Electronic Supplementary Information (ESI)

An Alternative Approach to Develop Highly Sensitive and Selective Chemosensor for the Colorimetric Sensing of Cyanide in Water

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Experimental Section

Materials and Instrumentations

All reagents were of analytical reagent grade and used without further purification. Doubly distilled water was used for all experiments. $Cu(NO_3)_2 \cdot 3H_2O$, NaCN, KSCN, NaCl, KBr, KI, $NaHSO_4$, Na_2SO_4, $NaH_2PO_4 \cdot 2H_2O$, $NaClO_4$, $NaNO_2$, $NaIO_3$, NaF, KOH and Zincon were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. UV-visible spectra were obtained using a Shimadzu UV-2550 spectrometer, and the pH values were determined by using a DELTA 320 PH dollar.

Preparation of solutions of metal ions and anions

0.1 mmol of each inorganic salt ($Cu(NO_3)_2 \cdot 3H_2O$, 24.2 mg; NaCl, 5.8 mg; KSCN, 9.8 mg; KBr, 11.9 mg; KI, 16.6mg; Na_2SO_4, 14.2 mg; $NaClO_4$, 12.2 mg; NaF, 4.2 mg; $NaNO_2$, 6.9mg; $NaHSO_4$, 12mg; $NaIO_3$, 19.8mg; $NaH_2PO_4 \cdot 2H_2O$, 15.6 mg; NaCN, 4.9mg; Zincon, 44mg) was dissolved in distilled water (10 mL) to afford 1×10^{-2} mol/L aqueous solution. The stock solutions could be diluted to desired concentrations with water when needed, and the pH values were adjusted by the addition of the concentrated solution of potassium hydroxide with the aid of a pH meter.

UV absorption changes of zincon by Cu^{2+}

UV absorption changes of zincon (5.0×10^{-5} mol/L) were recorded before and after the addition of Cu^{2+} to the solution of zincon. The same work was conducted at the pH value of 8.2 and 9.1.

UV absorption changes of zincon+Cu^{2+} with CN^-

The solution of zincon (5.0×10^{-5} mol/L) and NaCN (1×10^{-3} mol/L) were prepared in distilled water, and the pH values were adjusted by the addition of the concentrated solution of potassium hydroxide with the aid of a pH meter. A solution of zincon was placed in a quartz cell (10.0 mm width) and the UV Absorption spectrum was recorded. After the solution of Cu^{2+} (2.2×10^{-5} mol/L) was added to zincon (5.0×10^{-5} mol/L), the solution of NaCN was introduced in portions (the concentrations of the NaCN were 5.0×10^{-6}, 1.0×10^{-5}, 1.5×10^{-5}, 2.0×10^{-5}, 3.0×10^{-5}, 4.0×10^{-5}, 5.0×10^{-5}, 6.0×10^{-5}, 7.0×10^{-5} mol/L) and the UV absorption changes were recorded at room temperature each time. The same work was conducted at the pH value of 8.2 and 9.1.

UV absorption changes of zincon+Cu^{2+} with other anions

The solution of zincon (5.0×10^{-5} mol/L) and anions were prepared in distilled water, and the pH values were adjusted by the addition of the concentrated solution of potassium hydroxide with the aid of a pH meter. UV absorption changes of zincon (5.0×10^{-5} mol/L) + Cu^{2+} (2.2×10^{-5} mol/L) were recorded before and after the addition of anions to the solution of zincon. The same work was conducted at the pH value of 8.2 and 9.1.

UV absorption changes of zincon+Cu^{2+} with CN^- and other anions

Then UV absorption changes of zincon (5.0×10^{-4} mol/L) + Cu^{2+} (2.2×10^{-5} mol/L) were recorded before and after the addition of NaCN and all the other anions (5.0×10^{-5} mol/L). The same work was conducted at the pH value of 8.2 and 9.1.

UV absorption changes of zincon+Cu^{2+} with F^-

UV absorption changes of zincon (5.0×10^{-5} mol/L) + Cu^{2+} (2.2×10^{-5} mol/L) were recorded before and after the addition of F^- to the solution of zincon.

Equation S1: the reaction between Cu^{2+} and CN^-

$$2Cu^{2+} + 4CN^- = 2CuCN + (CN)_2 \quad \text{(CuCN is white precipitant).}$$

Equation S2: the reaction between CuCN and CN^-

$$CuCN + (x\text{-}1)CN^- = [Cu(CN)_x]^{1-x}, \ (x = 2, 3, \text{ or } 4)$$

The stability constants (K), $[Cu(CN)_2]^-$: $K = 1.00 \times 10^{24}$; $[Cu(CN)_4]^{3-}$: $K = 2.00 \times 10^{30}$.

