Electronic Supplementary Information

A reversible fluorescent chemosensor for the rapid sensing of CN^- in water: utilization of the intramolecular charge transfer blocking

Tai-Bao Wei,* Yuan-Rong Zhu, Hui Li, Guo-Tao Yan, Qi Lin, Hong Yao and You-Ming Zhang*

E-mail: weitaibao@126.com

E-mail: zhangnwnu@126.com

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

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

CONTENTS **PAGE**

1. Determination of association constant

The association constants (Ka) were also determined based on the fluorescent titration curve using the equation as follows: where **I** and $\mathbf{I_0}$ represent the intensity of host in the presence and absence of ions, respectively, $\mathbf{I_1}$ is the saturated intensity of host in the presence of excess amount of ions; $\mathbf{[A^-]}$ is the concentration of ions added.

$$\frac{1}{I - I_0} = \frac{1}{I_1 - I_0}\left[\frac{1}{Ka[A^-]} + 1\right]$$

2. ^{1}H NMR spectra of compound ZR

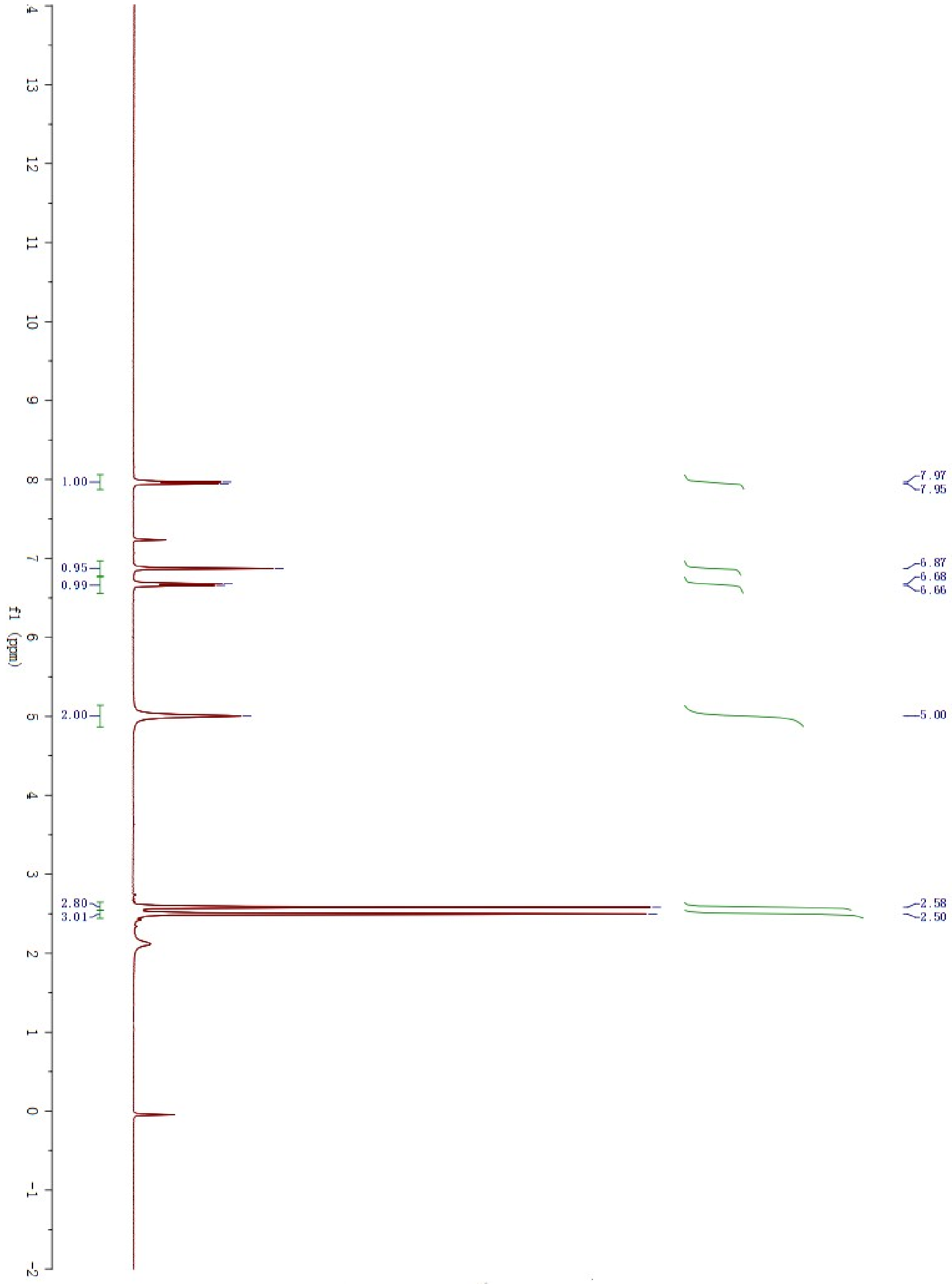


Fig. S1 ^{1}H NMR spectra of compound **ZR**.

