An alternative approach to develop a highly sensitive and selective chemosensor for the colorimetric sensing of cyanide in water†

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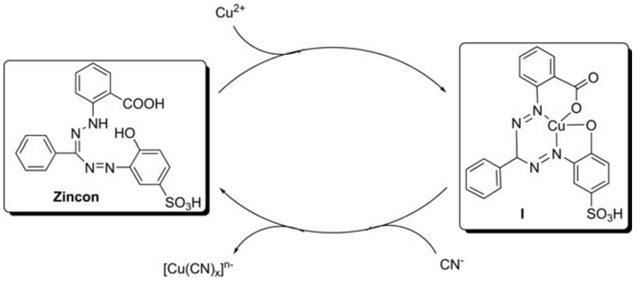
By utilizing a new indirect trick, an old and cheap compound, zincon (2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene), was found to be a "novel" highly sensitive and selective chemosensor for cyanide in pure aqueous solutions, with a detection limit of 0.13 ppm and a color change that could be observed by the naked eye.

New chemosensors capable of sensing target guests *via* changes in optical signals have attracted much attention due to their potential applications in the development of analytical devices. Especially, anion chemosensors are of particular interest, since they are involved in chemical, biological, and environmental processes of particular relevance.[1] However, in comparison with the relatively large number of cation chemosensors, the development of anion chemosensors that work in water is still a challenging area.[2]

Cyanide and fluoride are probably two of the most toxic anions. Despite its toxicity, cyanide is widely used industrially in gold mining, electroplating, metallurgy, the synthesis of nylon and other synthetic fibers and resins, and can be found in many foods and plants.[3–5] The US Environmental Protection Agency (EPA) has set the Maximum Contaminant Level (MCL) for cyanide in drinking water to be 0.2 ppm. Also, as excess fluoride can lead to fluorosis, the MCL for fluoride set by the EPA is 2 ppm in drinking water.[6] Although there are many chemosensors for cyanide and fluoride reported, highly sensitive ones that work *in water* are still very scarce. Especially, colorimetric chemosensors are most desirable, which could be widely used owing to the low cost and lack of equipment required, and a color change that can easily be observed by the naked eye, even at very low analyte concentrations.[7]

So far, most of the anion chemosensors have been based on the attachment of a dye to an anion-binding site; however, this mechanism does not always work well, leading to the comparatively scarce number of anion chemosensors as mentioned above. Considering that many anions can form stable complexes with cations, we are wondering if it is possible to probe anions by utilizing the reported good cation chemosensors. That is to say, the anions might snatch cations from the formed complex of the cations and their corresponding chemosensors, with a detectable optical signal. This is really possible, if the stability constant of the complex formed by the anion and the cation is larger than that of the complex of the cation and its chemosensor. Considering that cyanide could form very stable complex with copper ions [eqn (S1) and (S2)†],[8] we are wondering if there are some compounds that could form complex with Cu^{2+} and give optical signal with color change upon the addition of trace CN^-, sensitively and selectively. However, so far, there are no reports concerned with this idea. Thus, after thinking of some candidates, we focused our eyes on an old and very cheap compound, zincon (2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene) (Scheme 1), which is a widely accepted reagent for the detection of zinc and copper ions with a color change and possesses a high stability constant towards copper ions (log K 7.5 ± 0.1 in water).[9] Then, we expect that the added CN^- could snatch the Cu^{2+} from the formed complex of zincon and copper ions with a color change, as demonstrated in Scheme 1. To the best of our knowledge, this is the first example of cyanide colorimetric chemosensors, according to the above idea.

Based on the preliminary experiments (Fig. S1 and S2† shown as examples), the detecting conditions for Cu^{2+} and CN^- were optimized. As shown in Fig. 1, upon increasing the concentration of Cu^{2+}, the peak intensity of the maximum absorption (λ_{max}) at 463 nm decreased gradually, accompanying a new peak at about 600 nm. When the concentration of Cu^{2+} was 2.2×10^{-5} mol L^{-1}, the peak at 463 nm disappeared completely. This confirmed that complex **I** was formed completely. Then, we tried to add some cyanide to complex **I**. Fortunately, the peak at 463 nm, corresponding to zincon, that had disappeared upon the addition of Cu^{2+}, recovered and its intensity increased as the concentration of CN^-



Scheme 1 The speculated conversion cycle of zincon in the presence of Cu^{2+} and CN^-.

