A turn-on fluorescent chemosensor selectively detects cyanide in pure water and food sample

Tai-Bao Wei, Wen-Ting Li, Qiao Li, Jun-Xia Su, Wen-Juan Qu, Qi Lin, Hong Yao, You-Ming Zhang

PII: S0040-4039(16)30542-1
DOI: http://dx.doi.org/10.1016/j.tetlet.2016.05.028
Reference: TETL 47647

To appear in: *Tetrahedron Letters*

Received Date: 5 April 2016
Revised Date: 6 May 2016
Accepted Date: 9 May 2016

Please cite this article as: Wei, T-B., Li, W-T., Li, Q., Su, J-X., Qu, W-J., Lin, Q., Yao, H., Zhang, Y-M., A turn-on fluorescent chemosensor selectively detects cyanide in pure water and food sample, *Tetrahedron Letters* (2016), doi: http://dx.doi.org/10.1016/j.tetlet.2016.05.028

Tetrahedron Letters

journal homepage: www.elsevier.com

A turn-on fluorescent chemosensor selectively detects cyanide in pure water and food sample

Tai-Bao Wei*, Wen-Ting Li, Qiao Li, Jun-Xia Su, Wen-Juan Qu, Qi Lin, Hong Yao, You-Ming Zhang*

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, PR China

ARTICLE INFO

Article history:
Received
Revised
Accepted
Available online

Keywords:
Dihydroxy phenazine
Cyanide
Test strips
Food samples

ABSTRACT

A turn-on fluorescent chemosensor (**H-1**) for cyanide anions based on dihydroxy phenazine was designed and synthesised. The sensor **H-1** exhibits high sensitivity and good selectivity for cyanide in pure water. The CN^- response mechanism involves a hydrogen bonding and deprotonation process in the sensor, which induced prominent fluorescence enhancement. The detection limit of the sensor towards CN^- is 5.65×10^{-7} M, and other anions had nearly no influence on the probing behavior. In addition, test strips based on the sensor were fabricated, which also exhibit a good selectivity to CN^- in water. Notably, this sensor was successfully applied to detect CN^- in food samples, which proves a very simple and selective platform for on-site monitoring of CN^- in agriculture samples.

The cyanide (CN^-) has been continuously of concern all over the world due to its extreme toxicity and widespread use in metallurgy, plastics production, and silver or gold extraction.[1] Cyanide-containing substance, found in foods, plants, water, soil, polluted air, vehicle exhaust, and even cigarette burning gas, are extremely detrimental to living organisms and most animals by causing lethal effect to their central nervous system.[2] Uptake of toxic cyanide could occur through absorption by lungs and skin, and also from contaminated food and drinking water.[3] Therefore, much interest has been sparked in the design of new methods to monitor CN^- in biological and environmental samples.

Thanks to the enthusiastic efforts of scientists, a large number of good sensors for cyanide have been invented.[4] Among the various sensors, fluorescent chemosensors present numerous advantages, including high sensitivity, low cost, and easy operation.[5] Moreover, phenazine derivatives, which have dramatic fluorescent emissions, have been synthesized for a long time, but they were seldom been used in ions recognition field.[6] On the other hand, in biological and environmental systems, CN^- sensors interactions commonly occur in aqueous solution, therefore, much attention has been paid to develop the cyanide sensors that work in water. However, few, if any, CN^- sensors are able to display high selectivity over other anions such as F^-, AcO^-, and $H_2PO_4^-$ in pure water.[7] Recently, we have also reported 4-amino-3-hydroxynaphthalene-1-sulfonic acid (Scheme S2) and 2, 4-dimethyl-7-amino-1, 8-naphthyridine as the fluorescent cyanide sensors in pure water.[8]

In view of this requirement and as a part of our research interest in ion recognition.[9] Herein, we report a rationally designed, simple, and efficient fluorescent sensor **H-1** based on dihydroxy phenazine. The chemosensor **H-1** could act as a turn-on fluorescent sensor for cyanide anions in pure water. The recognition progress occurred via deprotonating between the hydroxyl of **H-1** and cyanide. When exposed **H-1** to the low concentration solution of cyanide anion there was a dramatically increase of the emission maximum of **H-1**, and the color of the solution changed from dim orange to bright yellow, which can be seen by naked-eyes under the UV lamp (365 nm). As practical applications, the chemosensor was successfully applied to the detection of CN^- in sprouting potatoes and bitter seeds, which prove a very simple and selective platform for on-site monitoring of CN^- in agriculture samples.

The 2, 5-dihydroxy-*p*-benzoquinone **(2)** was reacted with *o*-diaminobenzenes (1.1 equiv) in water to afford high yields of 2, 3-dihydroxyphenazines **H-1** (Scheme S1).[10] It was characterized by ^{1}H NMR, IR and ESI-MS (Fig. S5, S8, and S9 in SI).

In order to investigate the CN^- recognition abilities of the sensor **H-1** in water, we carried out a series of host-guest recognition experiments. The recognition profiles of the chemosensor **H-1** toward various anions, including F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, CN^- and SCN^-, were primarily investigated using fluorescence and UV-vis spectroscopy in water. When 50 equiv. of CN^- were added to the sensor **H-1** (20 μM), there was not a significant color change. Interaction of **H-1** with 50 equiv. of CN^- resulted in a negligible red shift in the absorption spectrum, which was not visible to the naked eye (Fig. S1 in SI).

As shown in Figure 1, in the fluorescence spectrum, the maximum emission of **H-1** appeared at 548 nm in water when excited at λ_{ex} = 415 nm. On the addition of 50 equivalents of CN^-, the fluorescence intensity of sensor **H-1** (20 μM) increased rapidly, and the maximum emission shifted to 568 nm. The color change from dim orange to bright yellow could be distinguished by the naked eye on UV lamp

* Corresponding author. Tel: +086 931 7973120;
E-mail address: weitaibao@126.com (T.-B. Wei); zhangnwnu@126.com (Y.-M. Zhang).