3. ^{13}C NMR spectra of compound ZR

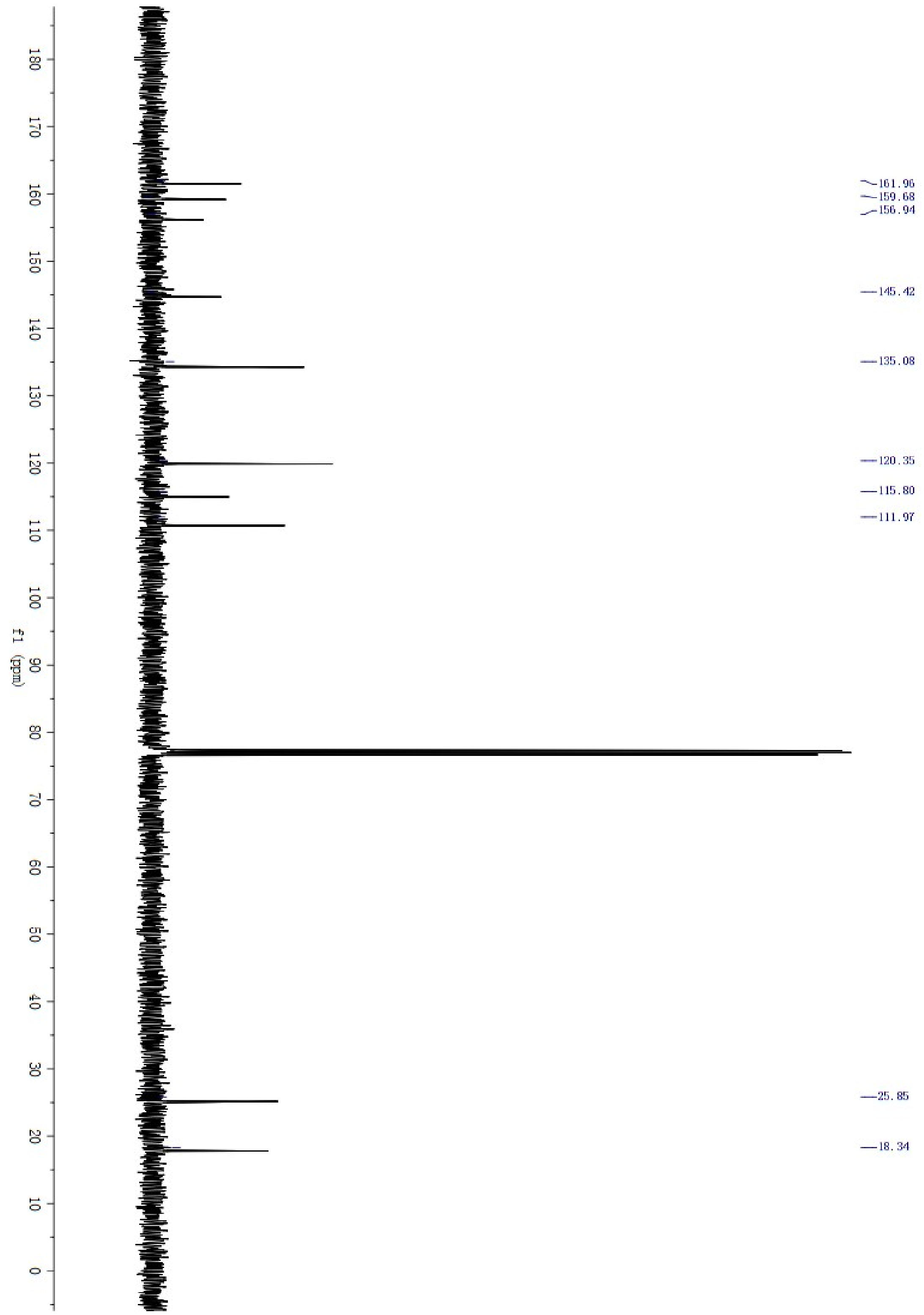
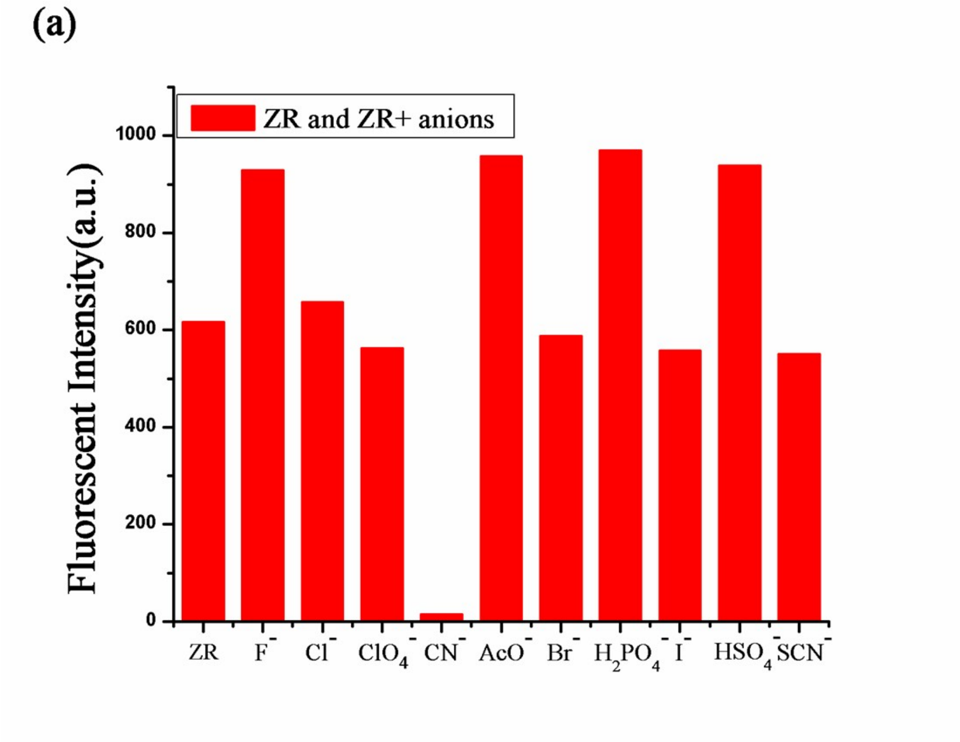