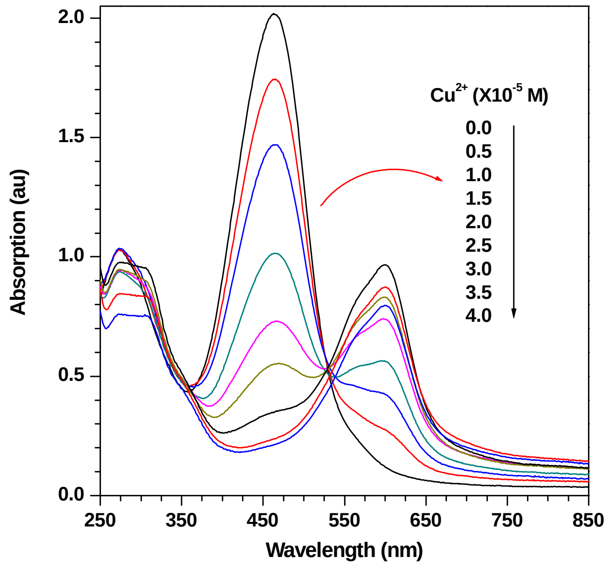

Figure S1. UV-vis spectra of zincon with increasing amounts of Cu^{2+} in water. The concentration of zincon was 1.0×10^{-4} mol/L.

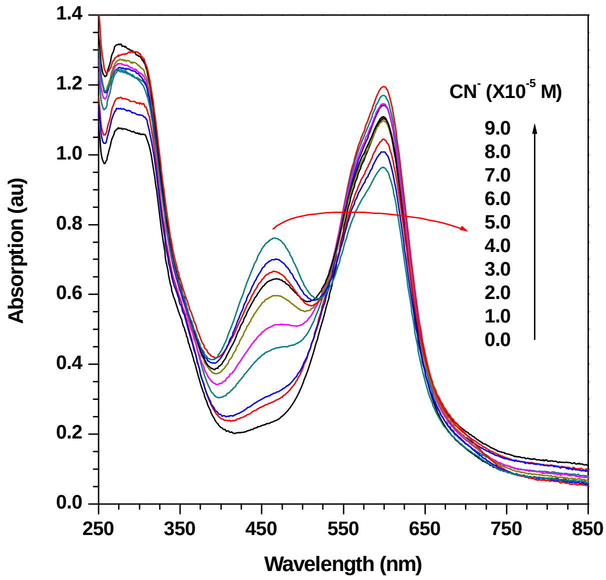

Figure S2. UV-vis spectra of the mixture solution of zincon (1.0×10^{-4} mol/L) and Cu^{2+} (4.0×10^{-5} mol/L) with increasing amounts of CN^- in water.

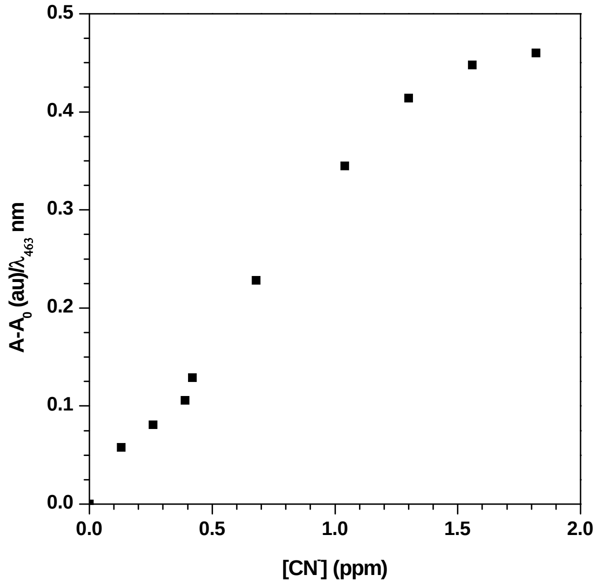

Figure S3. Absorption difference at λ= 463 nm versus the concentration of CN^- in water with the concentrations of zincon and Cu^{2+} at 5.0×10^{-5} and 2.2×10^{-5} mol/L , respectively.

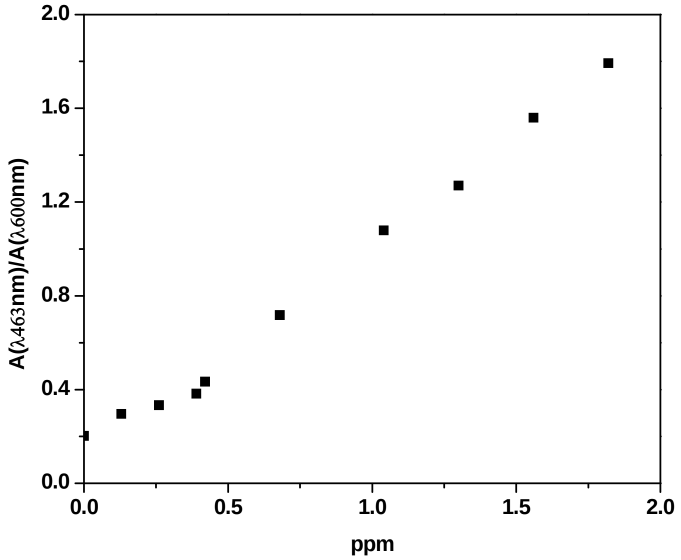

Figure S4. Absorption difference A(463nm)/A(600nm) versus the concentration of CN^- in water with the concentrations of zincon and Cu^{2+} at 5.0×10^{-5} and 2.2×10^{-5} mol/L , respectively.

