RSC Advances

PAPER

View Article Online
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Cite this: *RSC Adv.*, 2016, **6**, 86627

A highly selective colorimetric chemosensor for detection of iodide ions in aqueous solution†

Jie Chen, Qi Lin, Qiao Li, Wen-Ting Li, You-Ming Zhang and Tai-Bao Wei*

Received 20th July 2016
Accepted 30th August 2016

DOI: 10.1039/c6ra18490a

www.rsc.org/advances

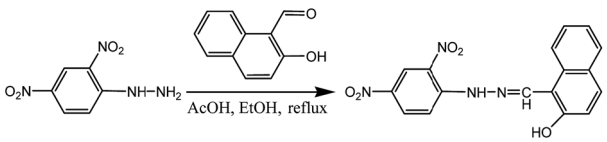
We synthesized a new iodide ion (I^-) chemosensor (**CS**) based on a hydrazone derivative obtained from the condensation of 2-hydroxy-1-naphthaldehyde and 2,4-dinitrophenylhydrazine. The **CS** showed selective colorimetric recognition of I^-, the miscellaneous competitive anions (F^-, Cl^-, Br^-, HSO_4^-, CH_3COO^-, $H_2PO_4^-$, SCN^-, CN^-, ClO_4^- and S^-) did not lead to any significant interference. The detection limits of the **CS** for I^- is 1.1×10^{-6} M. The sensor has been successfully applied to estimate the content of iodide ions in urine. Moreover, ion test strips based on **CS** were fabricated, which could act as a convenient and efficient I^- test kit for "in-the-field" measurement of iodide ions.

The selective sensing of important anions is highly significant because anions are widely distributed and play important roles in both environmental and life sciences.[1–7] Many efforts have been made to design chemosensors for anions such as F^-, CN^-, Cl^-, $H_2PO_4^-$, SO_4^-, AcO^-, *etc.*[8–19] However, most of the synthetic receptors operate in nonprotonic organic solvents while few in aqueous solution, and they often require convoluted and time-consuming syntheses.[20–24] It is particularly difficult to develop anion recognition systems that form hydrogen bonded complexes in aqueous solvent, for the obvious reason that the water competes strongly for the hydrogen bonding sites.

Iodine, as we know, is a crucial trace element on earth and mainly exists in seawater. Iodide is known an essential nutrient in the human body.[25] Iodine exists in the human body predominantly in the form of iodide (I^-), which is the bio-available form of iodine for thyroid.[26] As a major portion of iodine absorbed by the body is excreted in the urine, it acts as a sensitive marker of iodine intake in the body and iodine status change can be monitored through urine analysis. In addition, elemental iodine is used in a variety of applications, for example manufacturing of dyes, synthesis of some organic chemicals, and in medicine.[27] Therefore, it is of great importance to realize rapid, sensitive, and selective detection of iodide in food, pharmaceutical products, and biological samples such as urine. Nowadays, various methods based on different principles have been proposed to detect and determine iodide ions, including ion chromatography,[28,29] electrochemistry,[30–32] and organic chromophores or fluorophores.[33–39] Due to the large ionic radius, low charge density and low hydrogen bonding ability, iodide is the most difficult halide to be sensed. Therefore, the development of chemosensors for iodide based on hydrogen-bonding is very difficult, even that in aqueous solution.

In view of these, and as an research interesting in ions recognition,[40–42] herein, we report a new iodide ions (I^-) chemosensor (**CS**) based-on a hydrazone derivative obtained from the condensation of 2-hydroxy-1-naphthaldehyde and 2,4-dinitrophenylhydrazine (Scheme 1). In order to achieve the "naked-eye" detection for I^- stimuli, the 2,4-dinitrophenyl hydrazone moiety was introduced into the **CS** as the signal groups as well as binding sites. The chemosensor **CS** can optically and visually detect the presence of iodide over a wide range of other competent ions in an aqueous medium with high selectivity.

