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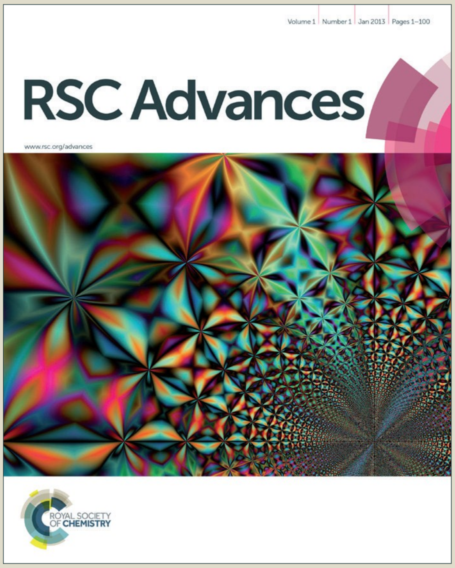

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PAPER

A simple chemosensor for the dual-channel detection of cyanide in water with high selectivity and sensitivity

Xiao-Bin Cheng, Hui Li, Feng Zheng, Qi Lin, Hong Yao, You-Ming Zhang and Tai-Bao Wei*

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We have synthesized a simple chemosensor (HY) of acylhydrazones and used it for colorimetric detection of cyanide anions (CN^-) in DMSO/H_2O (3:7, v/v) mixed solvent. The simple chemosensor displays specificity response for cyanide over other common anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, and SCN^-) in mixed solution. Upon treatment with cyanide, the HY displayed a remarkable naked-eye and fluorogenic response, simultaneously with the significant changes in its UV–visible and fluorescence spectra. Furthermore, competitive anions did not showed any significant changes both in colour and emission intensity, indicating the high selectivity of the sensor to CN^-. The absorption spectra detection limits of the chemosensor for cyanide was 8.34×10^{-7} M and the fluorescence spectra detection limit was 2.85×10^{-8} M. The cyanide test strips based on the chemosensor could serve as a convenient cyanide test kits. Furthermore, the chemosensor was successfully applied to the detection of cyanide in sprouting potatoes.

Introduction

The orientation on devising and synthesizing novel chemosensors for detecting anions have already been a potential subject due to the biological, surroundings and practical applications.[1] Among various anions, cyanide (CN^-) is one of the most researched focus anions owing to its high lethal effect on living body and the surroundings.[2] Nevertheless, cyanide anions (CN^-) are highly toxic to the organism,[3] while CN^- is widely used in industrial production, such as electroplating, gold mining, metallurgy, and the synthesis of fibers, nylon, and resins industry.[4] Strong complexation of CN^- to a heme cell of the cytochrome paralyzes cellular breathe and causes severely damages to the mid nervous system.[5] The cyanide standard in industrial wastewater is thence stringent requirements: for instance, Japan's Ministry of Environment sets its licensing standards at 38.5 mM.[6] Precise quantification of CN^- in the circumstance specimen is particularly necessary.[7] The majority of analytic methods such as potentiometry, chromatography, and voltammetry, have been used for CN^- detection.[8] These methods successfully detect very low standards of CN^- (<0.1 mM), but demand cumbersome sample preparation or costly analytical instruments.

Therefore, it is very necessary to develop sensitive, selective, cheap, simple, fluorometric and colorimetric chemosensors for detecting CN^-.[9] Optical chemosensors for CN^-, in which the change in the absorbance and fluorescence spectra is found, have been continually investigated due to their desirable features including simplicity, high selectivity and high sensitivity.[10] The design and synthesis of a colorimetric and fluorometric chemosensors for CN^- has attracted a great concern because it quantization in CN^- detection by easily absorbance on a UV–vis spectrophotometer and change in fluorescence on a fluorescence spectra. The general method for the cyanide detecting are summary as nucleophilic addition on the carbonyl units,[11] electron–deficient alkenes,[12] hydrogen bonding motifs,[13] cyanide complexation,[14] and so on. But they themselves all have their own drawbacks such as poor solubility in aqueous media, long responding time or poor application in the "naked eye" detecting.[15] So due to its operational simplicity, low cost, and rapid implementation, chromogenic sensor for the detection of cyanide is highly desirable.