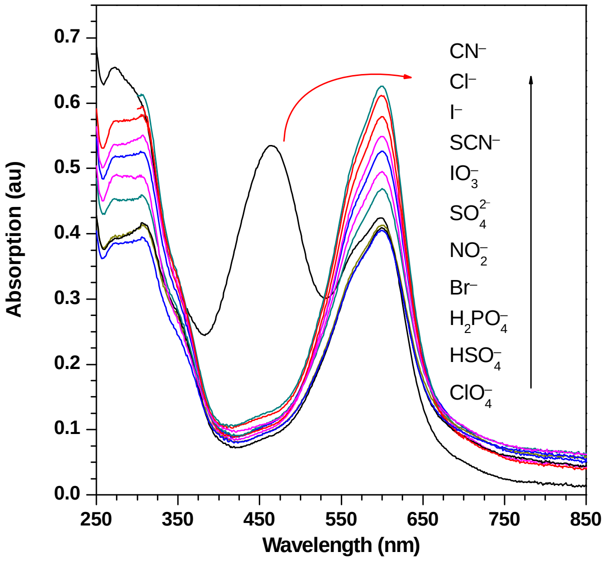

Figure S5. UV-vis spectra of zincon at the presence of different anions (5.0×10^{-5} mol/L) in water. The concentration of zincon was 5.0×10^{-5} mol/L.

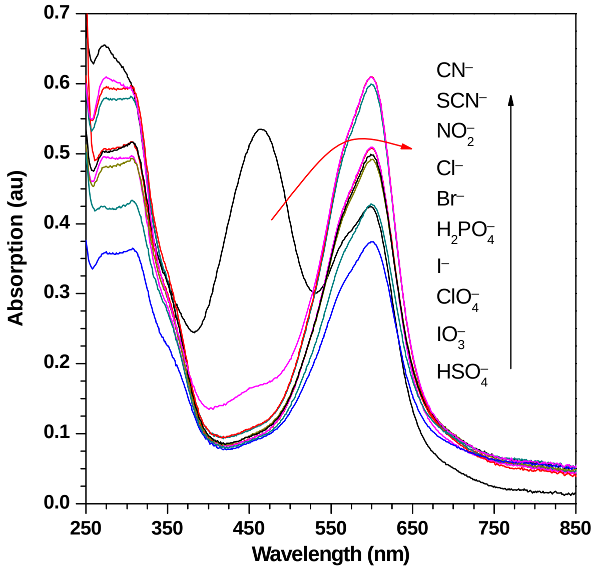

Figure S6. UV-vis spectra of zincon (5.0×10^{-5} mol/L) at the presence of different anions (2.5×10^{-4} mol/L) in water. The concentration of cyanide was 5.0×10^{-5} mol/L.

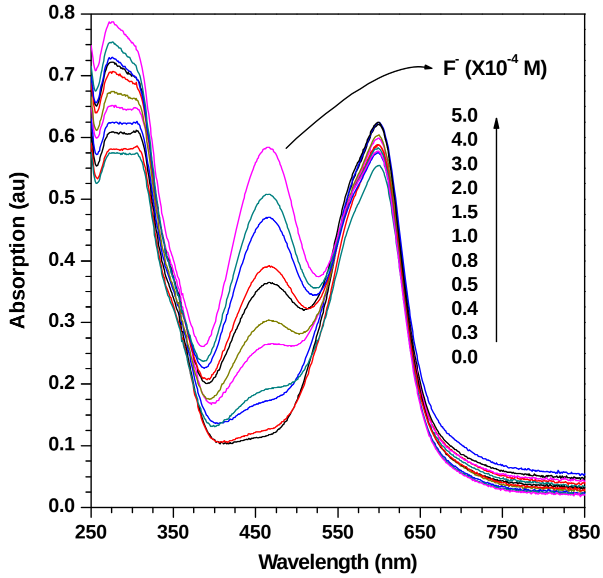

Figure S7. UV-vis spectra of the mixture solution of zincon (5.0×10^{-5} mol/L) and Cu^{2+} (2.2×10^{-5} mol/L) with increasing amounts of F^- in water. The stability constant (*K*) was calculated to be 4.8×10^4.