The sensing abilities of **CS** toward various anions (F^-, Cl^-, Br^-, I^-, HSO_4^-, CH_3COO^-, $H_2PO_4^-$, SCN^-, CN^-, ClO_4^- and S^-) were investigated by UV-vis spectroscopy. When 50 equivalents of these anions were added to the DMSO/H_2O (9 : 1, v/v)



Scheme 1 Structure and synthesis of the sensor **CS**.

Fig. 1 Color changes of **CS** (2×10^{-5} M) after addition of 50 equivalents of various anions in DMSO/H_2O (9 : 1, v/v). From left to right: only CS, I^-, F^-, Cl^-, Br^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, SCN^-, CN^- and S^{2-}.

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. E-mail: weitaibao@126.com; zhangnwnu@126.com; Fax: +86 9317973191; Tel: +86 9317973191

† Electronic supplementary information (ESI) available: Complete experimental procedures and some of the spectroscopic. See DOI: 10.1039/c6ra18490a

solutions of **CS** (2×10^{-5} M), respectively, at room temperature, a dramatic color change from purple to yellow was observed by the naked eye only upon the addition of I^- to sensor **CS** (Fig. 1).

An important feature of the sensor is its specific selectivity toward the analyte over other competitive species. The variations of UV-vis absorbance of **CS** in DMSO/H_2O binary solutions caused by the anions (F^-, Cl^-, Br^-, HSO_4^-, CH_3COO^-, $H_2PO_4^-$, SCN^-, CN^-, ClO_4^- and S^{2-}) were recorded in Fig. 2. More importantly, chloride, bromide, and iodide have a relatively high free energy of solvation, which indicates that the receptors have to compete with the medium effectively.[43,44] The results revealed that bromide and chloride did not exhibit any obvious color spectral changes. Other anions exerted no influence detection of iodide in the absorbance at 424 nm. In the presence of these ions, I^- still produced similar color and optical spectral changes (Fig. 3). The results showed that sensor **CS** selectivity toward I^- was not affected by the presence of other anions.

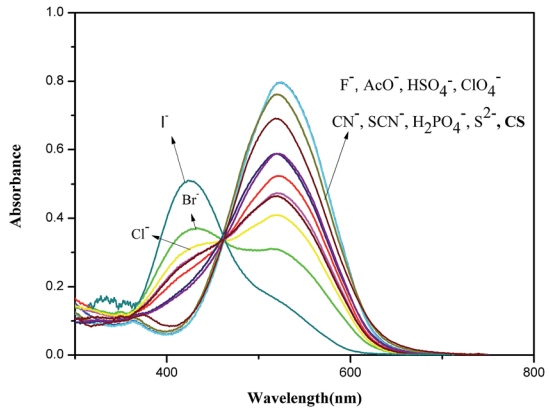


Fig. 2 Changes in the UV/vis spectra of **CS** (2×10^{-5} M) after addition of 50 equivalents of various anions in DMSO/H_2O (9 : 1, v/v).

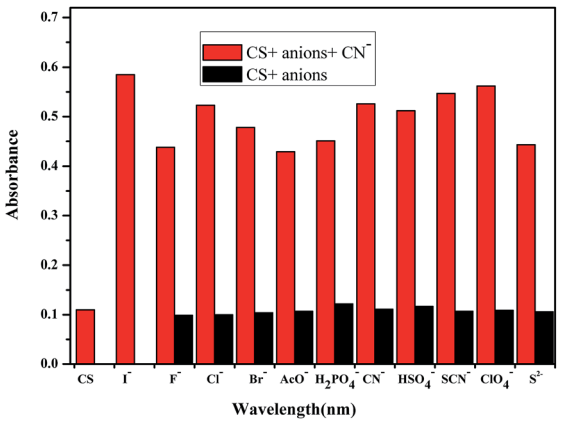


Fig. 3 Absorbance responses of **CS** (2×10^{-5} M) after addition of 50 equivalents of various anions in DMSO/H_2O (9 : 1, v/v) in the presence of 50 equivalents of I^- with 50 equivalents of various anions ions in DMSO/H_2O (9 : 1, v/v). Bars represent absorbance at 424 nm. The black bars represent the addition of the competing anions ions to the solution of **CS**. The red bars represent the addition of competing anions ions and I^- to the solution of **CS**.