In view of the above, and as a part of our research interest in ions recognition.[16] In this paper, we designed and synthesized a simple fluorescent and colorimetric sensor **HY** for cyanide anion based on a deprotonated mechanism. As its hydroxy (–OH) and amine group (–NH–) are effective targets for the deprotonated procedure, the cyanide can easily combine with it, inducing a remarkable change in spectroscopic properties. With the gradual addition of cyanide, the colour of the solution changed from colourless to yellow which offers the possibility for us to detect the cyanide by "naked eye". And the fluorescence colour of the sensor from yellow to colourless which similarly can detect cyanide by UV–lamps. Other anions such as F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, and SCN^- could not cause any interference.

Results and discussion

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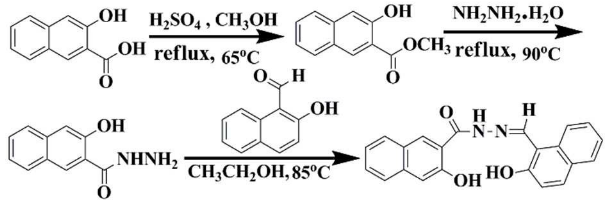

Scheme 1. Structure and synthesis of the chemosensor **HY**.

The synthetic procedure of chemosensor **HY** is shown in Scheme 1. The chemosensor **HY** has been characterized by ^1H NMR, ^{13}C NMR, IR and ESI–MS (Figure S1–S3).To detect the selectivity of **HY** towards CN^-, we carried out a series of spectral experiments, where 50 equiv. of various anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, CN^-, and SCN^-) were respectively added to 2.0 × 10^{-5} M of **HY** in mixed solution (DMSO/H_2O, 3:7, v/v). When adding 50 equiv. of CN^- to the solution of sensor **HY**, the **HY** responded with dramatic color changes from colorless to yellow (Fig. 1 inset). As shown in Fig. 1, in the corresponding UV–vis spectrum, a strong and broad absorption band from 378 to 460 nm was observed for the chemosensors **HY**. However, as shown in Fig. 2, a yellow fluorescence with one emission band centered at 512 nm appeared when the solution of chemosensors **HY** was excited at 378 nm. Upon the addition of CN^- solution, the yellow fluorescence emission band decreased remarkably. A variety of other anions, such as F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, and SCN^-, did not cause such a significant change.

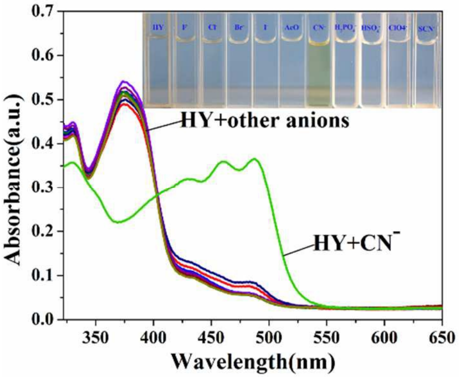

Figure 1. UV−Vis spectra of **HY** (c=2×10^{-5} M) after addition of 50 equivalents of various anions. Inset: UV−vis color changes of **HY** (c=2×10^{-5} M) after addition of 50 equivalents of various anions (c=1×10^{-2} M).

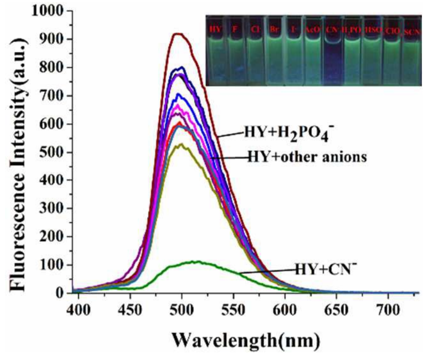

Fig. 2. Fluorescence spectra (λ_{ex}=378 nm) of **HY** (c=2×10^{-5} M) after addition of 50 equivalents of various anions. Inset: Fluorescent color changes of **HY** (c=2×10^{-5} M) after addition of 50 equivalents of various anions.

In order to estimate the specific properties for selective recognition of CN^- and colorimetric changes associated with the chemosensor **HY**, the chemosensor **HY** toward CN^- was studied by UV–vis absorption spectra titration experiments. Along with the increasing of concentration of CN^-, a significant increase of the UV–vis absorbance at 420 nm. Such a red shift led to the solution color changing from colorless to yellow. On the other hand, a clear isosbestic points are observed at 378 nm (Fig. 3). Similarly, the fluorescence spectra of the chemosensor **HY** change significantly along with the concentration increase of CN^-. The intensity of the fluorescence band centered at 512 nm of chemosensor **HY** decreased progressively along with the concentration increase of CN^-, and it was quenched almost completely after the addition of CN^- (**Fig. 4**). In the meantime, the detection limits of the **HY** for CN^- calculated on the basis of 3*δ*/S (Figure S4, S5) were 8.34×10^{-7} M for absorption spectra and 2.85×10^{-8} M for fluorescences spectra change respectively, which are both far lower than the WHO guideline of CN^- in drinking water (less than 1.9×10^{-6} M). In addition, the fluorescence quantum yields weakened from 0.64 to 0.007.