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† Electronic supplementary information (ESI) available: Details of the experimental procedure; UV-Vis spectra; equations; absorption difference of the diluted zincon solutions in the presence of copper ions and anions; photos of different solutions of zincon and copper ions in water in the presence of different concentrations of different anions. See DOI: 10.1039/b812746h

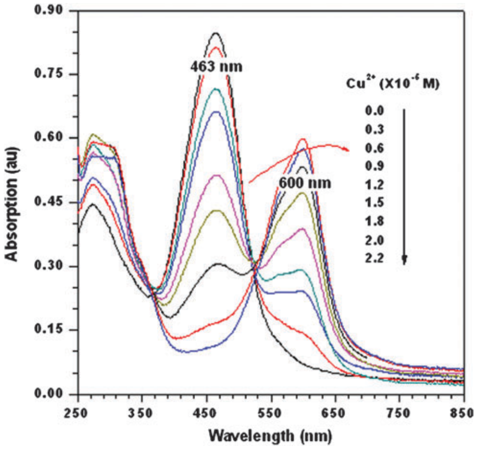

Fig. 1 UV-Vis spectra of zincon with increasing amounts of Cu^{2+} in water. The concentration of zincon was 5.0×10^{-5} mol L^{-1}.

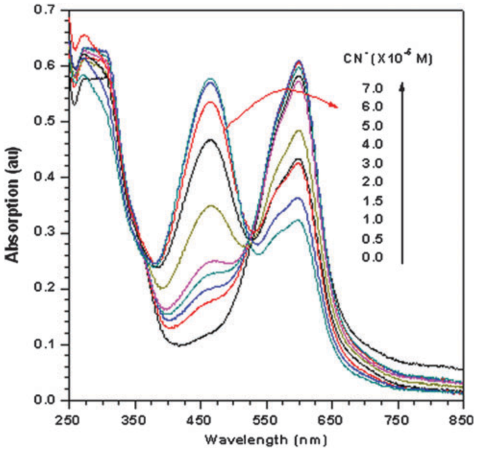

Fig. 2 UV-Vis spectra of the mixture solution of zincon (5.0×10^{-5} mol L^{-1}) and Cu^{2+} (2.2×10^{-5} mol L^{-1}) with increasing amounts of CN^- in water.

became higher (Fig. 2). Thus, the conversion cycle of zincon (Scheme 1) really did work in the presence of Cu^{2+} and CN^-, respectively, making the old, cheap zincon a "novel" sensitive CN^- chemosensor.

To see the sensitivity of zincon towards the cyanide anion more clearly, we presented the response of zincon for CN^- in water by another manner (Fig. S3†). It was easily seen that the absorption change at 463 nm was very obvious, for example, the absorbance change ($A - A_0$) was as big as 0.058 while the concentration of cyanide was only 0.13 ppm (namely at 0.5×10^{-5} M). And when the concentration of cyanide increased to 1.04 ppm (namely at 4×10^{-5} M), the change was much bigger (0.345). These results were relatively better to assure a limit of quantification below 0.2 ppm, fulfilling the EPA requirement. We also showed the response of zincon for CN^- by using the ratio of A_{463}/A_{600} (Fig. S4†), where the difference upon the addition of different amounts of cyanide was even more obvious, and the calculated change was as big as 0.094 while the concentration of cyanide was only 0.13 ppm, this was larger than the absorbance change ($A - A_0$) at 463 nm (0.058).

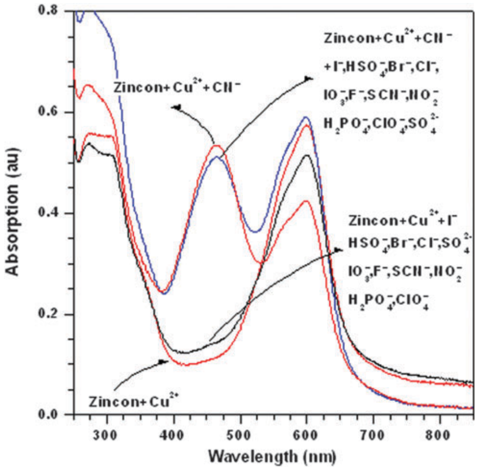

Fig. 3 UV-Vis spectra of zincon in the presence of different anions mixture (5.0×10^{-5} mol L^{-1}) in water. The concentration of zincon was 5.0×10^{-5} mol L^{-1} and Cu^{2+} was 2.2×10^{-5} mol L^{-1}.