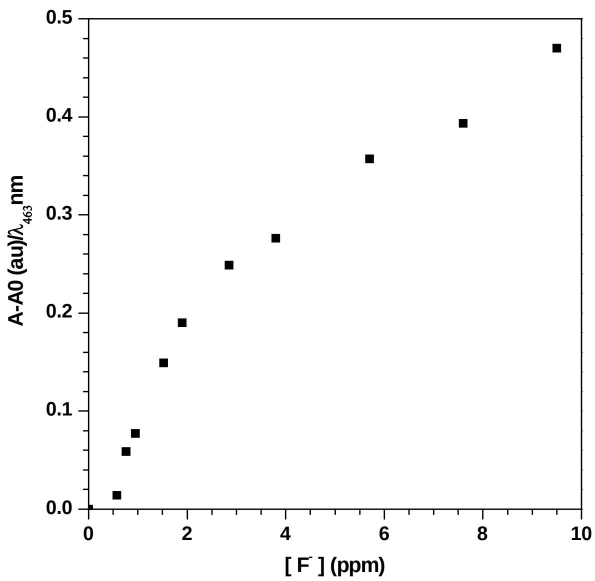

Figure S8. Absorption difference at λ= 463 nm versus the concentration of F^- in water with the concentrations of zincon and Cu^{2+} at 5.0×10^{-5} and 2.2×10^{-5} mol/L , respectively.

Figure S9. Different solutions of zincon and copper ions in water (5.0×10^{-5} and 2.2×10^{-5} mol/L, respectively) in the presence of anion (5.0×10^{-5} mol/L). From left to right: no anion, CN^-, Cl^-, I^-, IO_3^-, SO_4^{2-}, NO_2^-, Br^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-.

Figure S10. Different solutions of zincon and copper ions in water (5.0×10^{-5} and 2.2×10^{-5} mol/L, respectively) in the presence of different concentrations of F^-. From left to right ($\times10^{-5}$ mol/L): 0, 3.0, 5.0, 8.0, 10.0, 15.0, 20.0, 30.0, 40.0 and 50.0.

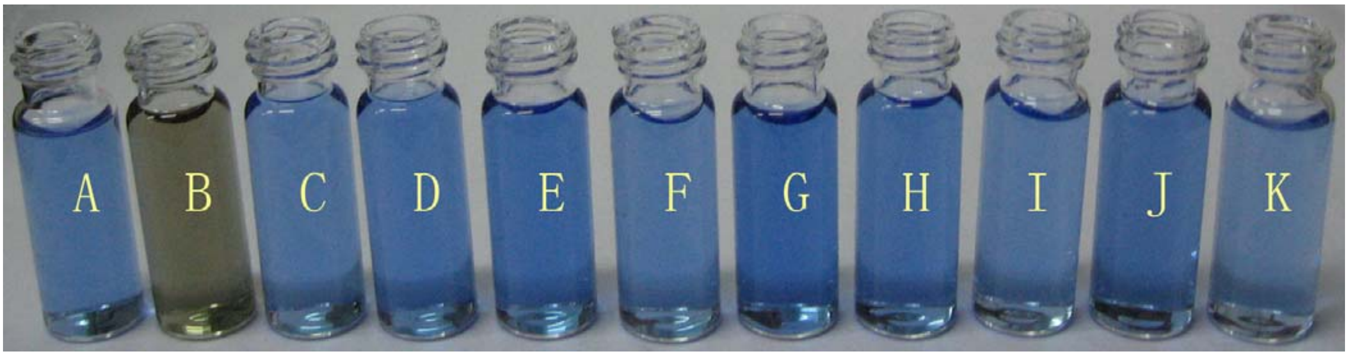

Figure S11. Different solutions of zincon and copper ions in water (5.0×10^{-5} and 2.2×10^{-5} mol/L, respectively) in the presence of anion (5.0×10^{-5} mol/L). From left to right: no anion, F^-, Cl^-, I^-, IO_3^-, SO_4^{2-}, NO_2^-, Br^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-.

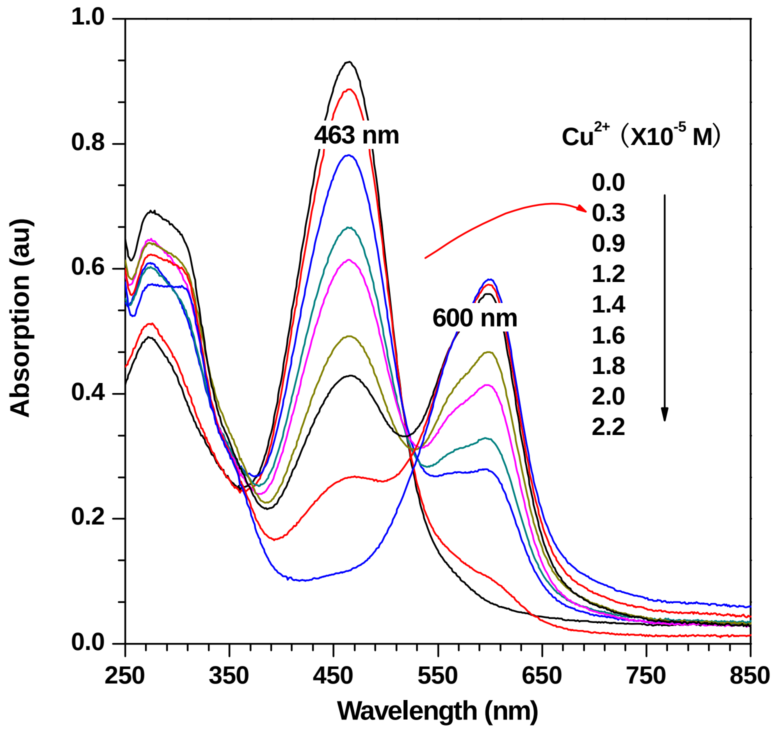

Figure S12. UV-vis spectra of zincon with increasing amounts of Cu^{2+} in water. The concentration of zincon was 5.0×10^{-5} mol/L. The pH value of the solution was about 8.2.