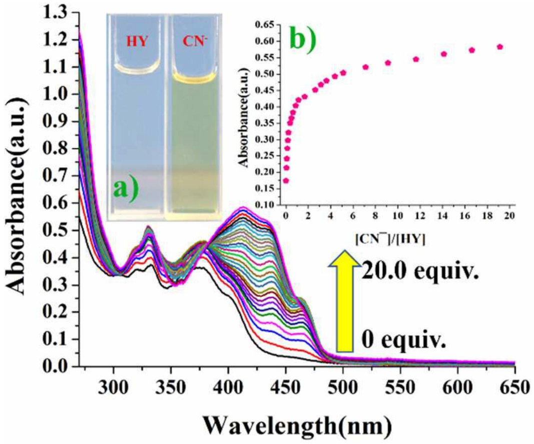

Fig. 3. UV–vis spectra of **HY** (2.0 × 10^{-5} M) in DMSO/H_2O (3:7, v/v) upon adding an increasing concentration of CN^- (0.1 M). Inset: a) Color change; b) a plot of absorption at 420 nm versus number of equivalents of CN^-.

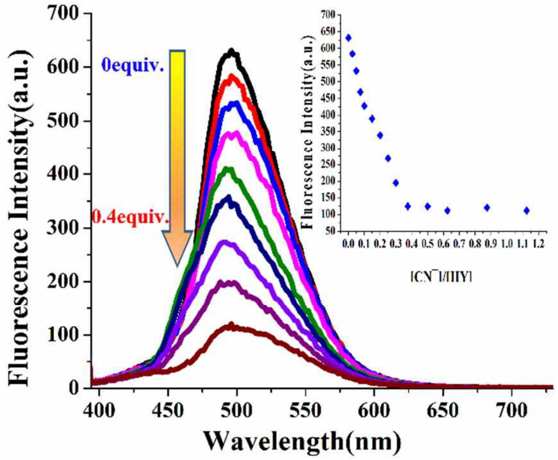

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Fig. 4. Fluorescence spectra of **HY** (2.0×10^{-5} M) in DMSO/H_2O (3:7, v/v) upon adding an increasing concentration of CN$^-$ (0.1 M). Inset: a plot of emission at 512 nm versus number of equivalents of CN$^-$.

To further exploit the utility of the chemosensor **HY** as anion-selective sensor for CN$^-$, competitive experiments were carried out in the presence of 50 equiv. of CN$^-$ and 50 equiv. of various anions in (DMSO/H_2O, 3:7, v/v) solution. As shown in Fig. 5, it is noticeable that the miscellaneous competitive anions did not lead to any significant interference. The fluorescence selectivity was examined at an excitation wavelength of 378 nm, as shown in Fig. 6, all the competing anions did not interfere in the detection of CN$^-$. This result displayed highly selectivity of the chemosensor **HY** toward cyanide anion over other analytes mentioned above.

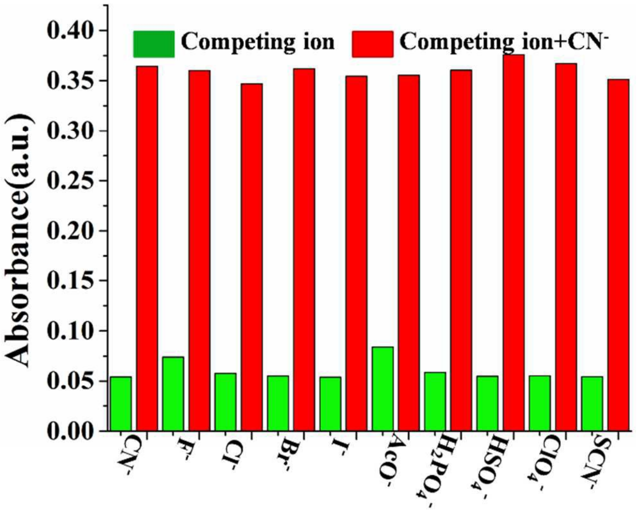

Fig. 5. UV–vis spectra of sensor **HY** at 460 nm with addition of 50 equiv. of CN$^-$ in the presence of 50 equiv. of other anions in DMSO/H_2O (3:7, v/v).

