

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 ($\Phi_R$ = 0.14). Changes in the spectral pattern were observed only in the presence of 50 equivalents of $CN^-$; chemosensor **L** produced a strong fluorescence response band shifted toward 530 nm, with an increase in quantum yield ($\Phi_R$ = 0.42), and responded with a dramatic color change, from pale colorless to yellow. No change in the 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 (Fig. 3 and 4).

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 spectroscopy. Among various anions, only cyanide displayed noticeable color changes from colorless to yellow. Fluorescence spectra showed that **L** had a high selectivity for the 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 (Fig. 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.

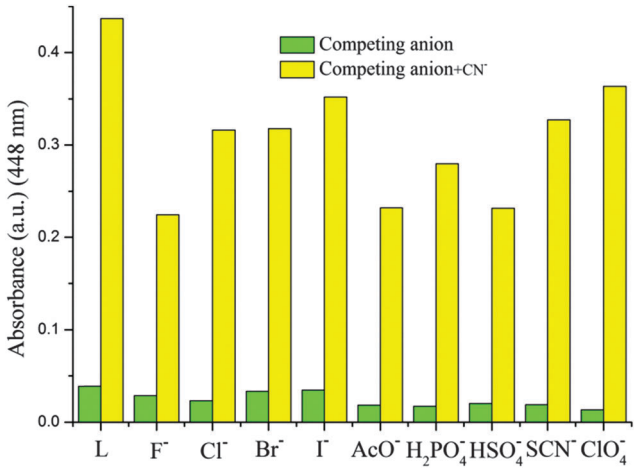



Fig. 5 Absorbance spectra of **L** ($2 \times 10^{-5}$ M) in the presence of various anions (50 equiv.) in DMSO/$H_2O$ (6 : 4, v/v) in response to $CN^-$ (50 equiv.).

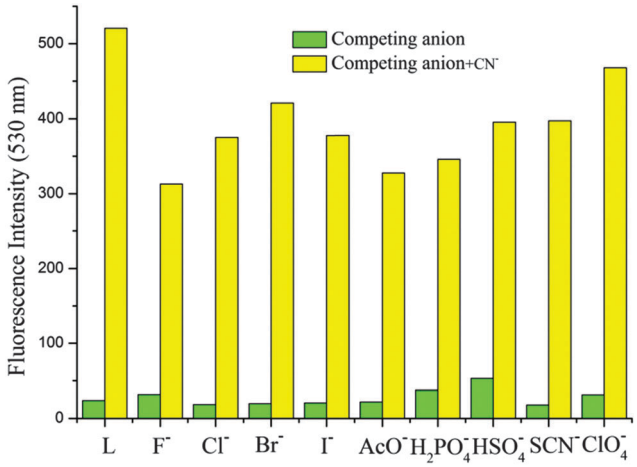



Fig. 6 Fluorescence spectra of **L** ($2 \times 10^{-5}$ M) in the presence of various anions (50 equiv.) in DMSO/$H_2O$ (6 : 4, v/v) in response to $CN^-$ (50 equiv.).

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 is calculated on the basis of $3S_B/S$ (ref. 24) (where $S_B$ is the standard deviation of the blank solution and $S$ is the slope of the calibration curve); Fig. 7 shows the detection limit of $1.20 \times 10^{-9}$ M for $CN^-$, which is far lower than the maximum level of $1.9 \times 10^{-6}$ M for cyanide in drinking water according to WHO guidelines.

The signaling mechanism of **L** (0.01 M) in the presence of cyanide (0.5 M) was based on the deprotonation of hydroxyl and amino groups. NMR spectra gave a strong evidence to support this assumption (Fig. 8). According to $^1$H NMR spectra of **L** and $CN^-$, the proton signals of –OH and –NH at 12.54 (s, 1H) and 12.42 (s, 1H) ppm completely disappeared, which clearly shows that –OH and –NH undergo deprotonation and the other aromatic proton chemical upfield shifts from 9.49–7.26 to

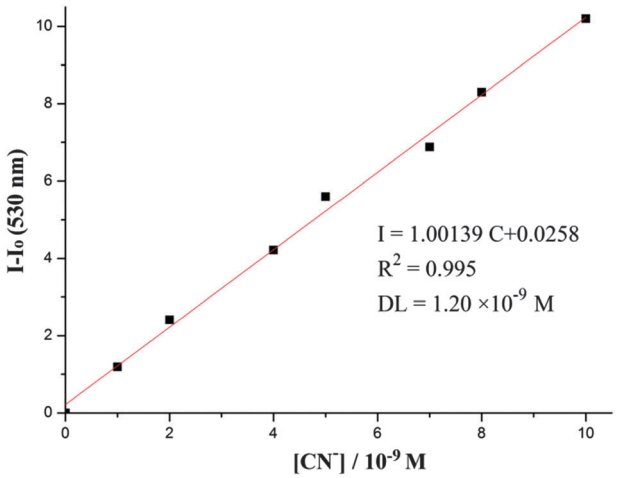



Fig. 7 Fluorescence detection limit spectra of **L** ($2 \times 10^{-5}$ M) in ($H_2O$/DMSO, 4 : 6, v/v) solution upon adding $CN^-$ ($1 \times 10^{-4}$ M).