To evaluate the cyanide-selective nature of zincon, possible absorption changes caused by other anions, including Cl^-, I^-, IO_3^-, SO_4^{2-}, NO_2^-, Br^-, $H_2PO_4^-$, SCN^-, HSO_4^- and ClO_4^-, were studied. As shown in Fig. S5†, anions other than cyanide did not cause significant changes in the absorption intensity. Increasing the concentration of these anions gave similar experimental results (Fig. S6†). Thus, the selectivity profile for CN^- over other anions was remarkably high. We further conducted experiments of competition using solutions containing cyanide and all the other anions. As shown in Fig. 3, the complex **I** could still report the presence of trace cyanide. Thus, this method for the probing of cyanide could still work in the presence of other anions.

Very interestingly, zincon responded sensitively to F^-, although not so high as towards cyanide. The absorption changes at 463 nm were recorded at different concentrations of F^- (Fig. S7†). Fig. S8† demonstrated the response of zincon for F^- in water: the limit of quantification was below 0.6 ppm (namely at 3×10^{-5} M), much lower than 2 ppm as required by the EPA. To find the possible reason, we calculated the stability constant of the complex formed after the addition of fluoride ions (Fig. S7†), which was much smaller than that of complex **I**. Thus, it was very difficult for the fluoride ions to snatch copper ions from complex **I**. Considering the fact that unlike in the case of cyanide, the peak at 600 nm almost remained unchanged upon the addition of fluoride ions, it was speculated that the added fluoride ions might coordinate with the copper ions together with zincon to form a new complex, in which the coordination number of copper ions might be five, not the normal four. However, further experiments should be conducted to prove this point.

As mentioned above, we would like to develop "naked eye" colorimetric sensors; thus, we wondered if the low detecting limit of the complex of zincon and copper ions towards cyanide and fluoride anions through an indirect trick could lead to the direct naked eye sensing of the two anions. Accordingly, we took photos of the resultant solutions at different concentrations of the anions and different solutions in the presence of different anions (Fig. 4 and S9–11†).

Fig. 4 Different solutions of zincon and copper ions (5.0×10^{-5} and 2.2×10^{-5} mol L^{-1}, respectively) in water in the presence of different concentrations of CN^-. From left to right ($\times 10^{-5}$ mol L^{-1}): 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0.

Although not so sensitive as measured by the UV-Vis spectrometer, we could easily observe the apparent color change at concentrations as low as 0.52 ppm for cyanide and 0.95 ppm for fluoride anions. And only in the presence of cyanide and fluoride anions, did the mixture solutions of zincon and Cu^{2+} show color changes. These results were relatively better, in comparison with most of those achieved in the literature so far. It should be pointed out that all the above experiments were conducted in pure water solutions, no organic solvents were needed any longer, and that many previously reported sensors worked in the mixture solution of organic solvents and water. Thus, this point should benefit the potential applications of zincon.

Considering that the addition of cyanide to a solution with too low a pH value would lead to the formation of cyanhydric acid, a highly toxic gas, we measured the pH value of the above used solutions and obtained the results: the pH value of the solution of zincon and copper ions was 6.73 with the concentrations the same as presented in Fig. 2. Thus, under the experimental conditions, it was safe for the operator.

Also, considering that usually, cyanide could be found in basic water with the pH range between 8.0 and 9.0, we further repeated the sensing experiments of zincon towards cyanide at the pH values of 8.2 and 9.1. As demonstrated in Fig. S12–22†, our reported indirect method for the detection of cyanide still worked, and the sensitivity and selectivity were nearly unchanged. However, the results of the experiments of competition were not as good as those at the pH value of 6.73.

In conclusion, we have successfully developed a "novel" anion chemosensor based on an old reagent. The preliminary results demonstrated that:

(1) For the first time, the well known cation colorimetric chemosensor was used to sense anions, cyanide and fluoride, sensitively and selectively, by utilizing an indirect trick. This perhaps is a novel idea to develop new anion chemosensors. And it was believed that many other good reported cation chemosensors could be found to be "novel" good anion chemosensors. Likewise, the anion chemosensors might also be applied to detect metal ions.

(2) The good selectivity and high sensitivity of the complex of zincon and copper ions towards cyanide and fluoride anions, coupled with the usage of pure water as the only solvent in the detection process, made a zincon promising candidate for the practical applications as a good chemical probe.

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