Electronic Supplementary Material

A simple Michael acceptor type quinoline derivative for highly selective sequential recognition of CN^- and Cu^{2+} in aqueous solution

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1. General Methods: Fresh double distilled water was used throughout the experiment. All reagents and solvents were commercially available at analytical grade and were used without further purification. ^{1}H NMR spectra were recorded on a Mercury-400BB spectrometer at 400 MHz and ^{13}C NMR spectra were recorded on a Mercury-400BB spectrometer at 150 MHz. Chemical shifts are reported in ppm down field from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Melting points were measured on an X-4 digital melting-point apparatus. Mass spectra was recorded on an esquire 6000 MS instrument equipped with an electrospray (ESI) ion source and version 3.4 of Bruker Daltonics Data Analysis as the data collection system.

All fluorescence spectra were recorded on a Shimadzu RF–5301 fluorescence spectrometer after the addition of tetrabutylammonium salts and perchlorate metal salts in water, while keeping the ligand concentration constant (2.0×10^{-5}M). The excitation wavelength was 358 nm. Solutions of anions were prepared from the tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, SCN^-, CO_3^{2-} and NaN_3, Na_2S, NaHS, NaCN. Metal ions were prepared from the perchlorate salts of Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+},

Pb^{2+}, Zn^{2+}, Cr^{3+} and Mg^{2+}.

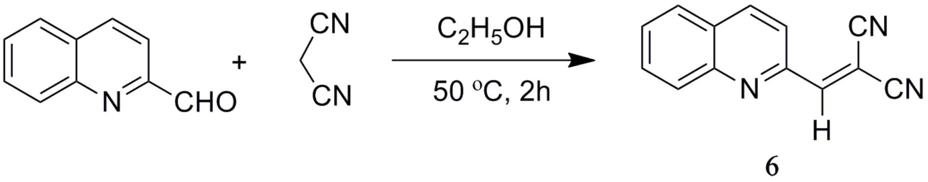
For ^{1}H NMR titrations, two stock solutions were prepared in DMSO-d_6, one containing the sensor **6** and the second containing an appropriate concentration of the anions. Aliquots of the two solutions were mixed directly in NMR tubes.

2. 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.

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

3. Synthesis of sensor 6



Scheme S1 Synthesis of the sensor molecule **6**.

General procedures for the synthesis of **6**: malononitrile (0.264 g, 4 mmol) and 2-Quinolinecarboxaldehyde (0.628 g, 4 mmol) were combined in 25 mL ethanol. The solution was stirred at 50 °C for 2 h. After cooling to room temperature, the atropurpureus precipitate was filtered, and recrystallized in ethanol to obtain 0.67g acicular product. Yield: 81.7%; m.p.: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.2 Hz, 1H), 8.24 (d, *J* = 7.9 Hz, 1H), 7.99 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.85 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.67, 148.52, 148.34, 137.72, 131.33, 130.67, 129.91, 129.29, 127.80, 122.33, 113.85, 112.31, 87.93; ESI-MS m/z: $(M+H)^+$ Calcd for $C_{13}H_7N_3$ 206.0640; Found 206.1000; Anal. Calcd for $C_{13}H_7N_3$: C, 76.08; H, 3.44; N, 20.48; Found C 76.27; H, 3.12; N, 20.61.