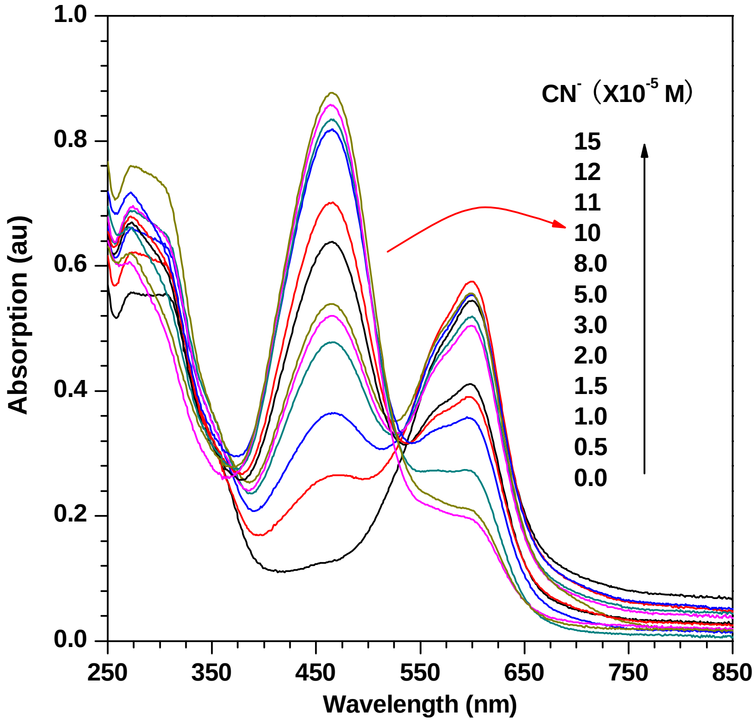

Figure S13. UV-vis spectra of the mixture solution of zincon (5.0×10^{-5} mol/L) and Cu^{2+} (2.2×10^{-5} mol/L) with increasing amounts of CN^- in water. The pH value of the solution was about 8.2.

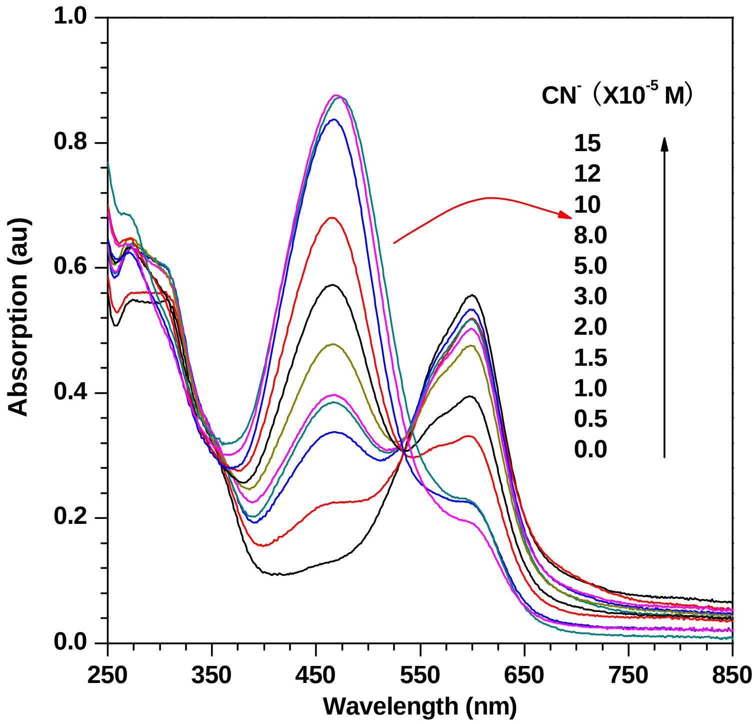

Figure S14. UV-vis spectra of the mixture solution of zincon (5.0×10^{-5} mol/L) and Cu^{2+} (2.2×10^{-5} mol/L) with increasing amounts of CN^- in water. The pH value of the solution was about 9.1.