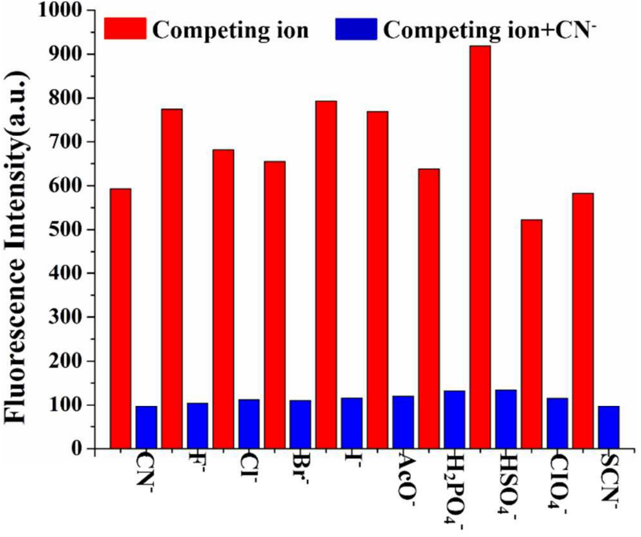

Fig. 6. Fluorescence of sensor **HY** at 512 nm with addition of 50 equiv. of CN$^-$ in the presence of 50 equiv. of other anions in DMSO/H_2O (3:7, v/v).

The pH dependence of the chemosensor in (DMSO/H_2O, 3:7, v/v) solution system was checked using its absorption spectrum at 420 nm (**Fig. 7**) and fluorescence spectroscopy emission at 512 nm (**Fig. 8**). Cyanide ion was added to the solution of **HY** at different pH values. The results indicated that **HY** binding with CN$^-$ occurred effectively in the range of pH 5–14.

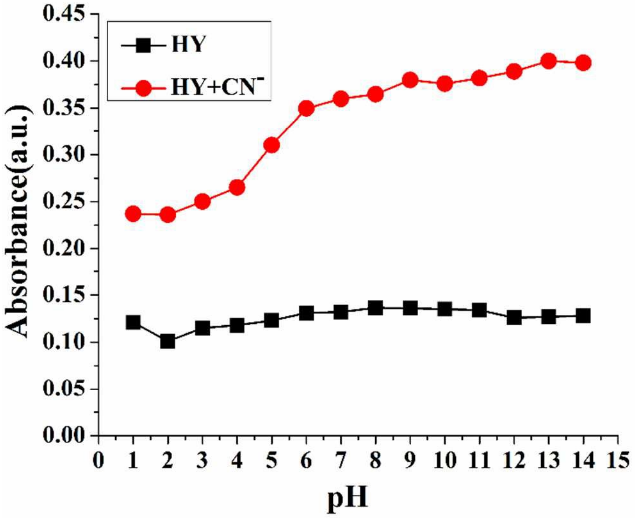

Fig. 7. Effect of pH on the absorbance spectra (460 nm) of **HY**+CN$^-$ (50 equiv.) from 1 to 14 in DMSO/H_2O (3:7, v/v) solution.

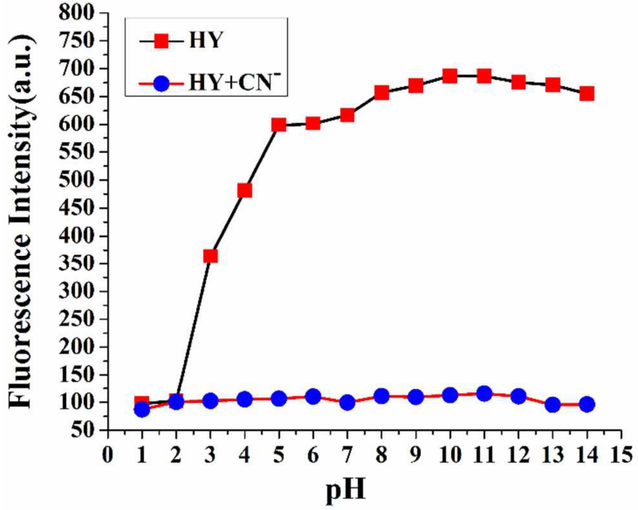

Fig. 8. Effect of pH on fluorescence spectra (512 nm) of **HY**+CN$^-$ (50 equiv.) from 1 to 14 in DMSO/H_2O (3:7, v/v) solution.

