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# A novel dual-channel chemosensor for $CN^-$ using asymmetric double-azine derivatives in aqueous media and its application in bitter almond

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**Abstract:**

In this paper, we have designed and synthesized a novel sensor **L1** based on asymmetric double-azine derivatives, which showed both "naked eye" recognition and fluorescence responses for $CN^-$ in DMSO/$H_2O$ (v/v=4:1, pH=7.20) solution. This simple sensor **L1** could distinguish $CN^-$ from coexisting anions via the way of deprotonation and sensing mechanism of intramolecular charge transfer (ICT), and the minimum detection limit on fluorescence response of the sensor **L1** towards $CN^-$ was down to $9.47\times10^{-7}$ M. Moreover, we have successfully utilized the sensor **L1** to detect $CN^-$ in bitter almond. Test strips containing **L1** were also prepared, which could act as a practical colorimetric tool to detect $CN^-$ in aqueous media.

**Key words**: Anion Sensor, Fluorescence, Cyanide, Test Strip, DFT

## 1. Introduction

Currently, the development of anions probes such as cyanide has been a subject of research hotspot, because anions play vital roles in environment pollutant and biological systems [1-6]. It is well known that cyanide as one of the most toxic anions can damage many biological functions including endocrine, vascular, central nervous and metabolic systems in addition to serious lead to eventually death [7-12]. However, cyanide is widely used in industry like gold extraction, synthetic fibers, electroplating and etc [13-18]. Thus, there is a need for developing an efficient sensing system to monitor cyanide concentration from contaminant sources.

In the past few decades, with the development of the detection techniques, many methods have been used to detect $CN^-$, such as titrimetric, potentiometric, electrochemical methods and ion chromatography [19-22] and etc. However, these methods usually suffer from a series of problems such as long response time and selectivity shortage. Hence, it is of great importance to design and develop efficient methods to solve above mentioned problems.

Up to now, a great deal of effort has been invested in developing fluorimetric and colorimetric sensors due to simplicity, low detection limit and practical application [23-27]. Fortunately, fluorimetric and colorimetric sensors based on various mechanisms (intramolecular charge transfer (ICT) [28-29], excited state intramolecular proton transfer (ESIPT) [30], photo-induced electron transfer (PET) [31], and metal-ligand charge transfer (MLCT) [32]) have been partly developed. Among the different intelligent strategies in designing sensors, the deprotonation approach is often used to detect $CN^-$ due to easy design and comprehension. In many

cases, sensors usually containing groups such as amide, thiourea, pyrrole and hydroxyl could detect $CN^-$ [33-34].

Our research group has a longstanding interest in molecular recognition [35-39]. Herein, we have synthesized a new chemosensor **L1** based on asymmetric double-azine derivatives, which could recognize $CN^-$ in DMSO/$H_2O$ (v/v=4:1, pH=7.20) solution. To the best of our knowledge, the double azine-based chemosensors reported so far are very few in the field of supramolecular chemistry. Here, the function of sensor **L1** for recognizing $CN^-$ is based on the appended salicylaldehyde hydrazone that act as binding sites as well as fluorescent signal group. Moreover, the sensor **L1** could successfully detect $CN^-$ in the bitter almond, and the detection limit was down to 9.47 $\times 10^{-7}$ M from fluorescence spectrum changes. The mechanism of this recognition was investigated by mass spectrometry and $^1$H-NMR.

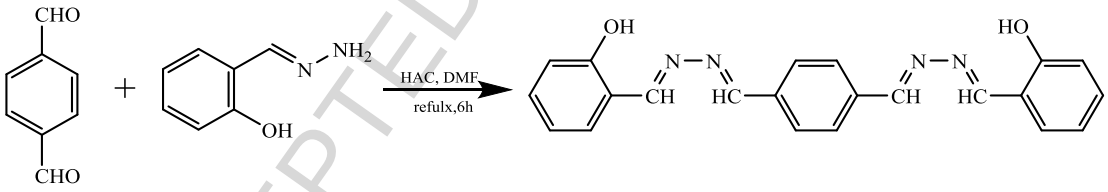
## 2. Materials and Instruments

$^1$H-NMR measurements were obtained from a Varian Mercury Plus-400MHz spectrometer and chemical shifts were recorded in ppm (DMSO-$d_6$ as solvent). Melting points were performed on an X-4 digital melting point apparatus and were uncorrected. $^{13}$C-NMR measurements were measured using a Mercury-400BB spectrometer at 100 MHz. UV-Vis absorption spectra was measured on a Shimadzu UV-2550 spectrometer. ESI-MS was measured on an Agilent 1100 LC-MSD-Trap-VL system. The photoluminescence spectra were performed on a Shimadzu RF-5301 fluorescence spectrophotometer.