4. ^{1}H NMR spectra of compound 6

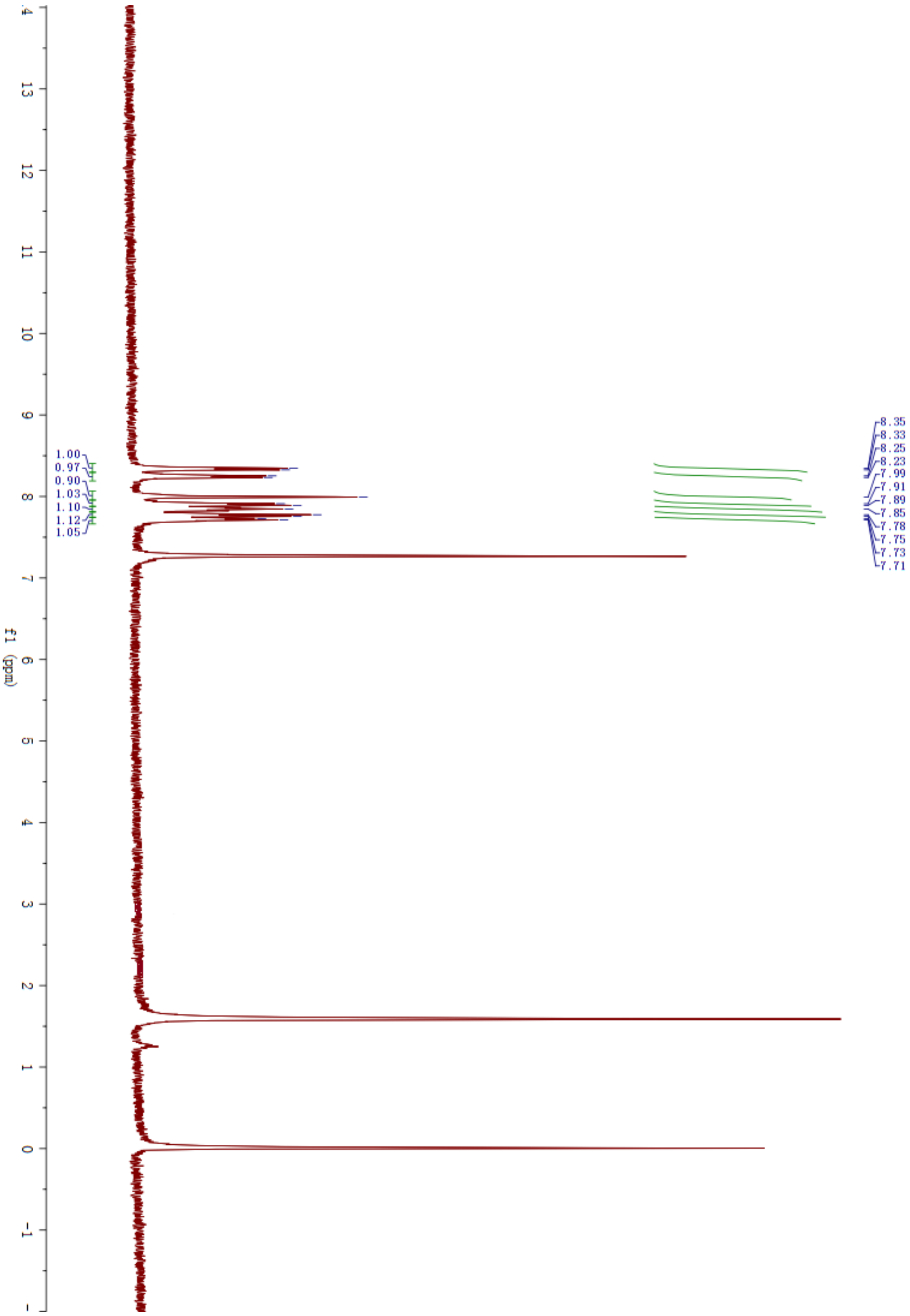


Figure S1 ^{1}H NMR spectra of compound **6**.