Fig. S2 ^{13}C NMR spectra of compound **ZR**

4. The Fluorescence Responses of ZR with anions

(a)



(b)

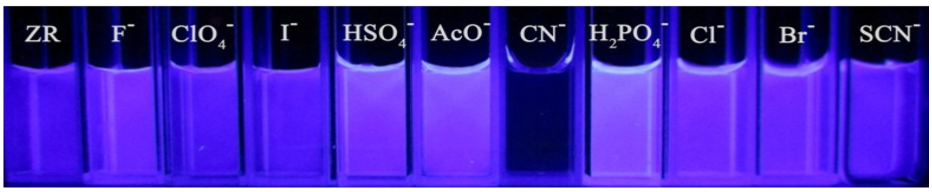


Fig. S3 (a) Fluorescence emission data for a 1:50 mixture of **ZR** (20 μM) and different anions in water (λ_{ex}=370 nm). (b) Visual fluorescence emissions of sensor **ZR** after the addition of various anions (50 equiv.) in water on excitation at 365 nm using UV lamp.

5. The Fluorescence Responses of ZR to CN^- with other competing anions

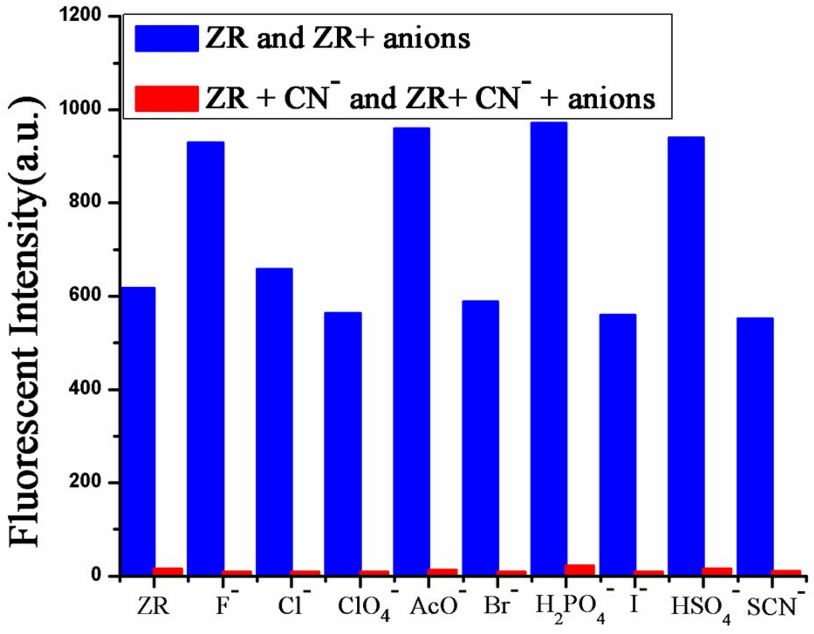


Fig. S4 Fluorescent intensity of the competition experiments between CN^- and other anions in water (λ_{ex}=370 nm).

6. A plot of fluorescence intensity Change of ZR with CN^-

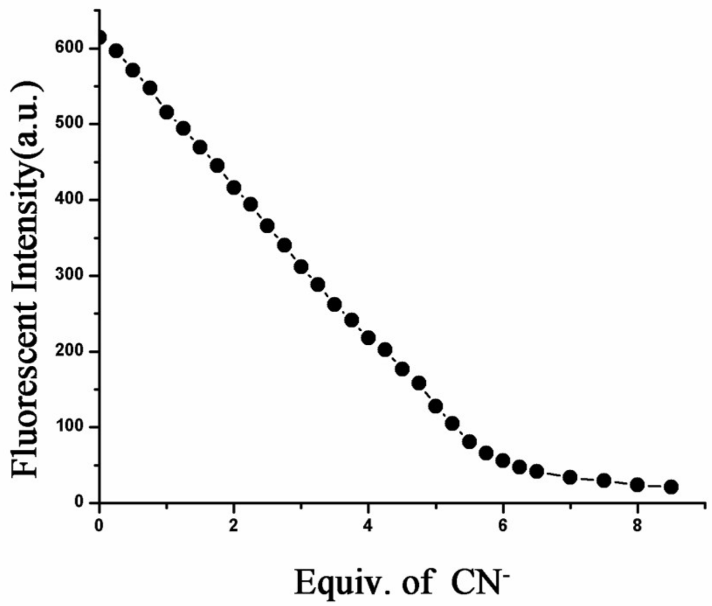


Fig. S5 A plot of fluorescence intensity depending on the concentration of CN^- in the range from 0 to 8.5 equivalents.