## 3. Experimental

3.1 Synthesis

The chemosensor **L1** was synthesized in good yields (72.3%) by one-step condensation of salicylaldehyde hydrazone (0.01 mol, 1.36 g), 1,4-phthalaldehyde (0.01 mol, 1.34 g) in DMF (20 mL). The reaction was refluxed for 6 h with 0.2 mL acetic acid as catalyst, and then cooling room temperature, the mixture was filtrated. Finally, the crude product was purified by recrystallisation with DMF/$H_2O$, obtaining the target compound **L1** (**Scheme 1**). Colour: yellow solid, mp: 247~249℃. $^1$H-NMR (DMSO-$d_6$, 400 MHz, ppm) δ: 11.26 (s, 2H), 9.00 (s, 2H), 8.88 (s, 2H), 8.00-7.99 (m, 4H), 7.72 (d, J=7.93 Hz 2H), 7.40 (m, 2H), 6.98-7.00 (t, J=8.32 Hz, 4H). $^{13}$C-NMR (DMSO-$d_6$, 100 MHz, ppm) δ: 163.88, 162.04, 159.22, 136.67, 133.72, 131.58, 129.36, 120.03, 118.64, 116.96. MS/ EI: m/z: 371.17 ($M+H^+$).




**Scheme 1** The synthetic procedure for sensor **L1**.

3.2 General procedure of spectroscopy

All UV-Vis spectroscopy and fluorescence spectroscopy were performed after adding tetrabutylammonium salt of anions ($F^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $H_2PO_4^-$, $HSO_4^-$, $ClO_4^-$, but $N_3^-$, $PO_4^{3-}$, $B_2O_7^{2-}$, $SCN^-$and $CN^-$ were added in the form of sodium salts) in DMSO solution, while keeping the host concentration constant ($2.0\times10^{-5}$ M).

For $^1$H-NMR titrations, **L1** and sodium cyanide were respectively prepared in DMSO-$d_6$, and the DMSO-$d_6$ solution of sodium cyanide was added to **L1** according

to different quantities.

4. **Results and Discussions**

The recognition of sensor **L1** towards anions ($F^-$, $Cl^-$, $Br^-$, $I^-$, $N_3^-$, $PO_4^{3-}$, $B_2O_7^{2-}$, $AcO^-$, $H_2PO_4^-$, $HSO_4^-$, $ClO_4^-$, $SCN^-$ and $CN^-$) in DMSO/$H_2O$ (v/v=4:1, pH=7.20) solution was investigated by UV-Vis spectroscopy and fluorescence spectroscopy. When adding 50.0 equiv. of various anions respectively to the solution of **L1**, we found that only $CN^-$ could induce an obvious color change from faint yellow to red, which could be easily distinguished under visible light. In the corresponding UV-Vis spectrum, an obvious red shift band from 412 nm to 500 nm was observed. Moreover, $F^-$ also gave rise to a red shift from 412 nm to 434 nm in the absorption spectrum, but it had no influence on detecting $CN^-$. In contrast, other examined anions didn't induce any dramatic color and spectra changes. These results suggested that sensor **L1** showed a specific selectivity for $CN^-$ in aqueous media (**Figure 1**).