Fig. 4 shows the family of absorption spectra obtained over the course of the titration of sensor **CS** with I^- (0.1 M) in DMSO/H_2O (9 : 1, v/v). With the gradual addition of I^- to sensor **CS**, the intensity of absorption bands at 424 nm increased, while the absorption band at 520 nm began to decrease until it reached a limiting value. Moreover the presence of one isosbestic points at 461 nm indicated that sensor **CS** reacts with I^- to form a stable complex. The association constant (K_a) of **CS** with I^- was determined using the Benesi–Hildebrand equation.[45–47] The measured absorbance $[1/(A-A_0)]$ varied as a function of $1/[I^-]$ in a linear relationship ($R^2 = 0.9919$) in Fig. 5. The association constant of **CS** with I^- in DMSO/H_2O (9 : 1, v/v) was calculated to be 1.53×10^6 M^{-1}. The detection limit of the absorption spectral changes calculated on the basis of $3\sigma/S$ was 1.1×10^{-6} M for the I^-.[48] As shown in Fig. 6, the minimum concentration of I^- for the color change observed by the naked eye was 1×10^{-4} M.

To further demonstrate the potential of **CS** probe for practical applications, we exemplified its ability to detect I^- ions in urine samples to realize its applicability in real sample analysis. Urine samples that were obtained from Lanzhou University Affiliated Hospital. For the urine samples, 2 ml of acetonitrile

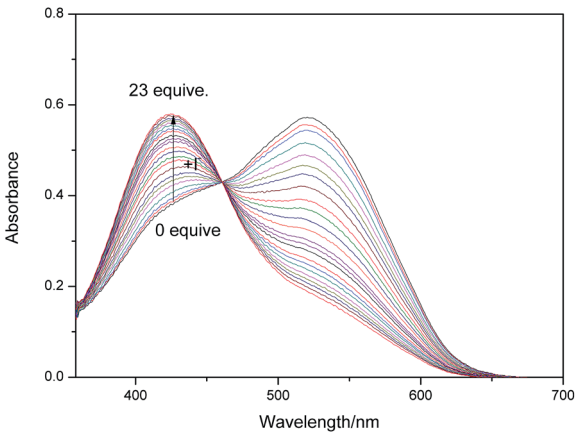


Fig. 4 UV-vis spectra of **CS** (2×10^{-5} M) in DMSO/H_2O (9 : 1, v/v) upon adding an increasing concentration of I^- (0.1 M).

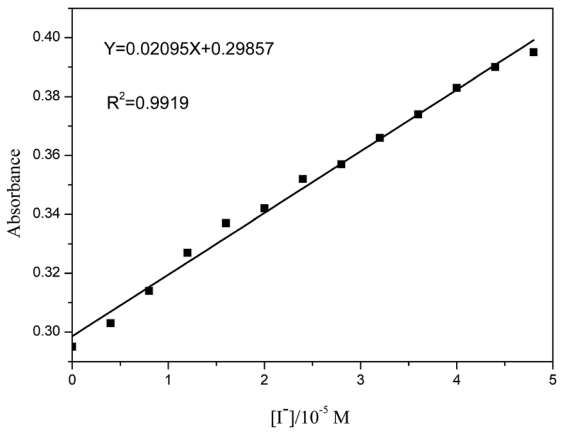


Fig. 5 Plot of the intensity at 424 nm for a mixture of **CS** (2×10^{-5} M) in DMSO/H_2O (9 : 1, v/v) and I^- in H_2O.