7. Calculation of binding constant Ka

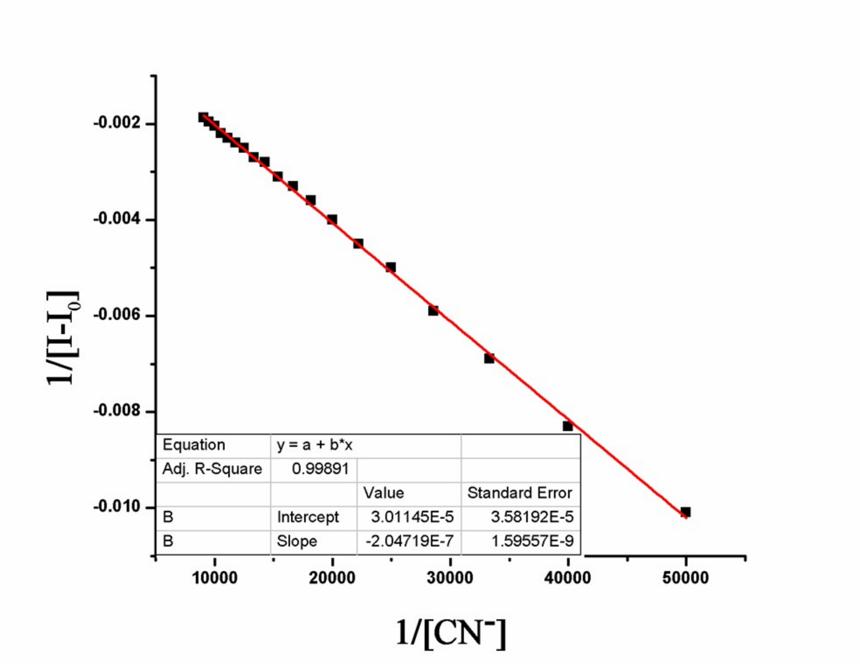


Fig. S6 Benesi-Hilderbrand plot of **ZR** with CN^-.

Linear Equation: $Y=-2.05\times10^{-7}\times X+3.01\times10^{-5}$

$R^2=0.9989$

$1/[\ K_a\ (I_1-I_0)]= -2.05\times10^{-7}$, $(I_1-I_0)=-590.6$

$K_a=8.26\times10^3\ M^{-1}$

8. Determination of Detection Limit of CN^-

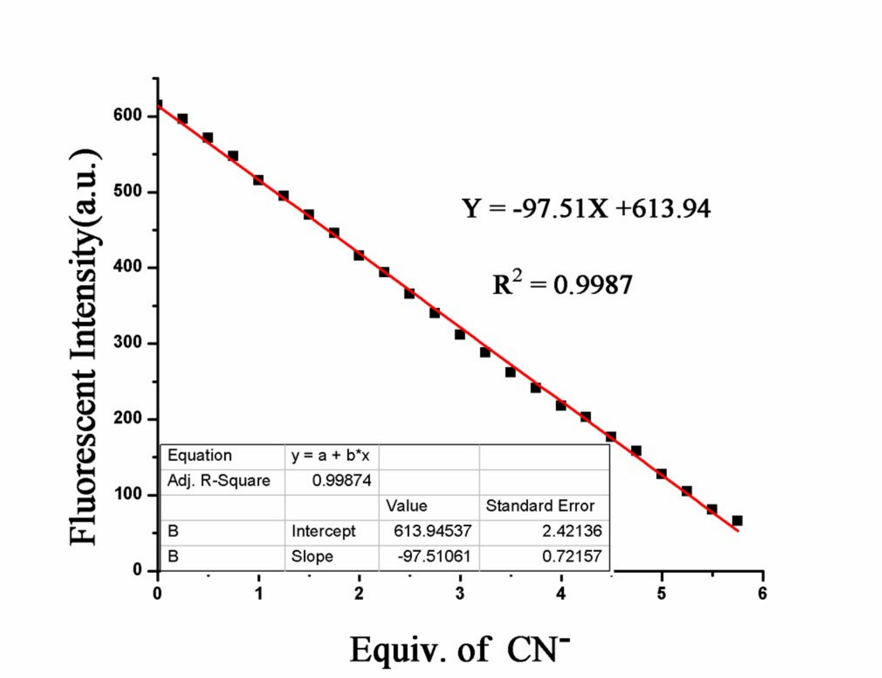


Fig. S7 Plot of the intensity at 464 nm for a mixture of **ZR** and CN^- in water solution in the range 0–5.75 equiv. (λ_{ex}= 370 nm).

Linear Equation: Y=-97.51×X+613.94, R^2=0.9987

$$\delta = \sqrt{\frac{\sum(F_0-F_1)^2}{N-1}} = 0.435 \ (N=10)$$

S=9.751×10^7, K=3

LOD=K×δ/S

LOD=1.34×10^{-8} M

F_0 is the fluorescence intensity of **ZR**; F_1 is the average of the F_0.