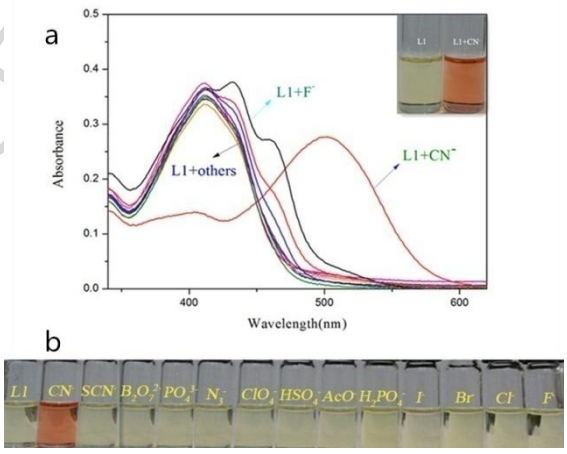



**Figure 1** (a) UV-Vis spectra of sensor **L1** (20 μM) with various anions (50 equiv.) in DMSO/$H_2O$ (v/v=4:1, pH=7.20) solution (b) Color changes of **L1** (20 μM) with various anions (50 equiv.) in DMSO solution.

The fluorescence measurements for sensor **L1** were performed in DMSO/$H_2O$ (v/v=4:1, pH=7.20) solution. The fluorescence spectrum of free **L1**, which was excited at 412 nm and showed a strong emission band at 554 nm in aqueous solution, when 50.0 equiv. of $CN^-$ were added to **L1**, a dramatic fluorescence quenching was observed. However, other anions could not induce any similar response. It showed that **L1** could be able to instantly and selectively detect $CN^-$ in DMSO/$H_2O$ (v/v=4:1, pH=7.20) solution. (**Figure 2**)

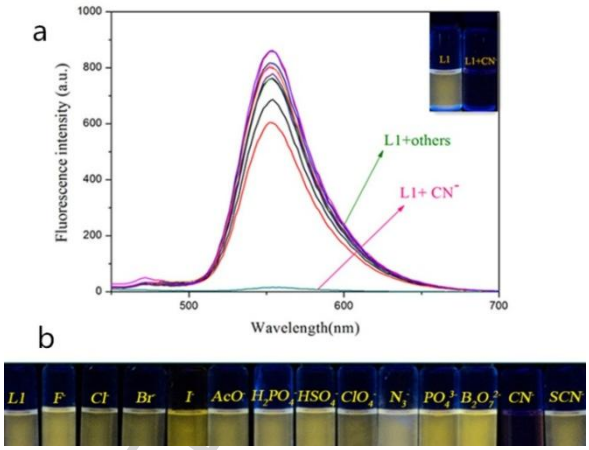



**Figure 2** (a) Fluorescence spectra of **L1** (20 μM) with various anions (50 equiv.) in DMSO/$H_2O$ (v/v=4:1, pH=7.20). (b) Color changes observed for **L1** (20 μM) with various anions (50 equiv.) in DMSO/$H_2O$ (v/v =4:1, pH=7.20) solution under the UV lamp.

In order to investigate the sensing behavior between **L1** and $CN^-$, we have worked absorption spectra titration. As shown in **Figure 3**, with an increasing amount of $CN^-$ from 0 equiv. to 55 equiv., the absorption band at 412 nm was gradually decreasing while the band at 500 nm was increasing little by little before obtaining the maximum value, which showed one red shift in the absorption band with $\Delta\lambda$=88 nm. Moreover, an isosbestic point at 450 nm clearly observed, which indicated that an

interconversion into single discrete chemical species during the titration process. In addition, we also have performed anti-interference experiments, results obviously showed that other coexisting anions had no or little influence on detecting $CN^-$ in aqueous solution. (**Figure. 4**)

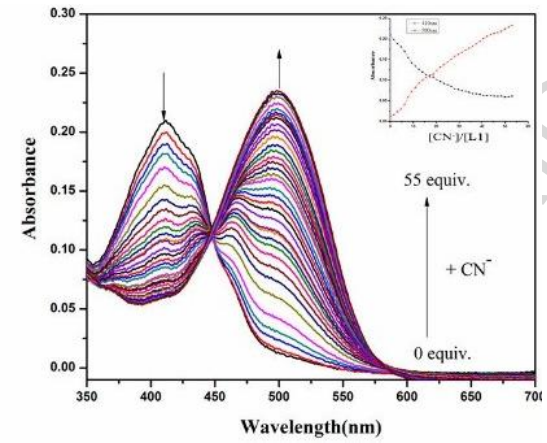



**Figure 3** Absorption spectra titration of sensor **L1** (20 μM) in presence of different concentration of $CN^-$ (0-55 equiv.) in DMSO/$H_2O$ (v/v =4:1, pH=7.20) solution. Inset: a plot of absorbance at 412 nm and 500nm depending on the concentration of $CN^-$ in the range from 0 equiv. to 55 equiv.