5. ^{13}C NMR spectra of compound 6

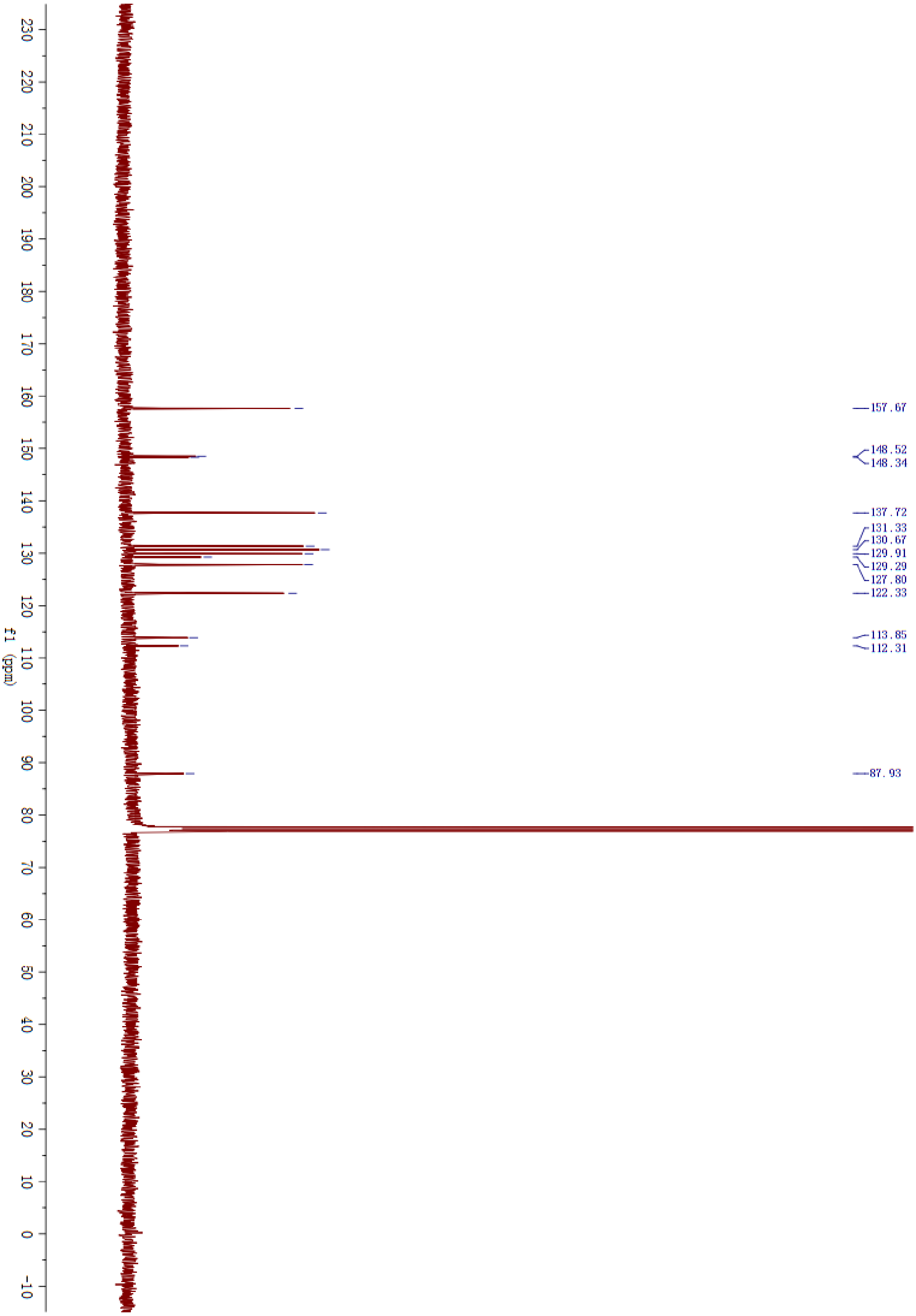


Figure S2 ^{13}C NMR spectra of compound **6**

6. The UV–vis spectroscopy of 6 with CN⁻

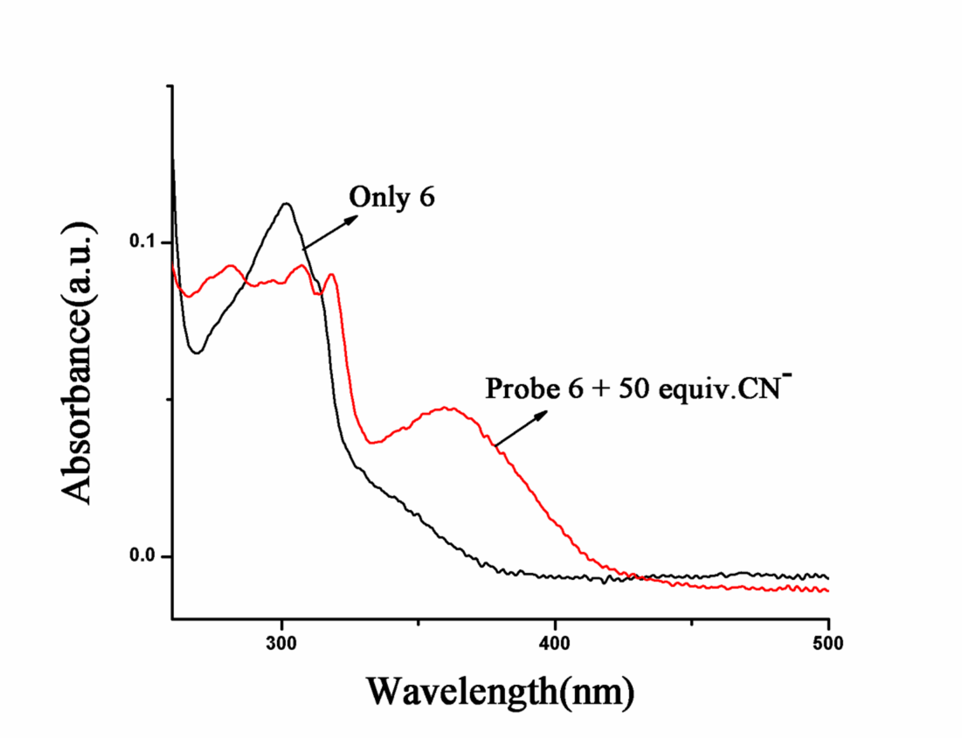


Figure S3 UV-vis spectra of compound **6** (20 μM) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH=7.2) upon addition of 50 equiv. of CN⁻

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7. The Fluorescence Responses of 6 with anions

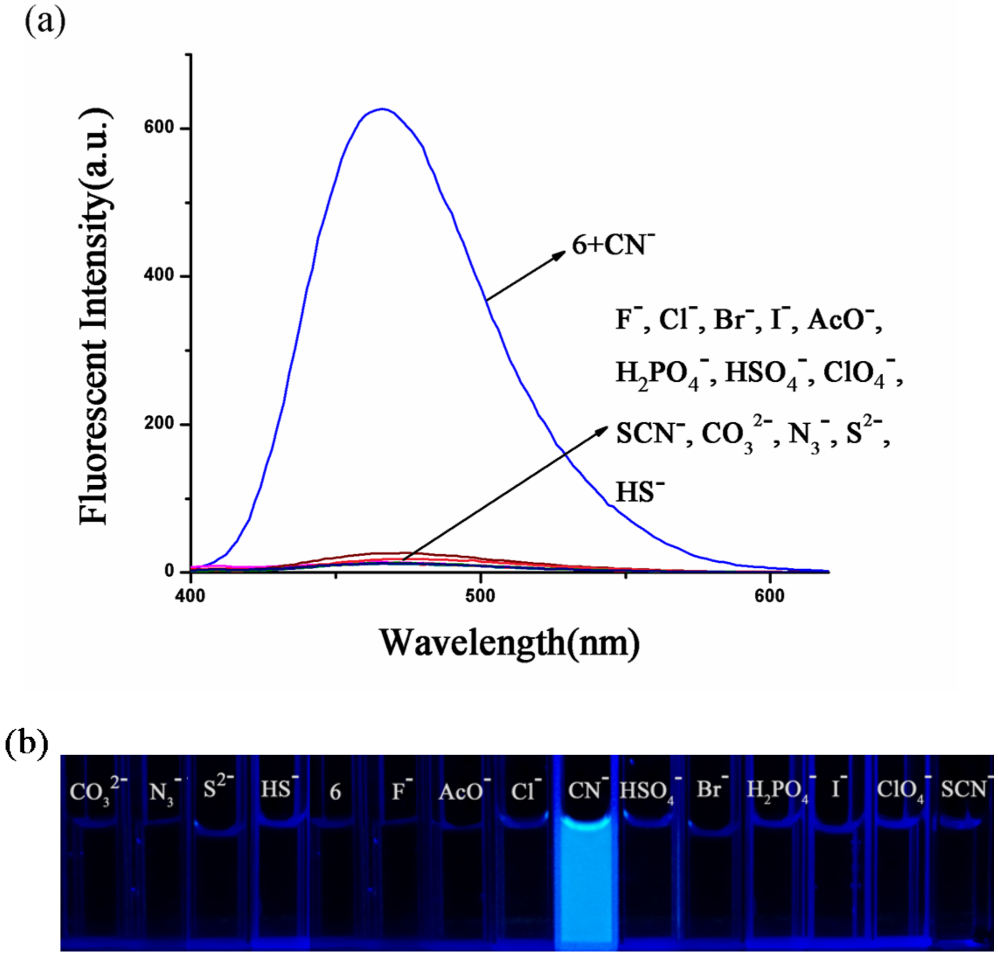


Figure S4 (a) Fluorescence emission data for a 1:50 mixture of **6** (20 μM) and different anions, as their tetrabutylammonium salts, in DMSO/H_2O (1:9, v/v) HEPES buffer (pH=7.2) solution (λ_{ex}=358 nm). (b) Visual fluorescence emissions of sensor **6** after the addition of various anions (50 equiv.) in water solution on excitation at 365 nm using UV lamp.