9. Influence of pH on ZR

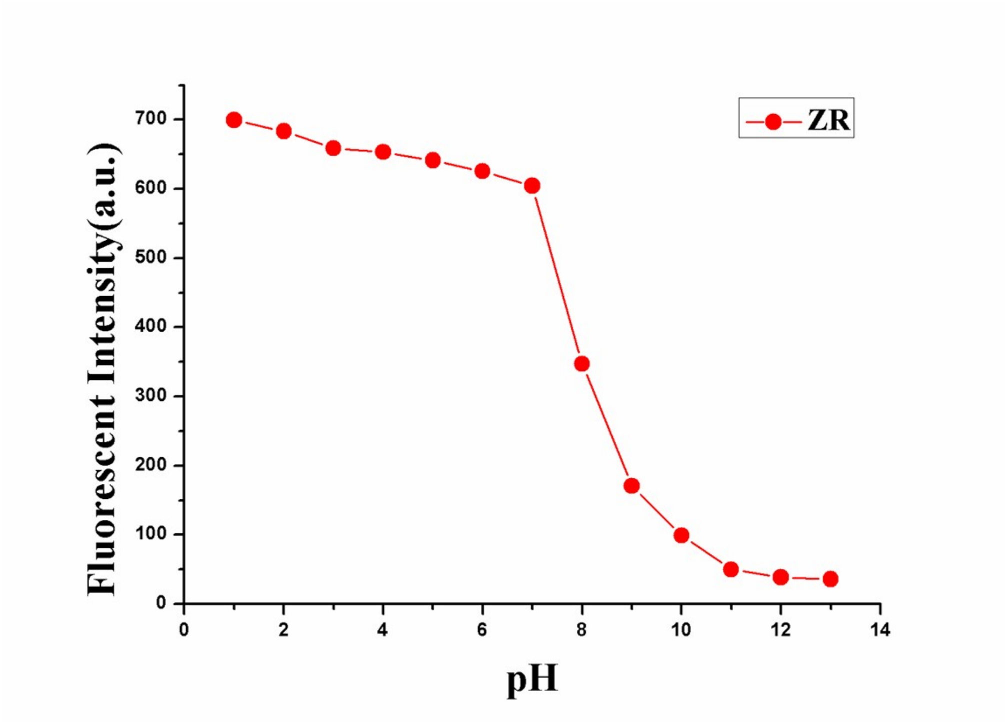


Fig. S8 Influence of pH on the fluorescence of **ZR**

10. The Fluorescence Intensity Changes of ZR in the Presence of CN^- and Cr^{3+}

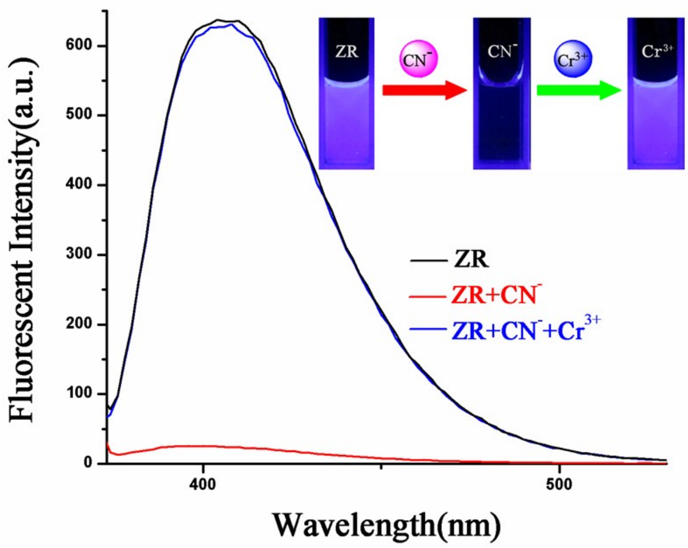


Fig. S9 Fluorescence emission spectra of **ZR** (20 μM) in the presence of CN^- (8.5 equiv.) or Cr^{3+} (2.5 equiv.) in water (λ_{ex}=370 nm). Inset: photograph from left to right shows the change in the fluorescence of only **ZR**, **ZR**+CN^- and **ZR**+CN^-+Cr^{3+} in water on excitation at 365 nm.