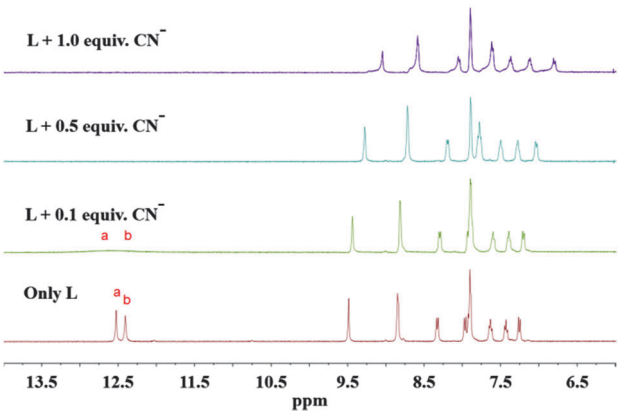
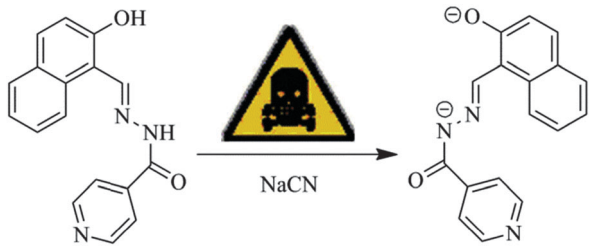



Fig. 8 Partial $^1$H NMR spectra of **L** (0.01 M) and in the presence of varying amounts of $CN^-$ (0.5 M).

9.02–6.79 ppm. This indicates that the aromatic protons were shielded by the negative charge of the deprotonated hydroxyl group.

This deprotonation caused a high charge separation between acceptor and donor units in **L**, and consequently caused a excellent electron delocalization to the 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 was possibly caused by a large charge separation between the 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 that chemosensor **L** selectively detects 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).

The selective detecting properties of **L** for $CN^-$ can be described by the basicity of anions. The charge transfer process




Scheme 2 Possible sensing mechanism.

could not occur in the case of a fluoride ion due to its high hydration enthalpy and low basicity ($\Delta H^0_{hyd}$ = −504 kJ mol$^{-1}$, p$K_a$ = 3.18) in an aqueous system.[25] Furthermore, the recognition properties of receptor **L** for $CN^-$ were determined by UV-vis and fluorometric titrations. The absorption spectral changes in **L** with the 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 appeared at 420 nm. 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** with the addition of $CN^-$ (0.1 M). When excited at 352 nm, the emission intensity at 533 nm remarkably increased upon changing the concentration of $CN^-$ from 0 to 3.8 μM.

To further investigate the interaction between sensor **L** and $CN^-$, the infrared spectra were recorded and are displayed in Fig. 11. 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) of sensor L compared with the N–H peak at 3218.90 cm$^{-1}$ of the **L** + $CN^-$ compound disappeared; at the same time, the peaks of (–C═O) and (C═N–H) at 1680.77 cm$^{-1}$ and 1576.92 cm$^{-1}$ moved to 1605.52 cm$^{-1}$ and 1536.29 cm$^{-1}$, respectively, which demonstrates that receptor **L** reacted with $CN^-$. Moreover, the mass spectrum obtained and confirmed that the ion peak of sensor **L** was detected at *m*/*z* 292.02, which corresponds to $[\mathbf{L} + H]^+$ (Fig. S2, ESI†). The probe with NaCN confirmed the revival of *m*/*z*

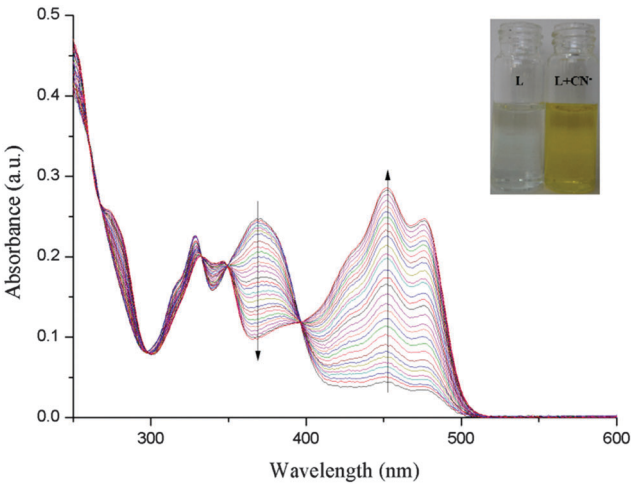



Fig. 9 UV-vis spectra of **L** ($2 \times 10^{-5}$ M) in DMSO/$H_2O$ (6 : 4, v/v) upon adding an increasing concentration of $CN^-$ (0.01 M).