8. Fluorescence and excitation spectra of the 6 and 6-CN⁻

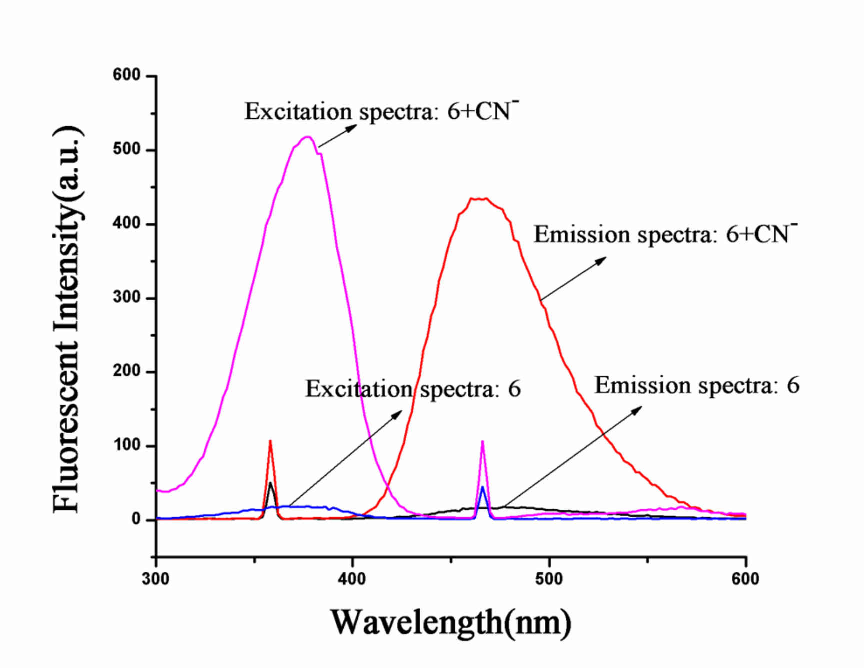


Figure S5 Fluorescence and excitation spectra of the **6** (20 μM) and **6**-CN⁻ were also tested in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.2) solution (λ_{ex}=358 nm).

9. A plot of fluorescence intensity Change of 6 with CN⁻

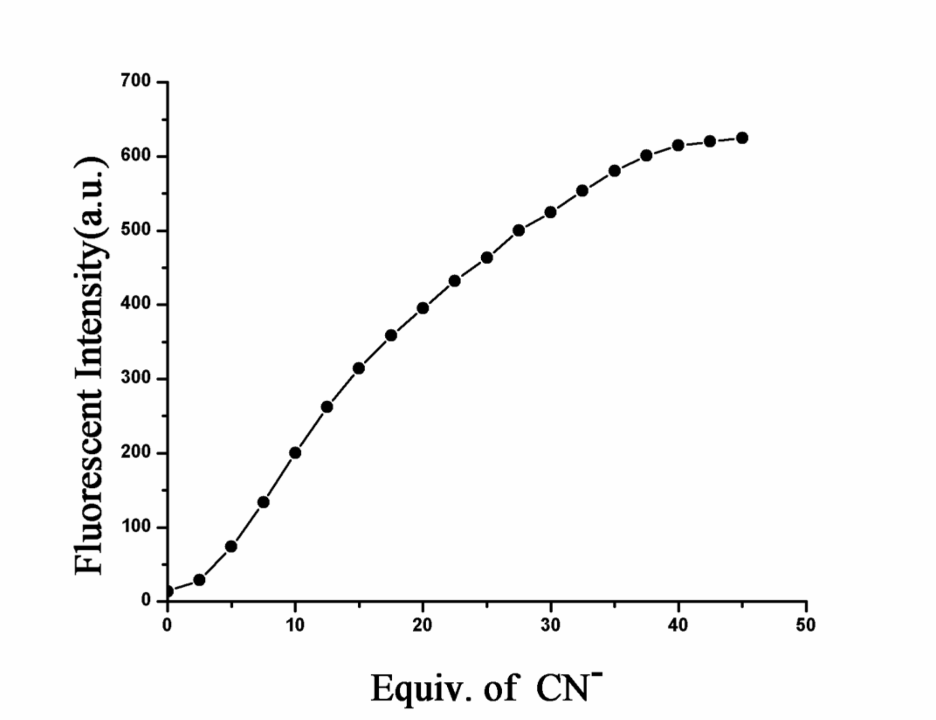


Figure S6 A plot of fluorescence intensity depending on the concentration of CN⁻ in the range from 0 to 45 equivalents.

10. Calculation of binding constant Ka

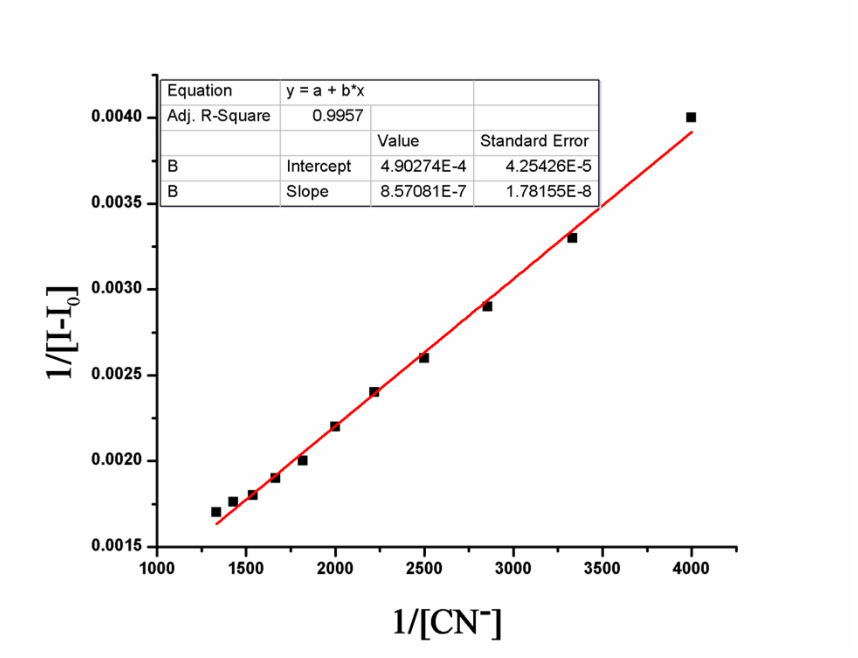


Figure S7 Benesi-Hilderbrand plot of **6** with CN^-.