11. Time-dependent Fluorescence Change of ZR with CN^-

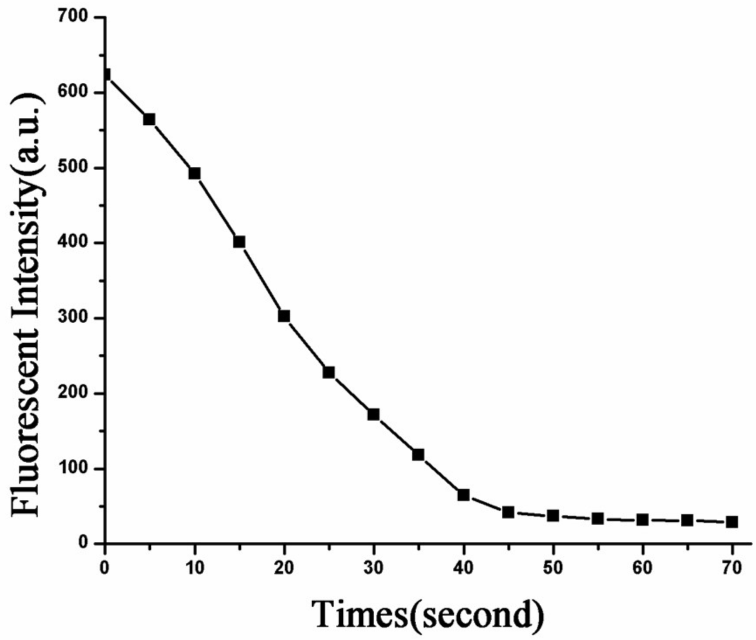


Fig. S10 Time-dependent fluorescence change of **ZR** (20 μM) in the presence of 12.5 equiv. of CN^- in water.

12. ^{1}H NMR spectra of ZR with addition of acid

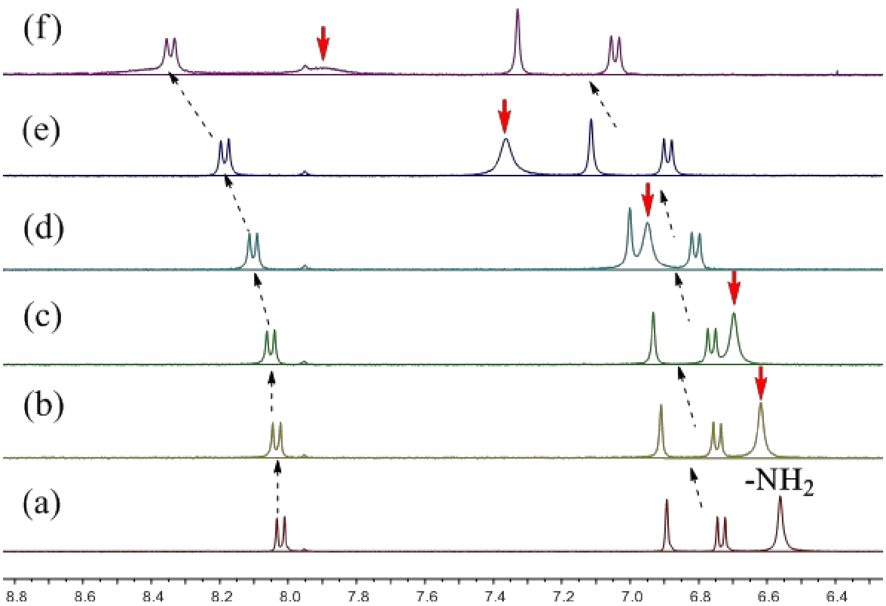


Fig. S11 Partial ^{1}H NMR spectra of: (a) **ZR**, (b) acid (0.1 equiv.), (c) acid (0.2 equiv.), (d) acid (0.5 equiv), (e) acid (1.0 equiv.), (f) acid (2.0 equiv.) in DMSO-d_6.

13. IR spectra of compound ZR and ZR+CN⁻

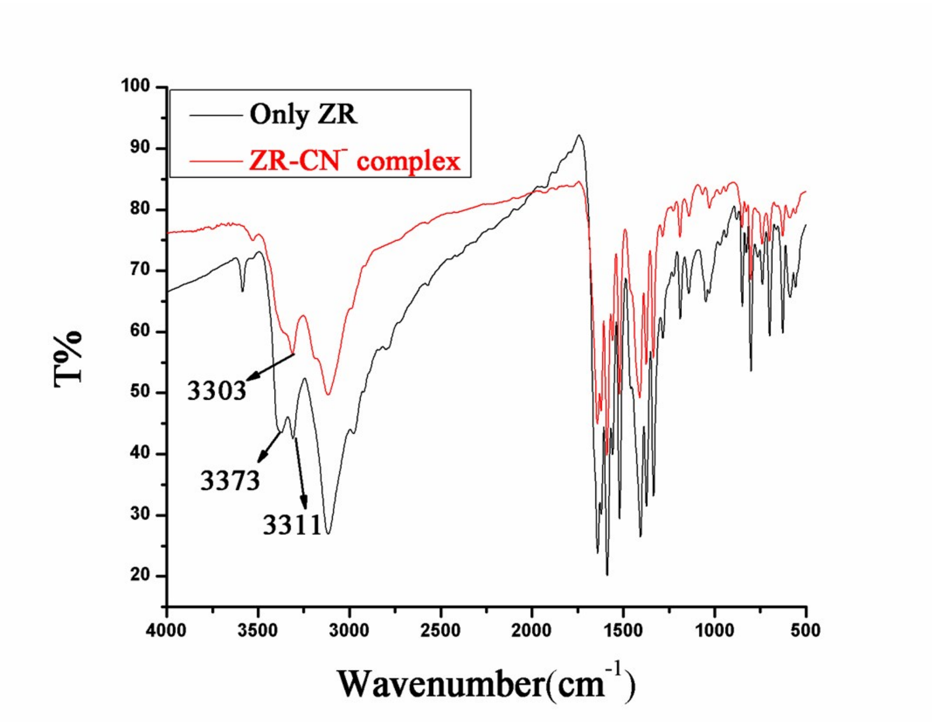


Fig. S12 IR spectra of compound **ZR** and **ZR**+CN^- complex in KBr disks.