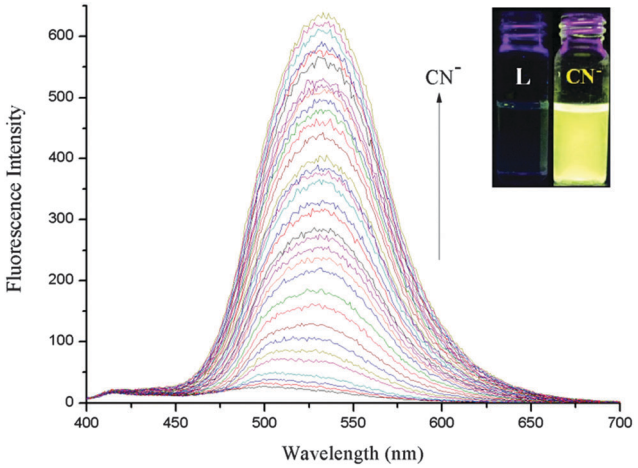



Fig. 10 Fluorescence titration spectra ($\lambda_{ex}$ = 368 nm) of **L** ($2 \times 10^{-5}$ M) in ($H_2O$/DMSO, 4 : 6, v/v) solution upon adding an increasing concentration of $CN^-$ (0.1 M). The inset shows a fluorescence change of **L** observed upon excitation at 365 nm after the addition of $CN^-$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

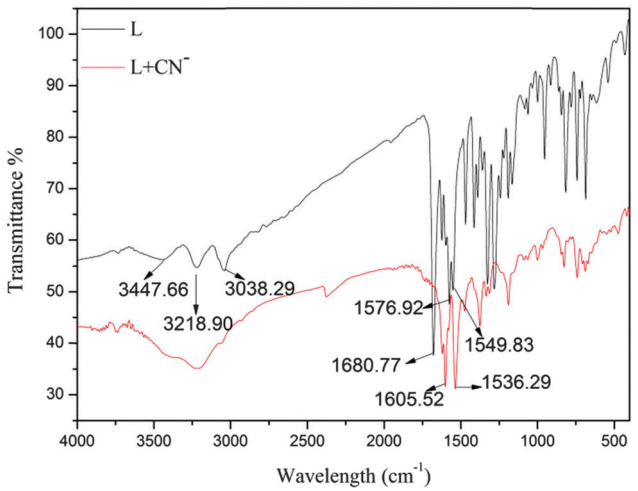



Fig. 11 Infrared spectra of **L** (black line) and its complex **L** + $CN^-$ (red line).

313.97 and also demonstrated the presence of compound [**L** – 2H + $Na^+$ + H]$^+$ (Fig. S3, ESI†). In conclusion, the IR and mass spectroscopy experiments suggested the sensing mode of chemosensor **L** and cyanide.

The pH dependence of sensor **L** in the HEPES buffer system was also checked by UV-vis and fluorescence spectroscopy. Cyanide ions were added to the buffer solution of **L** at different pH values. No apparent changes in the spectra were observed, indicating that the binding of **L** with the $CN^-$ cannot work well in the pH range of 1.0–12.0 (Fig. S5, ESI†).

The realization of quick response to cyanide is quite meaningful for the sensor for 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) followed by its exposure to air for drying. Intriguingly, the fluorescence color changed immediately from blue to mazarine once the test papers were immersed into an aqueous solution (5 μM) of cyanide under UV irradiation

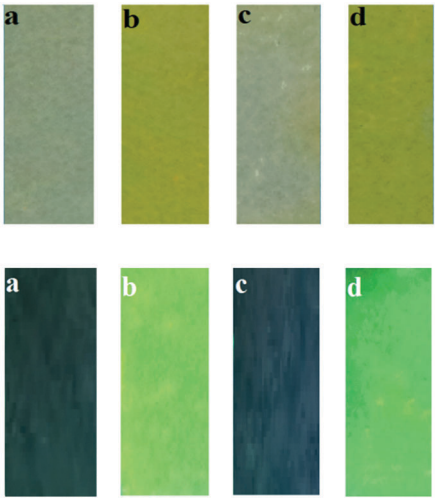



Fig. 12 Photographs of **L** (0.01 M) on test strips (a) only **L**, (b) after immersion into water solutions with $CN^-$, (c) after immersion into water solutions with other anions, (d) after immersion into water solutions with $CN^-$ and other anions at room temperature and irradiation under UV light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

(Fig. 12). Therefore, 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 of cyanide ions.

## 4. Conclusions

In conclusion, we have presented a facile, rapid and efficient chemosensor **L**, which showed special selectivity and high sensitivity UV-vis absorption and fluorescence recognition for $CN^-$ in DMSO/$H_2O$ (6 : 4, v/v) solutions. Moreover, the sensor demonstrates that the detection limit on fluorescence response of the sensor to $CN^-$ is down to $1.20 \times 10^{-9}$ M, which is far lower than the maximum level of $1.9 \times 10^{-6}$ M for cyanide in drinking water according to 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 a colorimetric and fluorimetric sensor for $CN^-$.

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