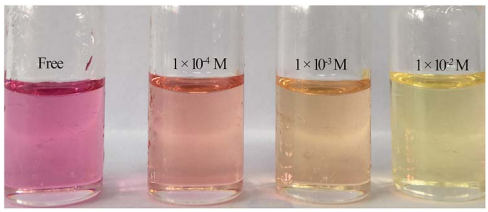


Fig. 6 Naked-eye detection limit.

Table 1 Determination of iodide content in urine samples (n=3)

Urine sample	Amount of I^- before adding I^-	Adding I (μM)	Foumd (μM)	Recovery (%)	RSD (n = 3, %)
1	—	20	21.2	106	0.93
2	—	50	52.2	104	1.3

and 6 ml of deionized water were added along with 2 ml urine in centrifuge tubes. The tubes were vortex for 2 minutes and centrifuged at 1500 rpm for 20 minutes. The supernatant of these solutions were taken and filtered through 0.22 μm membrane prior to use. Urine samples were analyzed using the standard addition method. The results show an average recovery of 105% with Relative Standard Deviation (RSD) of 1.12% for urine samples (Table 1). The experimental results indicate that the sensor possessed excellent applicability for real sample analysis. The development of a "dip-sticks" approach was extremely attractive for "in-the-field" measurements that did not require any additional equipment. The test strips were prepared by immersing filter papers into a DMSO/H_2O (9 : 1, v/v) solution of **CS** (1×10^{-3} M) then drying in air. As shown in Fig. 7, when the different amount of I^- (5×10^{-3} M, 1×10^{-2} M, 2×10^{-2} M) was added on the test kits, the obvious color changes from purple to yellow were observed. Therefore, the test strips of **CS** have excellent application value in the detection of I^-.

To explore the sensing mechanism of **CS** to I^-, the IR, ^1H NMR titration and ESI-MS were investigated, which illustrated the characteristic structural changes occurring upon interaction with I^-. In the IR spectra of **CS**, the stretching vibration absorption peaks of N–H, and H–C=N appeared at 3267 cm^{-1}, 1612 cm^{-1} respectively. However, when **CS** coordinated with I^-, the stretching vibration absorption peaks of N–H shifted to 2960 cm^{-1}, while, the stretching vibration absorption peaks of H–C=N shifted to 1619 cm^{-1} (Fig. 8). These phenomena

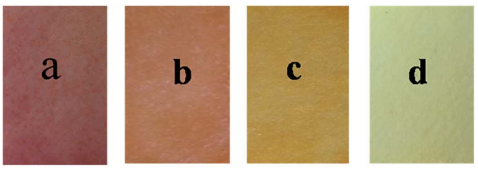


Fig. 7 Photographs of test strips (a): only **CS**, (b) **CS** + I^- (5×10^{-3} M) (c) **CS** + I^- (1×10^{-2} M) (d) **CS** + I^- (2×10^{-2} M).

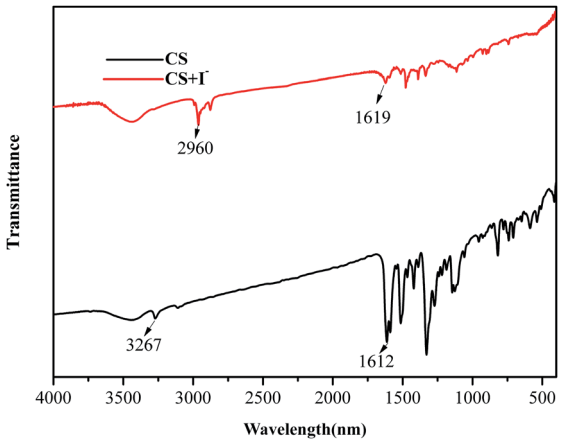
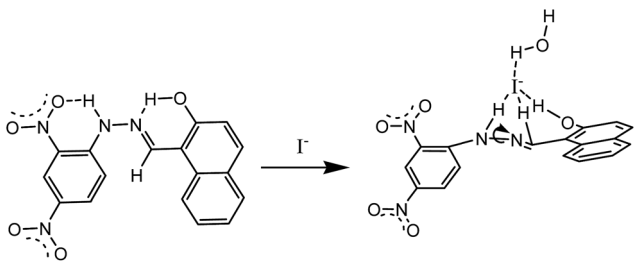