Linear Equation: $Y=8.57\times10^{-7}\times X+4.9\times10^{-4}$

$R^2=0.9957$

$1/[K_a (I_1-I_0)]=8.57\times10^{-7}$, $(I_1-I_0)=611.47$

$K_a=1.9\times10^3$ M^-

11. Determination of Detection Limit of CN^-

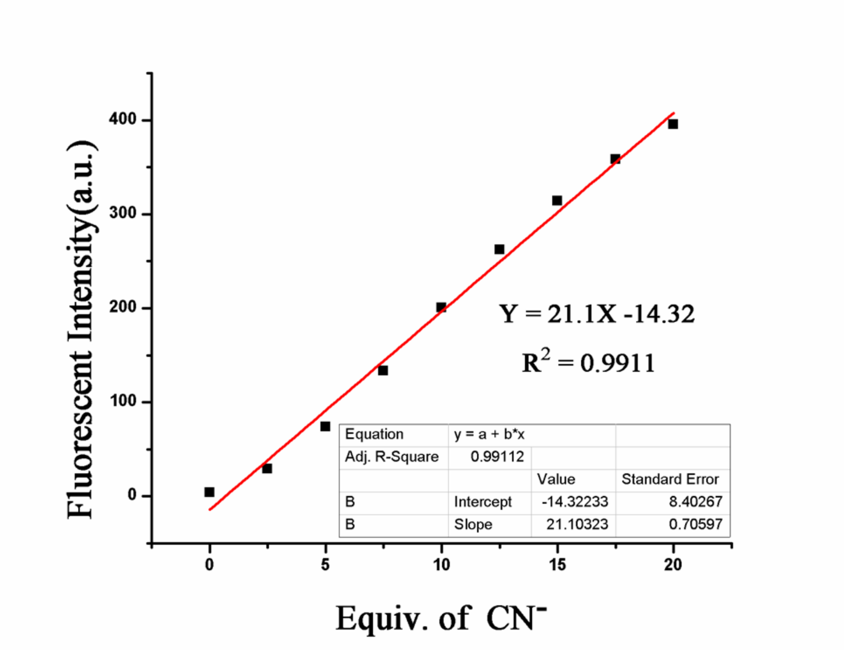


Figure S8 Plot of the intensity at 464 nm for a mixture of **6** and CN^- in water solution in the range 0–20 equiv. (λ_{ex}= 358 nm).

Linear Equation: $Y=21.1\times X-14.32$, $R^2=0.9911$

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

K=3

$S=2.11\times10^7$, $\delta=$ =0.358 (N=10)

$LOD=K\times\delta/S$

$LOD=5.09\times10^{-8}$ M

F_0 is the fluorescence intensity of **6**; F_1 is the average of the F_0.

12. Time-dependent Fluorescence Change of 6 with CN⁻

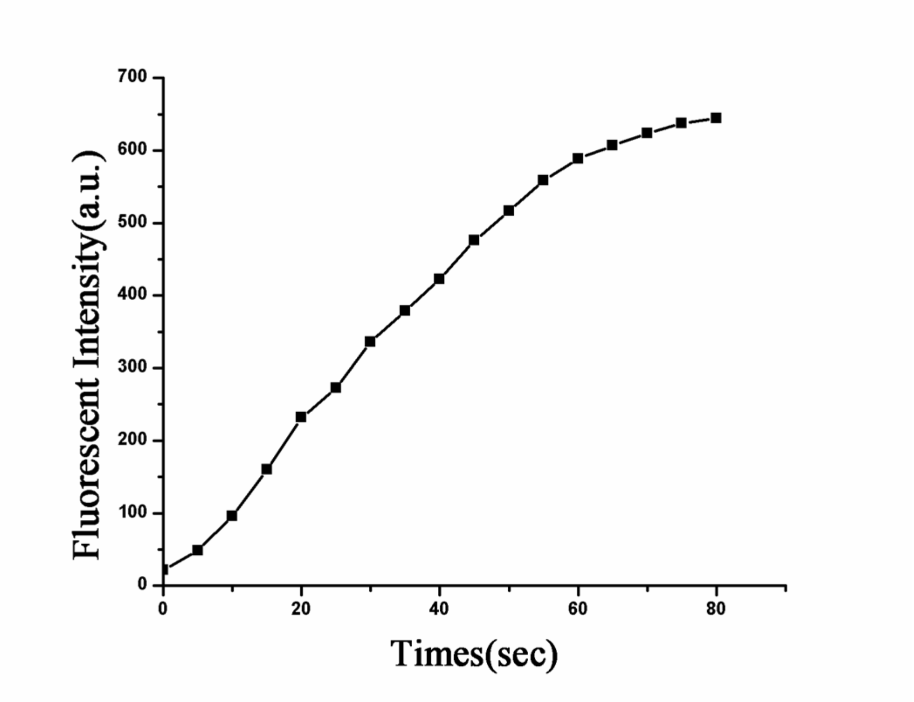


Figure S9 Time-dependent fluorescence change of **6** (20 μM) in the presence of 50 equiv. of CN⁻ in DMSO/H_2O (1:9, v/v) HEPES buffer (pH=7.2) solution (λ_{ex}=358 nm).