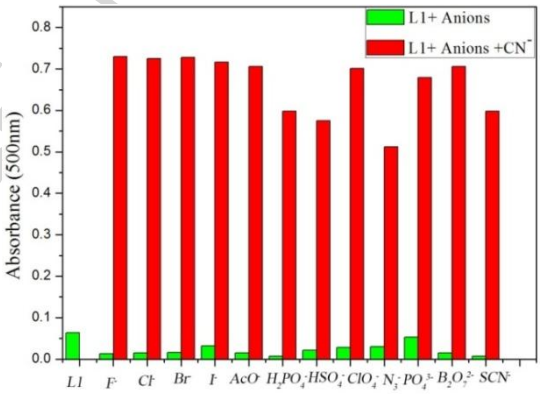



**Figure 4** Absorption spectra change for a 1:20 mixture of **L1**-$CN^-$ upon addition of 20 equiv. of other examined anions in DMSO/$H_2O$ (v/v =4:1, pH=7.20) solution.

Similarly, the variation in fluorescence emission spectral of sensor **L1** was measured by titrations methods. As shown in **Figure 5**, the fluorescence intensity at

554 nm of **L1** decreased steadily on changing the concentration of $CN^-$ from 0 equiv. to 76 equiv, and it was quenched almost completely after the addition of 76 equiv. $CN^-$. Furthermore, the fluorescence intensities at 554nm were plotted to obtain a calibration graph, which clearly showed an excellent linear relationship between fluorescence intensity and $CN^-$ concentration. Moreover, we have also validated the selectivity of sensor **L1** towards $CN^-$ in the context of coexisting anions ($F^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $H_2PO_4^-$, $N_3^-$, $PO_4^{3-}$, $B_2O_7^{2-}$, $HSO_4^-$, $ClO_4^-$ and $SCN^-$), which clearly showed that other examined anions had little impact on $CN^-$ detection. (**Figure 6**)

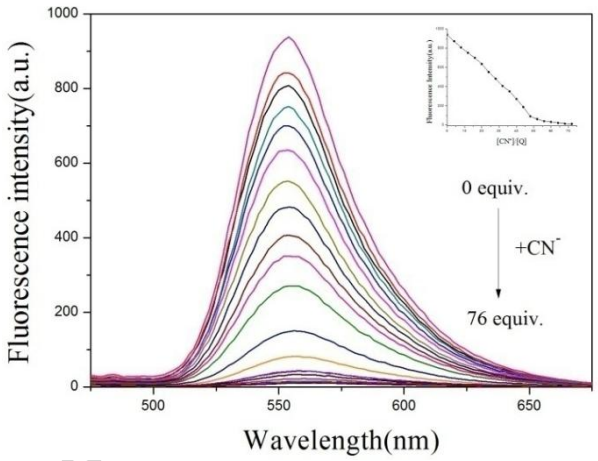



**Figure 5** Fluorescence titration of sensor **L1** (20 μM) with different concentration of $CN^-$ (0-76 equiv.) in DMSO/$H_2O$ (v/v=4:1, pH=7.20) solution. Inset: the change of fluorescence 554 nm depending on the concentrations of $CN^-$

Since the charge distribution and inherent fluorescence properties of a sensor are affected by pH value. Thus, the effect of pH to **L1**-$CN^-$ was also studied by emission spectra (**Fig. S1**). Results suggested that single **L1** had no fluorescence response when pH was between 2.0 and 8.0, but the **L1**-$CN^-$ systems showed a significant fluorescence response when pH was between 7.0 and 8.0, which indicated that **L1**

showed an excellent fluorescence response for $CN^-$ within the basic pH range (pH=7.0–8.0).