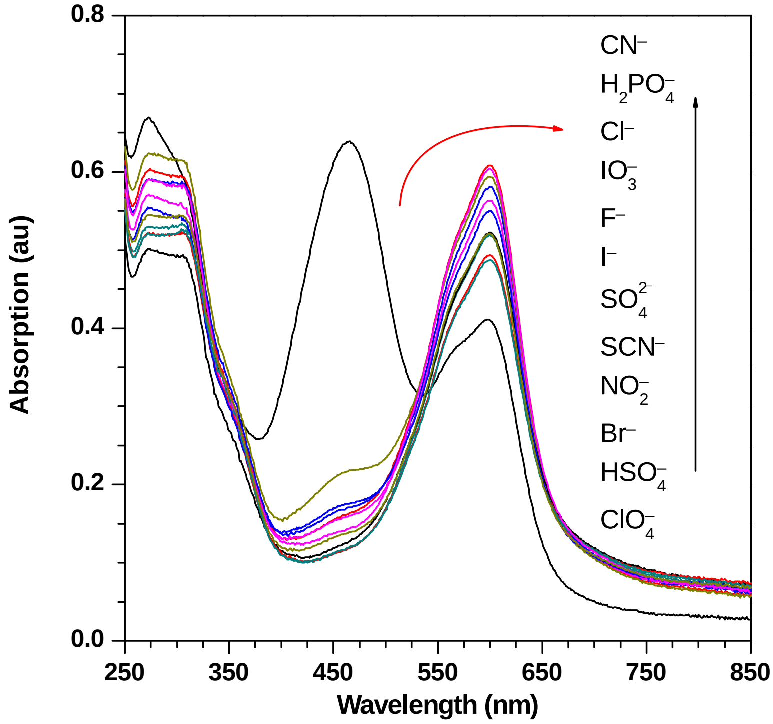

Figure S15. UV-vis spectra of zincon at the presence of different anions (5.0×10^{-5} mol/L) in water. The concentration of zincon was 5.0×10^{-5} mol/L. The pH value of the solution was about 8.2.

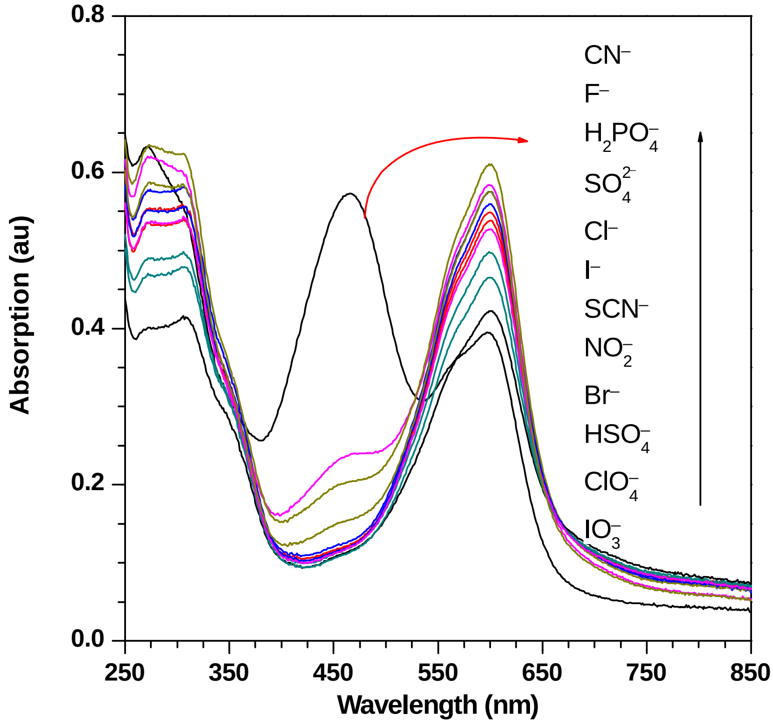

Figure S16. UV-vis spectra of zincon at the presence of different anions (5.0×10^{-5} mol/L) in water. The concentration of zincon was 5.0×10^{-5} mol/L. The pH value of the solution was about 9.1.

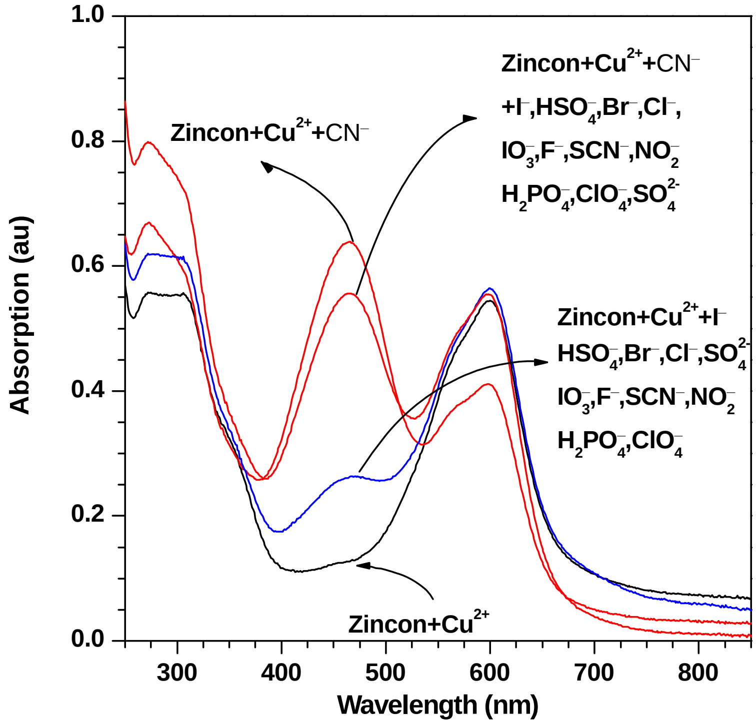

Figure S17. UV-vis spectra of zincon at the presence of different anions mixture(5.0×10^{-5} mol/L) in water. The concentration of zincon was 5.0×10^{-5} mol/L and Cu^{2+} was 2.2×10^{-5} mol/L. The pH value of the solution was about 8.2.