13. The Fluorescence Responses of 6 with Metal ions

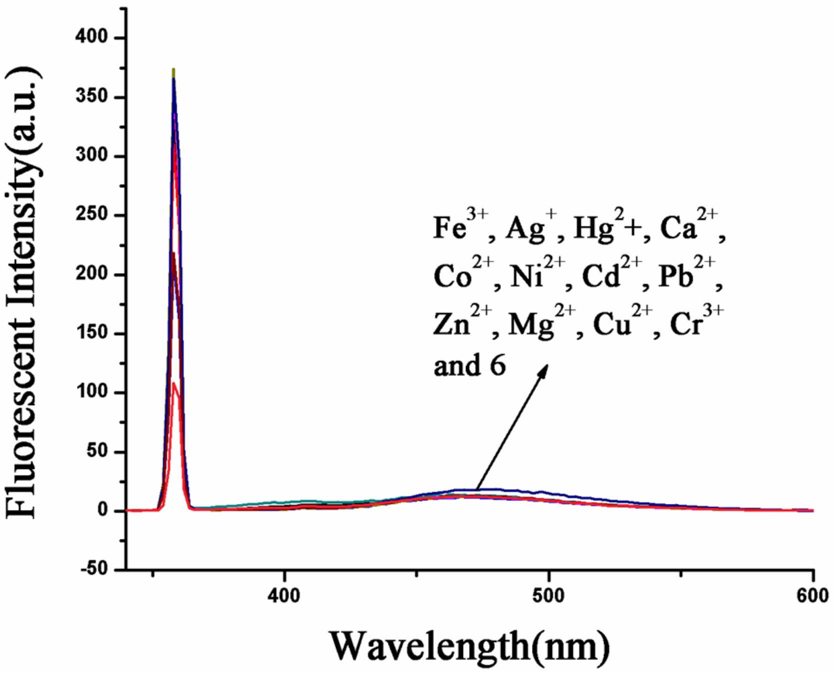


Figure S10 Fluorescence emission data for a 1:20 mixture of **6** (20 μM) and different metal ions in DMSO/H_2O (1:9, v/v) HEPES buffer (pH=7.2) solution (λ_{ex}=358 nm).

14. The Fluorescence Responses of 6-CN⁻ with Metal ions

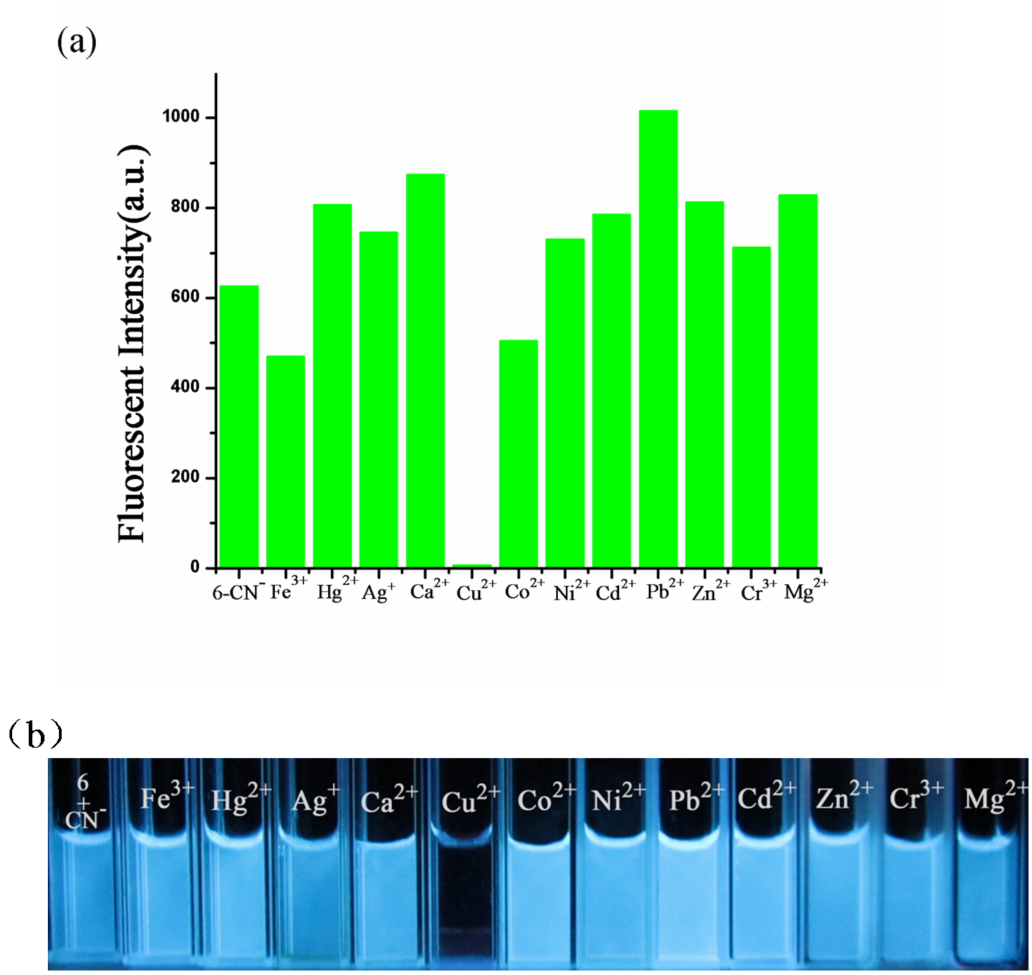


Figure S11 (a) Fluorescence emission data for a 1:20 mixture of **6-**CN⁻ (20 μM) and different metal ions, as their perchlorate metal salts, in DMSO/H_2O (1:9, v/v) HEPES buffer (pH=7.2) solution (λ_{ex}=358 nm). (b) Visual fluorescence emissions of sensor **6-**CN⁻ after the addition of various metal ions (20 equiv.) in water solution on excitation at 365 nm using UV lamp.