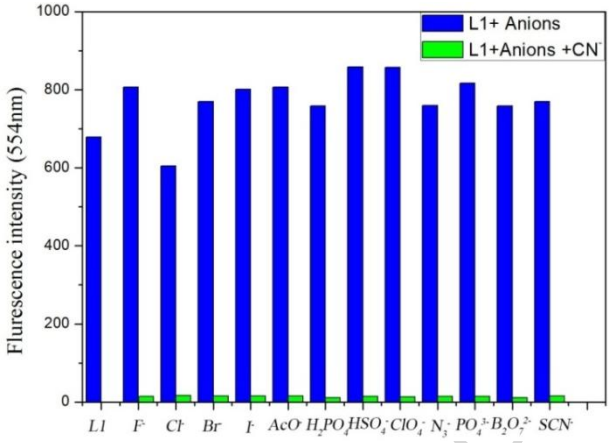



**Figure 6** Fluorescence spectra of **L1** (20 μM) in presence of 20 equiv. of $CN^-$ and 20 equiv. of various interference anions.

The reversibility of a chemosensor is one of the essential aspects for its applications. Therefore, the reversibility of sensor **L1** was performed by respectively addition of $H^+$ and $CN^-$. To our delight, this switching process was repeated more than six times in the absence of fluorescence loss, which indicated that **L1** showed an excellent reversibility to $CN^-$ (**Figure 7**).

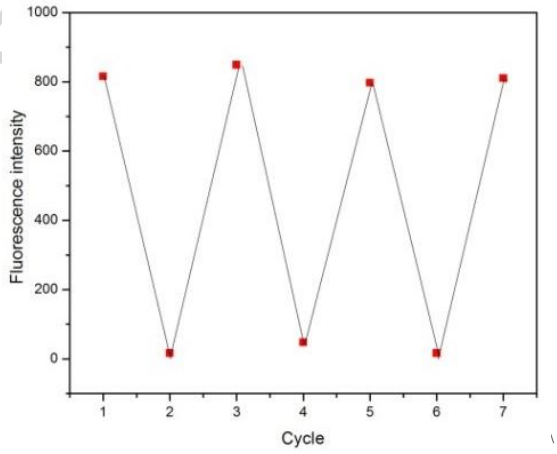



**Figure 7** Switching cycles of **L1** controlled by alternating addition of $H^+$ and $CN^-$.

Moreover, the fluorimetric detection limit on sensor **L1** for $CN^-$ was also tested.

As shown in **Figure 8**, the fluorescence detection limits on sensor **L1** for $CN^-$ was down to $9.47\times10^{-7}$ M according to the basis of 3σ/s (where σ and s represent respectively the standard deviation of blank solution and the slope of calibration curve), indicating that the sensor **L1** could detect very low concentration of $CN^-$.

In addition, a lot of experiments have been done to investigate the stoichiometry between **L1** and $CN^-$. As shown in **Figure 9**, as expected, a job plot was implemented, demonstrating a stoichiometry for **L1-$CN^-$** was 1:2.