Fig. 8 IR spectra of compound **CS** and **CS**–I^- in KBr disks.

indicated that the N–H group and the H–C=N group formed $I^-\cdots$H–C=N and N–H$\cdots I^-$ hydrogen bond (Scheme 2).

As shown in Fig. 9, before the addition of I^-, there were two intramolecular hydrogen bonds in the molecular structure of **CS**. The formation of these hydrogen bonds led to the ^1H NMR chemical shifts of –OH, N–H and HC=N appeared at 11.80, 11.10 and 9.59 ppm, respectively. Upon gradual addition of I^-, the –OH peak at 11.80 ppm and N–H 11.10 ppm became broad. At the same time, the HC=N peak at 9.59 ppm decreased gradually that is ascribed to the molecular structure underwent an intramolecular rotation, which induced the breaking of



Scheme 2 A possible sensing mechanism of the sensor **CS** to I^-.

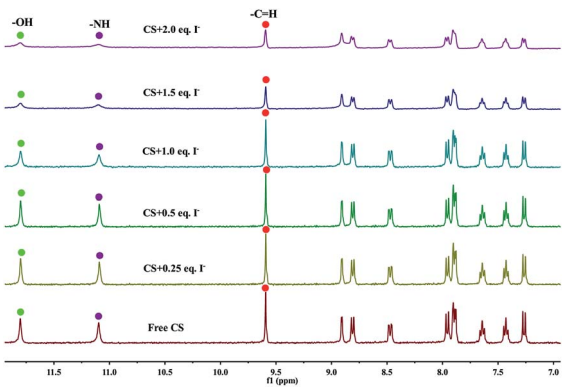


Fig. 9 Partial ^1H NMR spectra of **CS** (0.01 M) in DMSO upon addition of I^-.

N–H···O=N and N–H···O–H, simultaneously, the I^-–**CS** complex was formed *via* the coordination of I^- with O–H, N–H and hydrogen atoms of HC=N on **CS** (Scheme 2). Further evidence obtained by ESI-MS experiments also supports this proposed mechanism. In the ESI-MS spectra of **CS** (Fig. S1, ESI†), the $[\mathbf{CS}–H]^-$ (m/z calcd = 351.1250). However, when 1 equivalent of I^- was added to the solution of **CS**, coinciding well with that for the species $[\mathbf{CS} + H_2O + I^-]^-$ (m/z calcd = 496.0906) and indicating the formation of the stabilized anions species **CS**–I^- (Fig. S2, ESI†).

In summary, we have developed a new chemosensor **CS**, which could detect I^- in aqueous solution with specific selectivity and high sensitivity. A unique colorimetric response to I^- is realized through the coordination with **CS**. In particular, competitive anions such as F^-, AcO^-, and $H_2PO_4^-$ did not afford any obvious interference response. The detection limits of I^- were found to be 1×10^{-4} M and 1.1×10^{-6} M from the naked-eye color changes and absorption spectral changes respectively. So this recognition behaviour makes **CS** as a potential probe to detect I^- in environmental and life sciences.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21064006, 21262032 and 21161018), the Program for Changjiang Scholars and Innovative Research Team in University of Ministry of Education of China (No. IRT1177), the Natural Science Foundation of Gansu Province (No. 1010RJZA018), the Youth Foundation of Gansu Province (No. 2011GS04735) and NWNU-LKQN-11-32.

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