To gain better insight into the sensing mechanism of chemosensor **HY** to CN$^-$, the ^{1}H NMR titration, IR spectrum and ESI–MS were carried out. In the ^{1}H NMR titration spectra (**Fig. 9**), before the addition of cyanide anions, the ^{1}H NMR chemical shifts of the O–H_a, O–H_b and –NH_c– protons on **HY** were at δ 12.75, 12.23 and 11.29 ppm. With the addition CN$^-$, the hydroxy proton H_a and H_b, –NH– proton H_c completely disappeared by the deprotonation. Upon the gradual addition of CN$^-$, all naphthalene ring protons exhibited an upfield shift on different levels, which suggest the increase in the electron density in naphthalene ring through charge delocalization in the conjugated system. Meanwhile, we also did the infrared spectroscopy experiments to prove mechanism. In the IR spectrum of **HY**, the stretching vibration absorption peaks of hydroxyl O–H and HC=N appeared in 3409 cm^{-1}, 1607 cm^{-1}, respectively. However, when **HY** met with CN$^-$, the stretching vibration peaks of hydroxy (O–H) and HC=N absorption miraculously disappeared (Figure S6). This is clear proof of

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the **HY** encounter CN^{-} occurred deprotonation effect. Moreover, from the ESI–MS data, we can also see an obvious peak at m/z 422.9846 assignable to [**HY**–3H^{+}+3Na^{+}] (m/z called = 422) (Figure S7). This similarly supports the deprotonation phenomena of **HY**. These common phenomenon could be explained from the propose sensing mechanism show in Scheme 2.

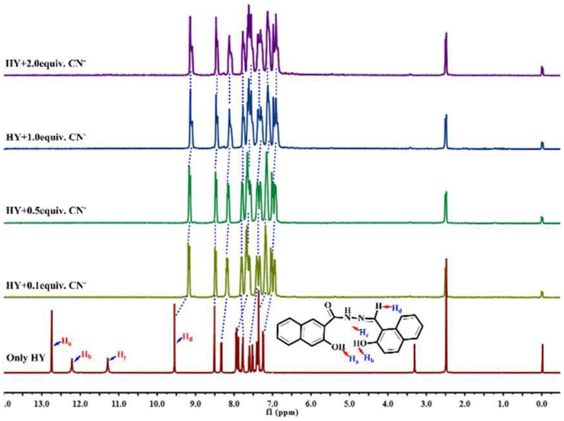
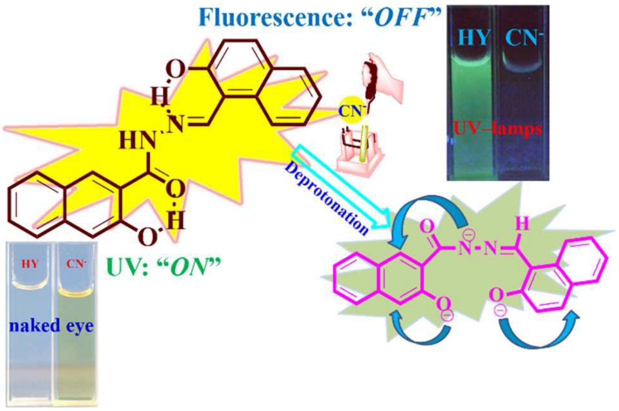


Fig. 9. ^{1}H NMR spectra of **HY** (0.1 M, DMSO–d_6) and in the presence of varying amounts of CN^{-}.



Scheme 2. The sensing mechanism of the chemosensor **HY** to CN^{-}.

Motivated by the favourable CN^{-} recognition properties of chemosensor **HY**, we prepared test strips by immersing filter papers into the DMSO/H$_2$O (3 : 7) solution of the chemosensor **HY** (1×10^{-3} M) and then dried them in air. The test strips could conveniently detect CN^{-}, similar to that commonly used for the pH measurement. Upon the addition of CN^{-} solutions to the test strips, the test strips shown obvious color change from colorless to yellow, meanwhile, under the UV–lamp, the yellow fluorescence were disappear that can be clearly observed (**Fig. 10**). Therefore, the test strips of **HY** have excellent application value in detection CN^{-}.