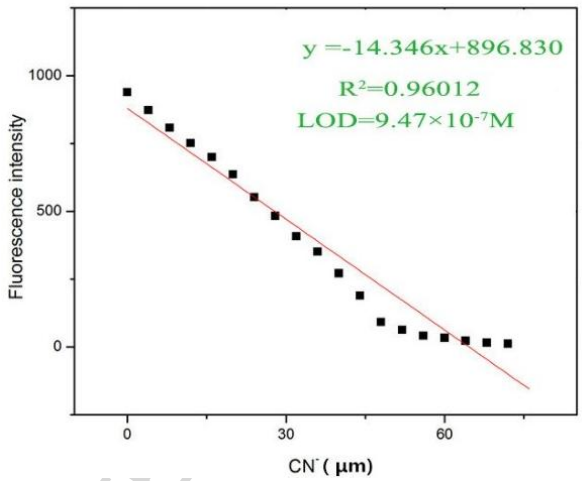



**Figure 8** Fluorescence detection limit of **L1** (20 μM) towards $CN^-$ in DMSO/$H_2O$ (v/v= 4:1, pH=7.20) solution.

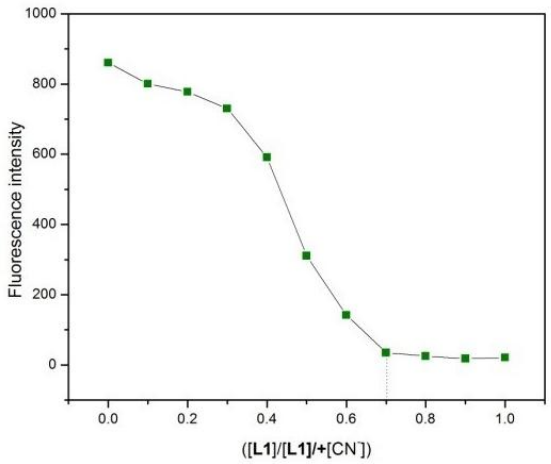



**Figure 9** Job plots of **L1** and $CN^-$.

The recognition mechanism was finally investigated by ESI-MS, $^{1}$H-NMR titration methods and Job plot of **L1**-$CN^{-}$. As shown in **Figure 10**, the –OH peak at 11.25 disappeared when adding 0.5 equiv. of $CN^{-}$ to the DMSO-$d_6$ solution of **L1**, which clearly showed that –OH undergo deprotonation. With the increasing amount of $CN^{-}$, the proton chemical of aromatic gradually showed upfield shift that indicated the aromatic of protons were shielded by the increase of electron density through charge delocalization in the conjugated system.

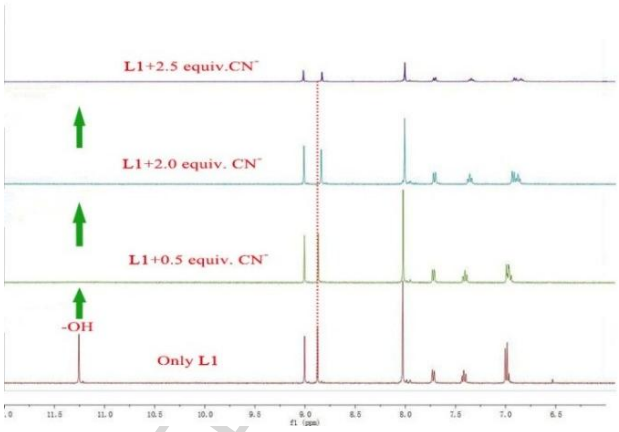
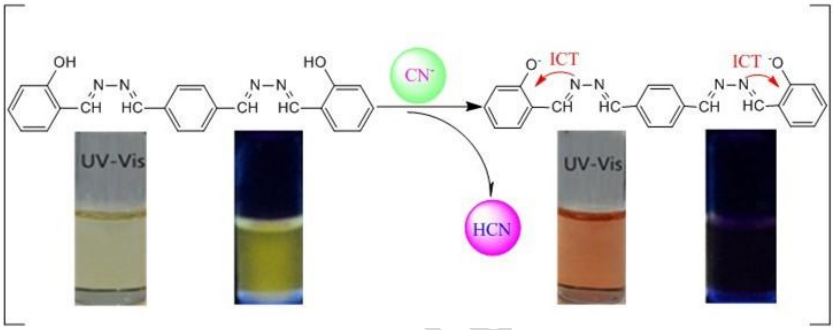



**Figure 10** $^{1}$H-NMR spectra of free **L1** (DMSO-$d_6$) and in the presence of different amounts of $CN^{-}$

Moreover, ESI-MS further gave a strong support to above result. As shown in **Fig. S2**, **L1** ion peak was detected at m/z 371.17 (ESI. **L1**+$H^{+}$), and it appeared at m/z 413.2716 (ESI. **L1**-2$H^{+}$+2$Na^{+}$-$H^{+}$) when the addition of $CN^{-}$ to the solution of **L1** (**Fig. S3**), simultaneously, according to the stoichiometry of **L1**-$CN^{-}$, which clearly suggested that **L1** did undergo deprotonation and lost two protons.

This deprotonation caused a high charge separation between acceptor and donor units in **L1**, which led to a bathochromic shift in the absorption band with Δλ=88 nm nm for **L1** upon the addition of $CN^{-}$. Moreover, we observed that the fluorescence

intensity at 554nm was quenched, which was possibly caused by a large charge separation resulting in a strong intramolecular charge transfer (ICT) in **L1**. Furthermore, according to the change of mass spectrum after the addition of $CN^-$ and the stoichiometry of **L1**-$CN^-$ 1:2, we proposed that a possible interaction mechanism between **L1** and $CN^-$. (**Scheme 2**)




**Scheme 2** A possible mechanism of **L1** and $CN^-$.

In order to realize quick response of sensor **L1** for cyanide, test strips were fabricated by immersing filter papers into the DMSO solution of **L1** ($2\times10^{-3}$ M) and then drying in air, as shown in **Figure 11**, the color of test strip changed from faint yellow to red under visible light; and the fluorescence color also changed from yellow to black under UV lamp. Herein, the test strips could be used to conveniently detect $CN^-$ in solutions.