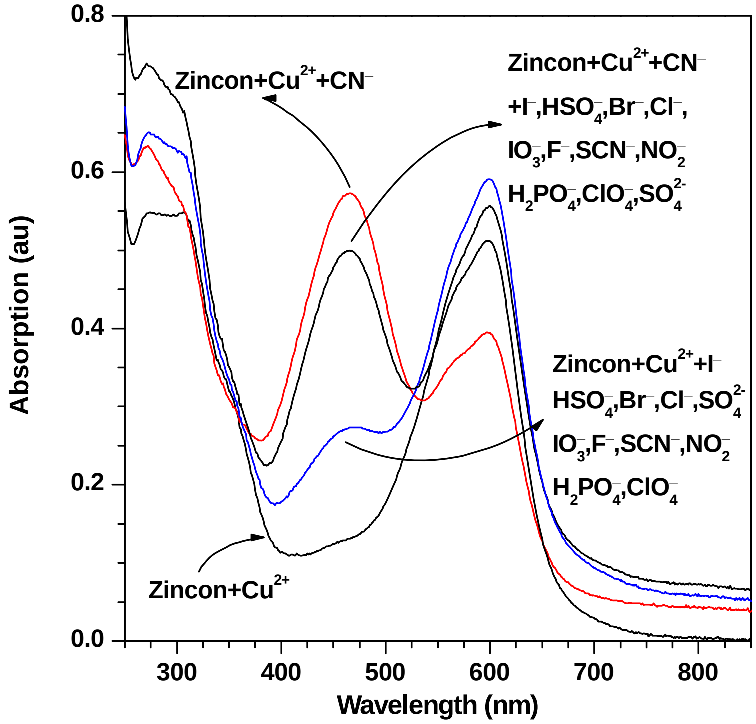

Figure S18. UV-vis spectra of zincon at the presence of different anions mixture(5.0×10^{-5} mol/L) in water. The concentration of zincon was 5.0×10^{-5} mol/L and Cu^{2+} was 2.2×10^{-5} mol/L. The pH value of the solution was about 9.1.

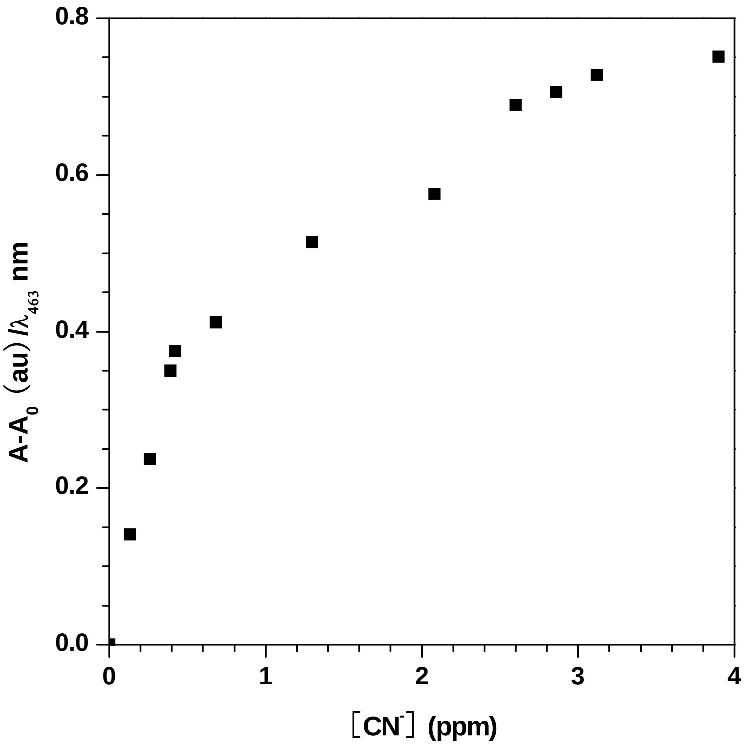

Figure S19. Absorption difference at λ= 463 nm versus the concentration of CN^- in water with the concentrations of zincon and Cu^{2+} at 5.0×10^{-5} and 2.2×10^{-5} mol/L , respectively. The pH value of the solution was about 8.2.