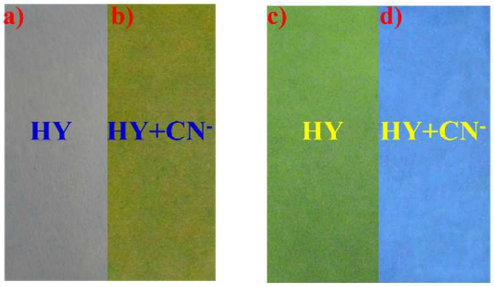


Fig. 10. Left: color change of test strips upon addition of CN^{-}. Right: the detection of test strips upon addition of CN^{-} under an UV lamp at 365 nm.

It is worth mentioning that we also investigated the practical utilities of the sense in our daily life, we selected the sprouting potatoes to carry out the below experiment. The sprouting potato (187 g) was first mashed before being soaked in water (400 mL) for 5 days until the extract became muddy. The mixture was filtered and the filtrate was washed with 60 mmol/L NaOH solution (150 ml) to get the cyanide–containing solution. As shown in Figure 10, upon the addition cyanide–containing solution into **HY**, An obvious colour change from colourless to yellow this can be directly observed by the naked eye (**Fig. 11a**). And with imagine the unanimous yellow fluorescent disappear under the UV lamp confirming that **HY** is a promising CN^{-} probe for practical applications (**Fig. 11b**).

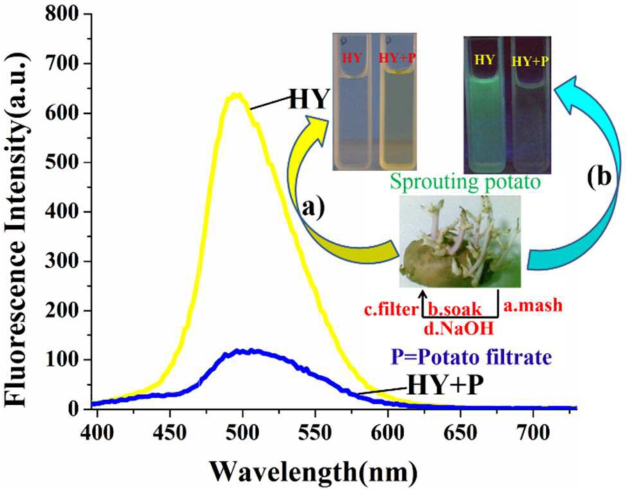


Fig. 11. Fluorescence emission data for the chemosensor **HY** to detect cyanide in sprouting potato. Inset: a) color changes observed for **HY** upon the addition of cyanide–containing ; b) color changes observed for **HY** upon the addition of cyanide–containing under the UV lamp and photograph of sprouting potato.

Conclusions

In summary, we have developed a novel CN^{-} chemosensor, which could detect CN^{-} through UV "turn–on" and fluorescent quenching with specific selectivity and high sensitivity. The investigation of the recognition mechanism indicated that the chemosensor **HY** recognized CN^{-} by a deprotonated procedure. It's worth noting that the competitive anions did not afford any obvious interference response. The absorption spectra detection limits of the **HY** for CN^{-} was 8.34 × 10^{-7} M and the fluorescence spectra detection limit was 2.85×10^{-8} M, which is far lower than the WHO guideline of CN^{-} in drinking water (less than 1.9×10^{-6} M). Moreover, test strips based on this chemosensor were fabricated, which could serve as practical colorimetric and fluorescence test kits to detect CN^{-} for simple and fast measurement and the chemosensor **HY** is a good way to detect cyanide aqueous extracts of sprouting potatoes.

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Notes and references

Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China; Key Laboratory of Polymer Materials of Gansu Province; College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070, P. R. China Fax: +86 9317973191; Tel: +86 9317973191; E-mail: weitaibao@126.com.

†Electronic Supplementary Information (ESI) available: [details of any supplementary information of complete experimental procedures]. See DOI:10.1039/b000000x/

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A simple chemosensor for the dual-channel detection of cyanide in water with high selectivity and sensitivity

Xiao-Bin Cheng, Hui Li, Feng Zheng, Qi Lin, Hong Yao, You-Ming Zhang and Tai-Bao Wei*
Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China; Key Laboratory of Polymer Materials of Gansu Province; College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070，P. R. China

By a deprotonated mechanism, the simple chemosensor **HY** showed high sensitivity and selectivity for cyaniade in aqueous media. Moreover, the chemosensor **HY** is a good cyaniade test kits. It could detect cyanide in aqueous extracts of sprouting potatoes.