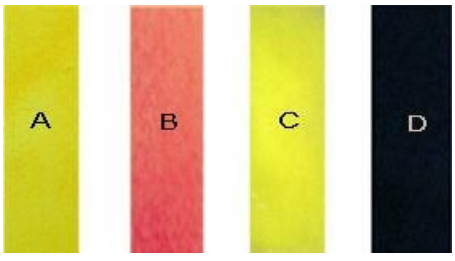



**Figure 11** Photographs of test strips containing **L1** under different conditions; (A) only **L1** (B) **L1** with $CN^-$ by naked eyes, (C) only **L1** under UV lamp, (D) **L1** with $CN^-$ under UV lamp.

Finally, we have investigated its applicability of **L1** in our lives. 30 g of crushed bitter almond were put into a flask by adding 100 mL of water and 0.5 g of NaOH. And the mixture solution was filtered after stirring 20 min. Then we made the pH=9 which diluted the solution with fresh double water. When addition of the solution into **L1**, we found that the fluorescence of **L1** quenched. This result indicated that could be applied successfully for detecting $CN^-$ in bitter almond.

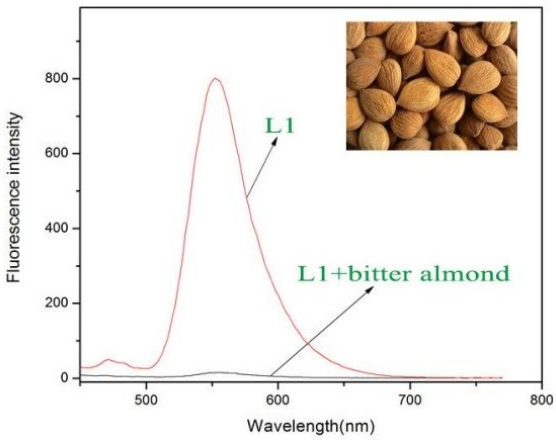



**Figure 12** Fluorescence spectral response of **L1** (20 μM) in diluted bitter almond.

Comparison with reported $CN^-$ receptors, **L1** could detect $CN^-$ in solution with high water content, as shown in **Table S1**, so **L1** could act as a preferable fluorescence sensor for $CN^-$.

### 4.1. Theoretical Calculations

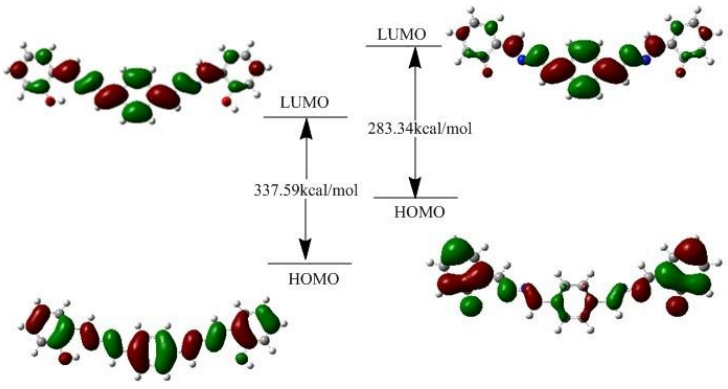



**Figure 13** The DFT computed HOMO and LUMO diagram of **L1** and **L1**-$CN^-$

complex.

The mechanism of sensor **L1** with $CN^-$ was further confirmed by DFT (Density Functional Theory) calculations. As shown in **Figure 13**, the HOMO–LUMO energy band gap of **L1** and **L1**-$CN^-$ complex were 337.59 kcal/mol and 283.34 kcal/mol respectively, it is obviously that the former was higher than the latter, which led to the red shift of **L1** in absorption spectra.