14. ESI-MS spectrum of ZR

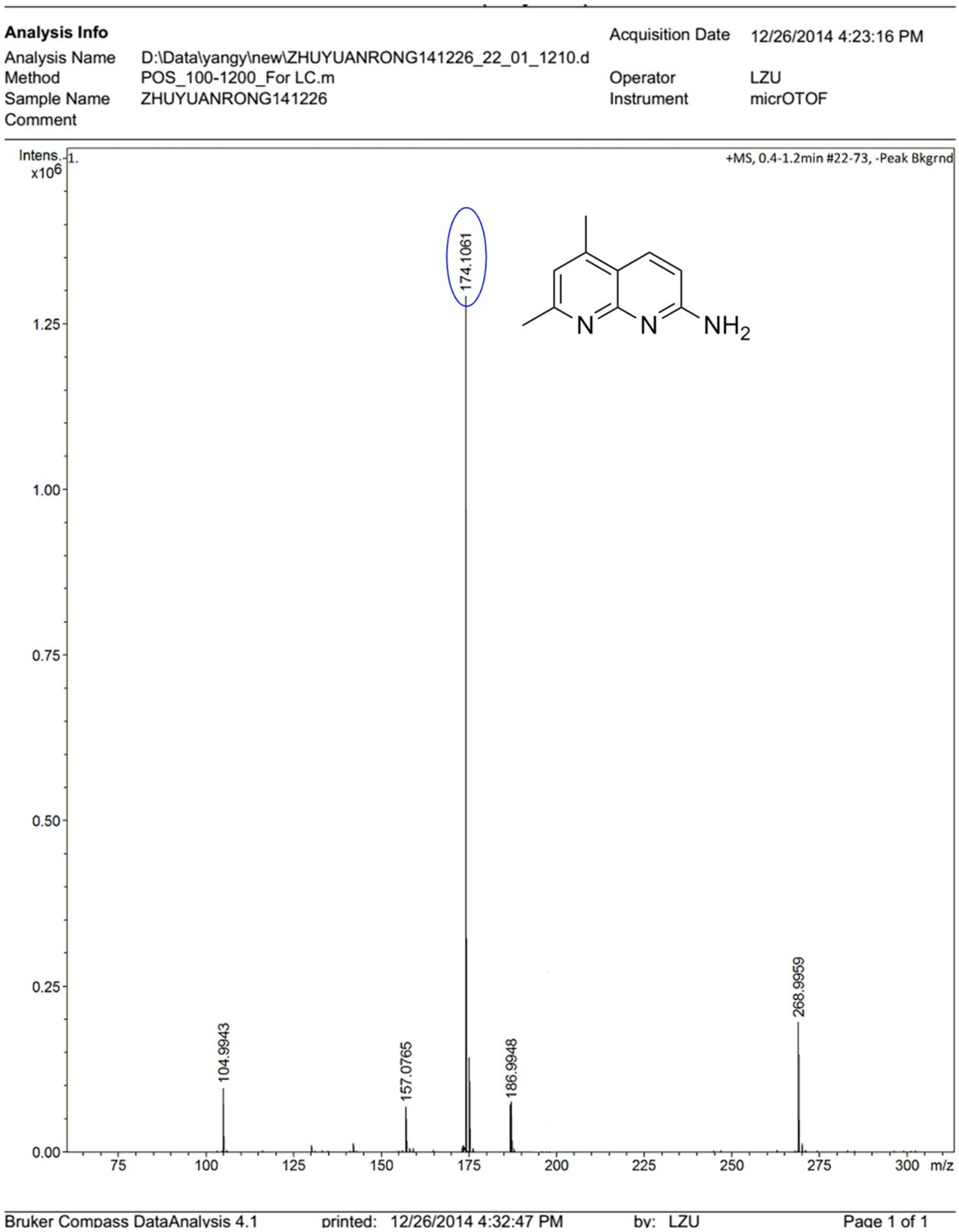


Fig. S13 ESI-MS spectrum of **ZR**.