15. The Fluorescence Responses of 6 with different adding order

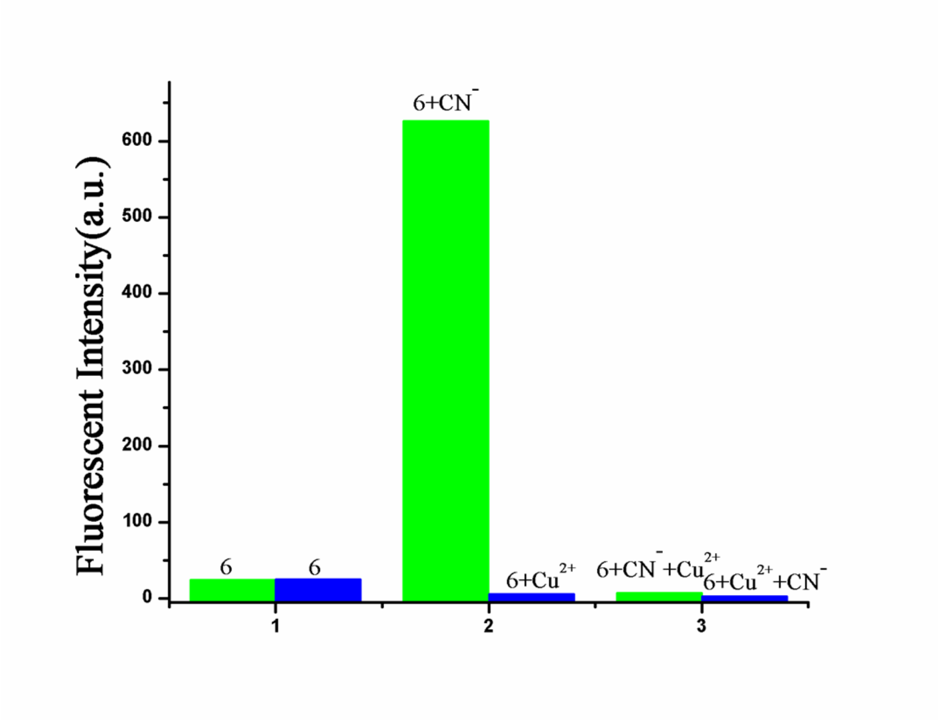


Figure S12 Fluorescence emission data for a different adding order of **6**, CN^- and Cu^{2+}.

16. The Fluorescence Responses of 6-CN⁻ with other competing metal ions

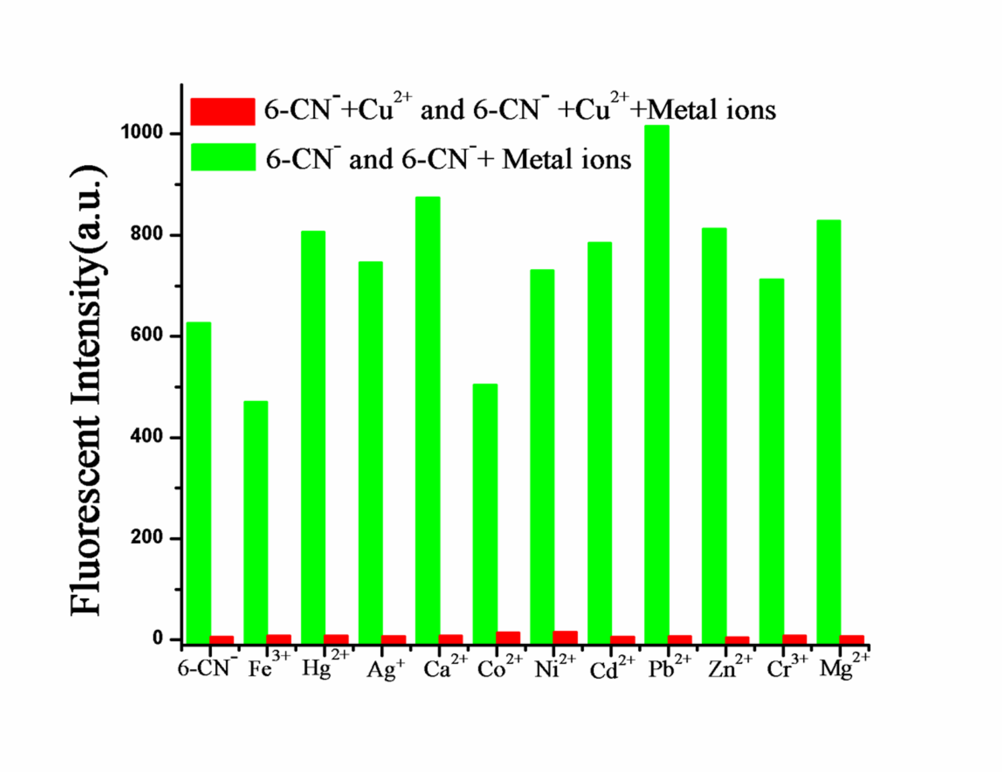
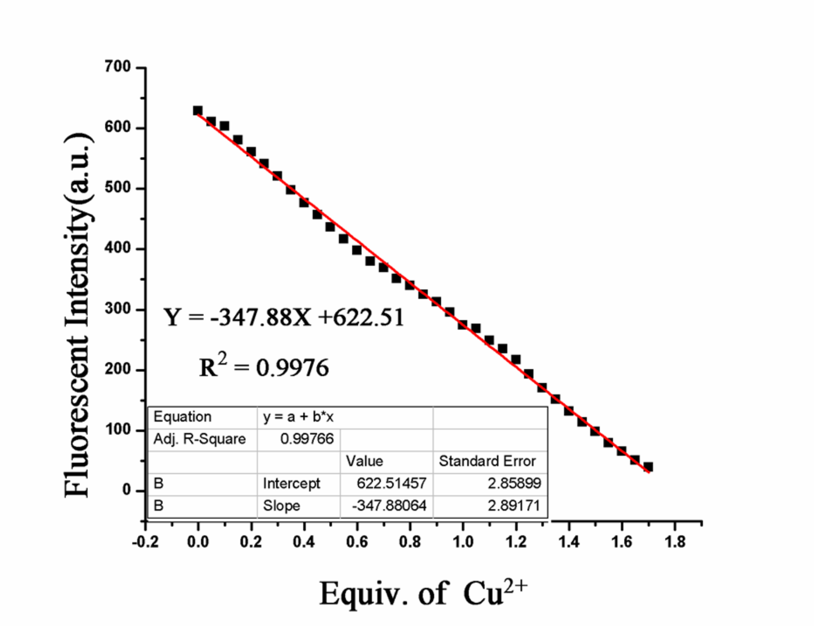


Figure S13 Fluorescence response of **6**-CN⁻ (20 μM) in the presence of Cu^{2+}, (20 equiv.) and additional other competing metal ions (20 equiv.) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH=7.2) solution (λ_{ex}=358 nm).

17. Determination of Detection Limit of Cu^{2+}



Equation	y = a + b*x		
Adj. R-Square	0.99766		
		Value	Standard Error
B	Intercept	622.51457	2.85899
B	Slope	-347.88064	2.89171

Figure S14 Plot of the intensity at 464 nm for a mixture of **6-**CN^{-} and Cu^{2+} in water solution in the range 0–1.7 equiv. (λ_{ex}= 358 nm).