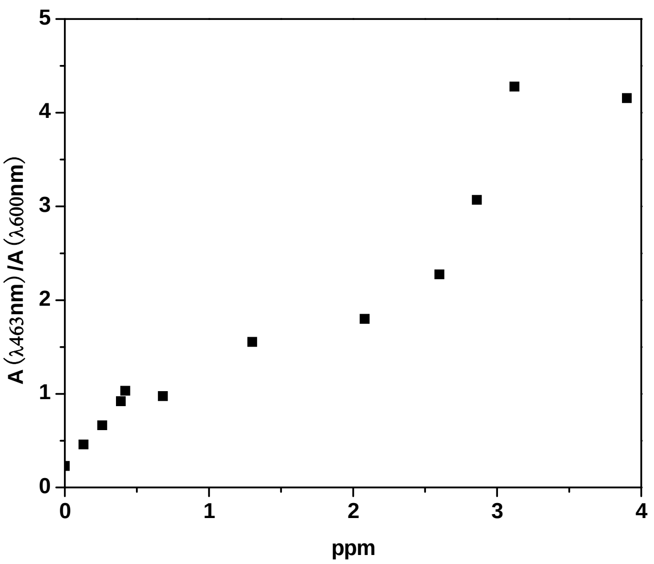

Figure S20. Absorption difference A(463nm)/A(600nm) versus the concentration of CN^- in water with the concentrations of zincon and Cu^{2+} at 5.0×10^{-5} and 2.2×10^{-5} mol/L , respectively. The pH value of the solution was about 8.2.

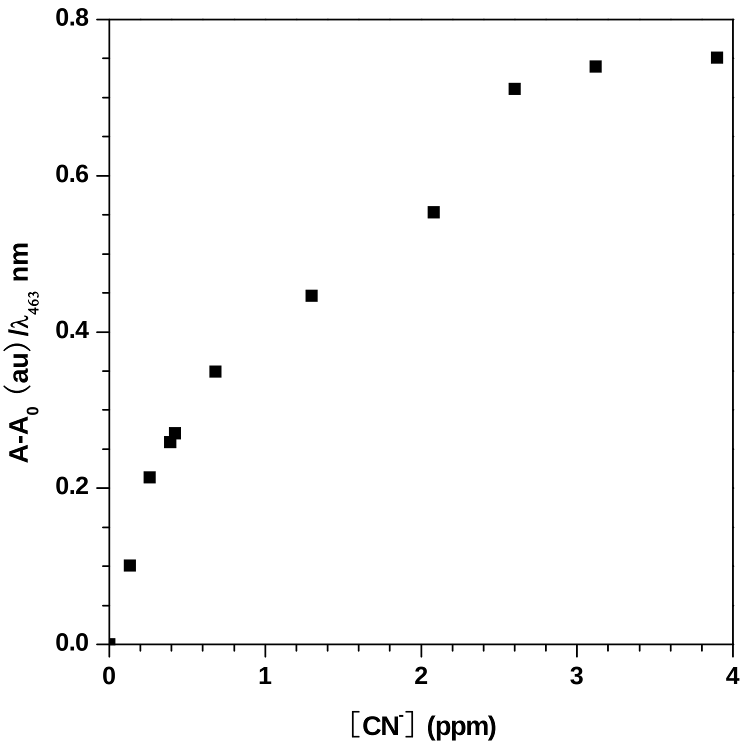

Figure S21. Absorption difference at λ= 463 nm versus the concentration of CN^- in water with the concentrations of zincon and Cu^{2+} at 5.0×10^{-5} and 2.2×10^{-5} mol/L , respectively. The pH value of the solution was about 9.1.

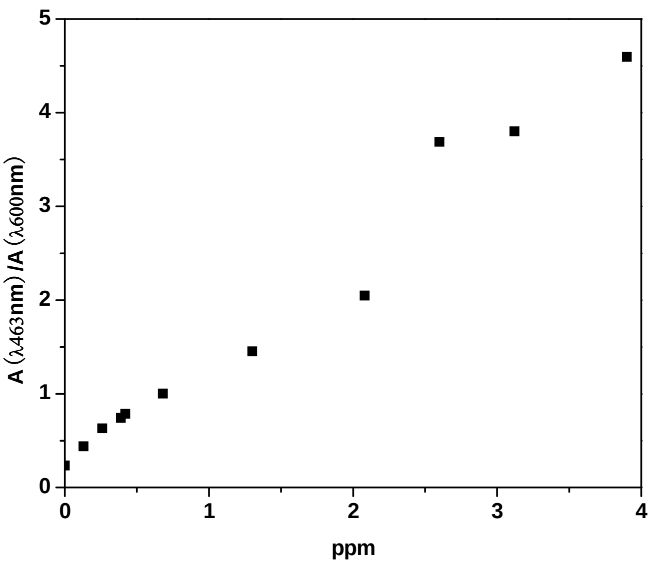

Figure S22. Absorption difference A(463nm)/A(600nm) versus the concentration of CN^- in water with the concentrations of zincon and Cu^{2+} at 5.0×10^{-5} and 2.2×10^{-5} mol/L , respectively. The pH value of the solution was about 9.1.