15. ESI-MS spectrum of ZR+CN⁻ complex

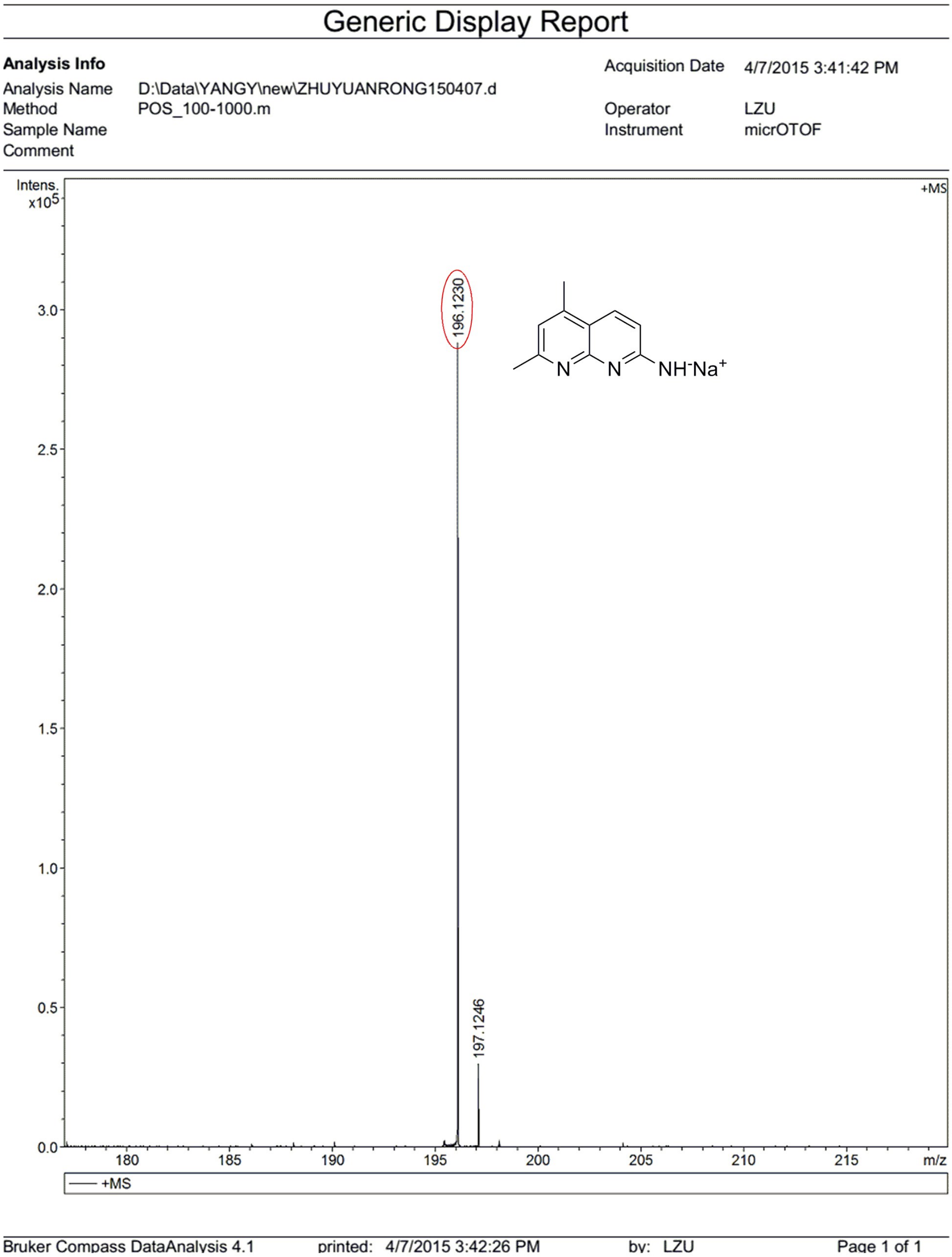


Fig. S14 ESI-MS spectrum of **ZR**+CN^- complex.

16. A complementary IMP logic function

INP_1 (CN^-)	INP_2 (Cr^{3+})	OUTPUT (emission) 406nm
0	0	1
0	1	1
1	0	0
1	1	1

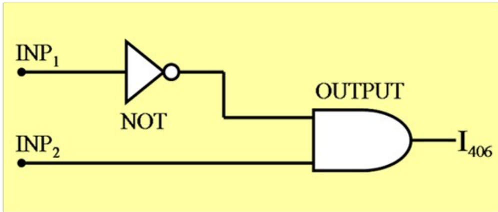


Fig. S15 The complementary IMP logic gate and its truth table. INP1 and INP2 represent input CN^- and input Cr^{3+}, respectively.

17. Performance of ZR in the IMP gate mode

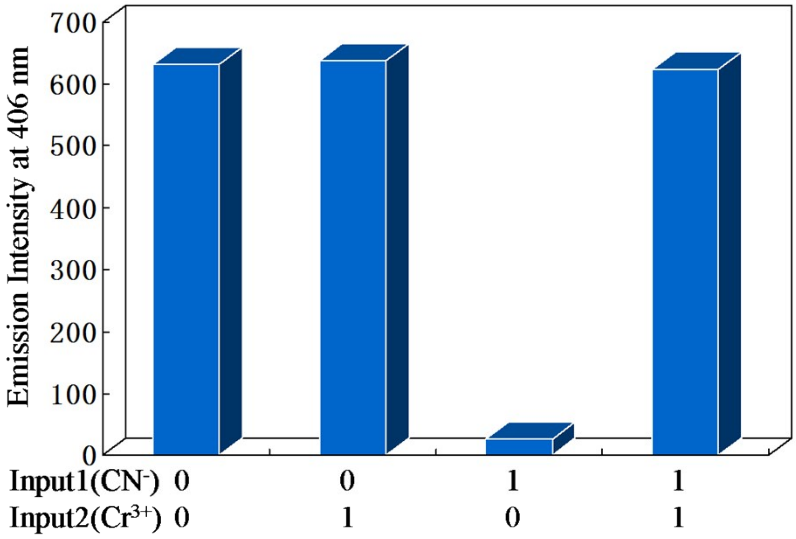


Fig. S16 Performance of **ZR** in the IMP gate mode. The bars show the emission intensity at 406 nm after each input combination in water (λ_{ex}=370 nm).