## 5. Conclusion

In summary, we have designed and synthesized a colorimetric and fluorescence sensor **L1**, which could selectively sense $CN^-$ in DMSO/$H_2O$ (v/v=4:1) solution within the basic pH range (pH=7.0–8.0), and the detection limit of sensor **L1** to $CN^-$ is down to $9.47 \times 10^{-7}$ M from fluorescence spectrum changes. The $CN^-$ induced fluorescence process could be reversed by adding $H^+$ and the switching process could be repeated more than six times without a large fluorescence loss. Moreover, test trips based on sensor **L1** could be utilized to detect $CN^-$ in aqueous solution. Above all, the probe was successfully applied to the detection of cyanide in bitter almond. On account of those advantages, we believe that **L1** as a $CN^-$ sensor makes it more conspicuous for its potential applications.

## Acknowledgment

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# A novel dual-channel chemosensor for $CN^-$ using asymmetric double-azine derivatives in aqueous media and its application in bitter almond

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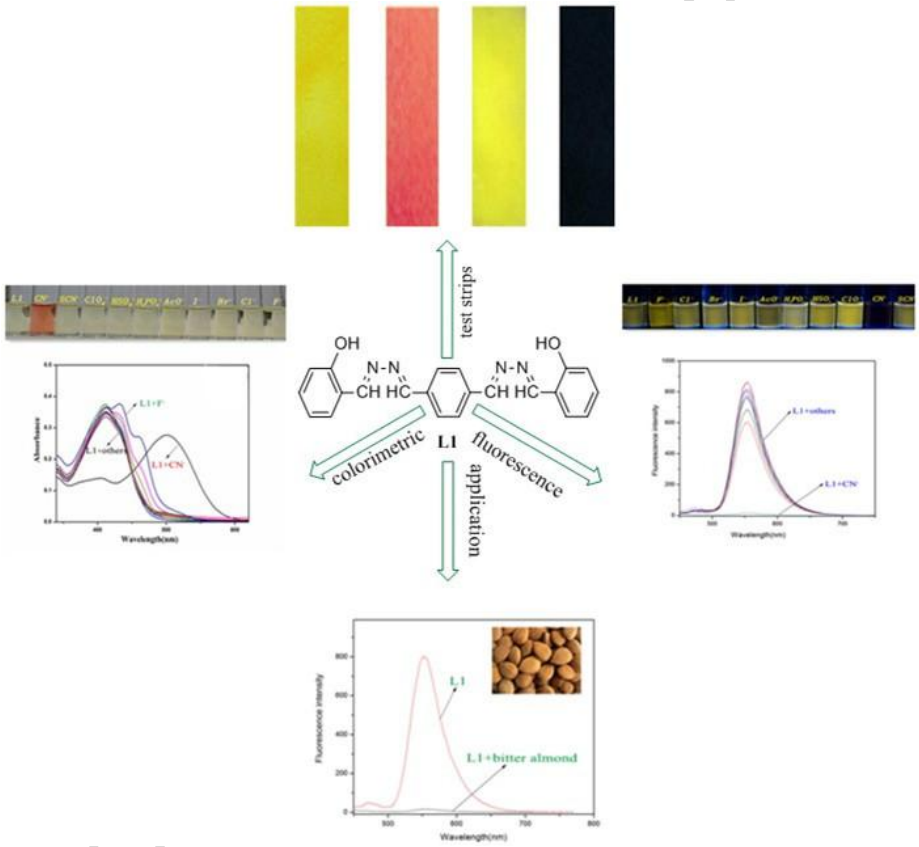


**Graphical abstract**: A novel cyanide specifically selective and highly sensitive fluorescence enhanced chemosensor **L1** based on asymmetric double-azine derivatives had been designed and synthesized.

**Highlights**

**1** Chemosensor **L1** is based on asymmetric double-azine derivatives.

**2** Sensor L1 demonstrates specifically selective “naked eye” recognition and fluorescence response for $CN^-$

**3** Receptor **L1** shows highly selective colorimtric and fluorimetric response for $CN^-$.

**4** The probe **L1** responds with $CN^-$ in aqueous solution system.

**5** The probe L1has been detected successfully $CN^-$ in bitter almond.

**6** Test strips of **L1** was prepared and convenient and rapidly detected $CN^-$.