Linear Equation: Y=-347.88×X+622.51, R^2=0.9976

$\sqrt{\frac{\sum(F_0-F_1)^2}{N-1}}$K=3

S=3.47×10^{8}, δ= =1.429 (N=10)

LOD=K×δ/S

LOD=1.23×10^{-8} M

F_0 is the fluorescence intensity of **6-**CN^{-}; F_1 is the average of the F_0.

18. IR spectra of compound 6, 6-CN⁻ and 6-CN⁻-Cu^{2+}

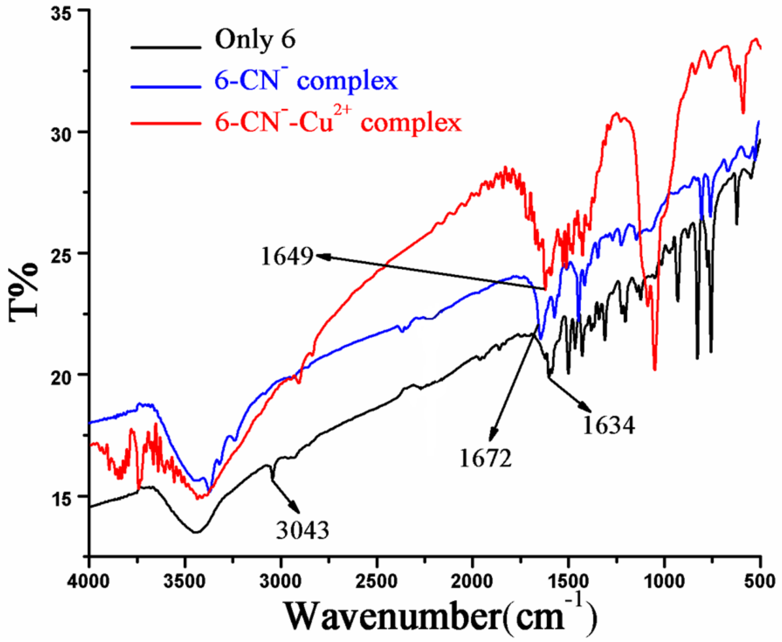
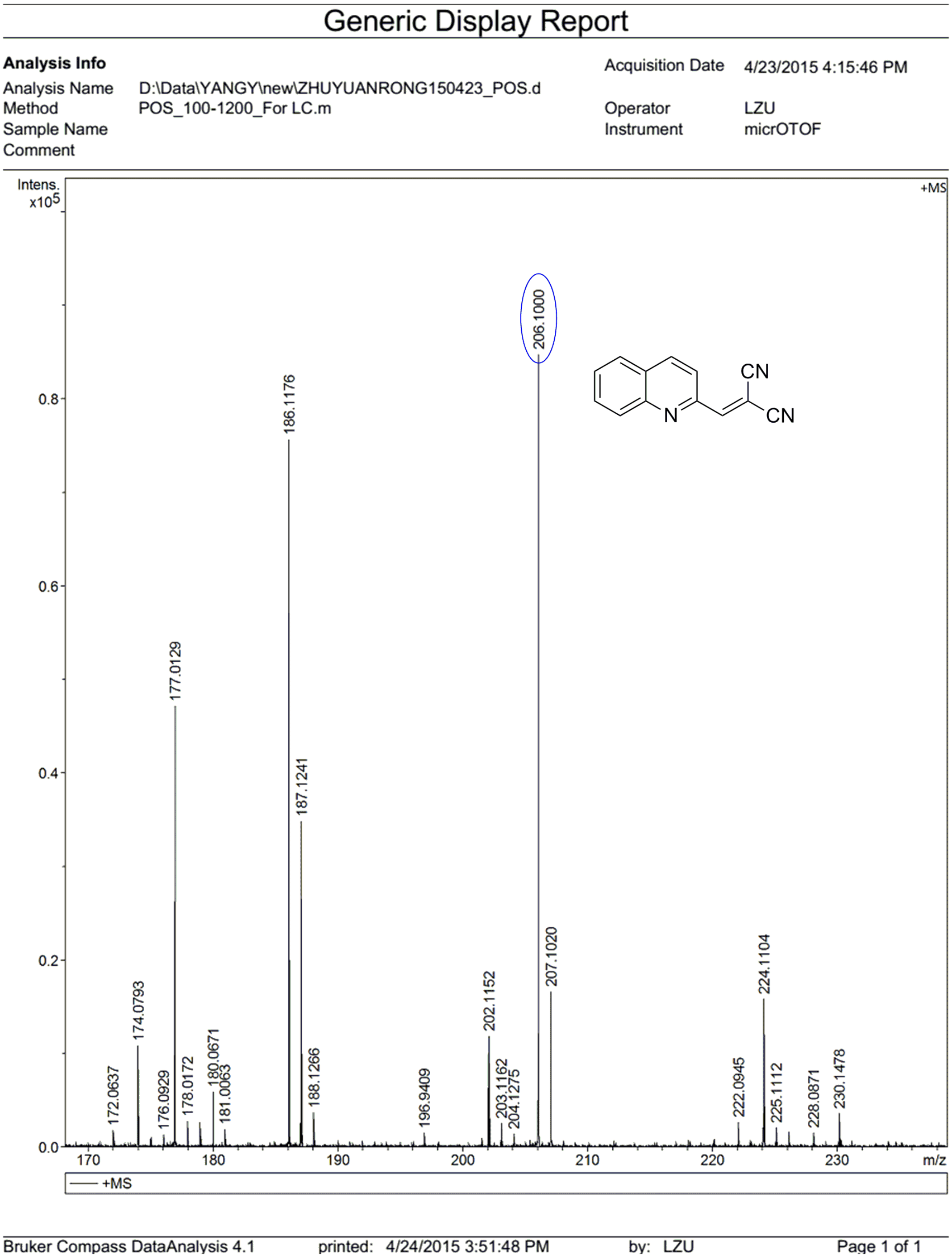


Figure S15 IR spectra of compound **6**, **6**-CN⁻ and **6**-CN⁻-Cu^{2+} complex in KBr disks.

19. ESI-MS spectrum of 6



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Instrument micrOTOF

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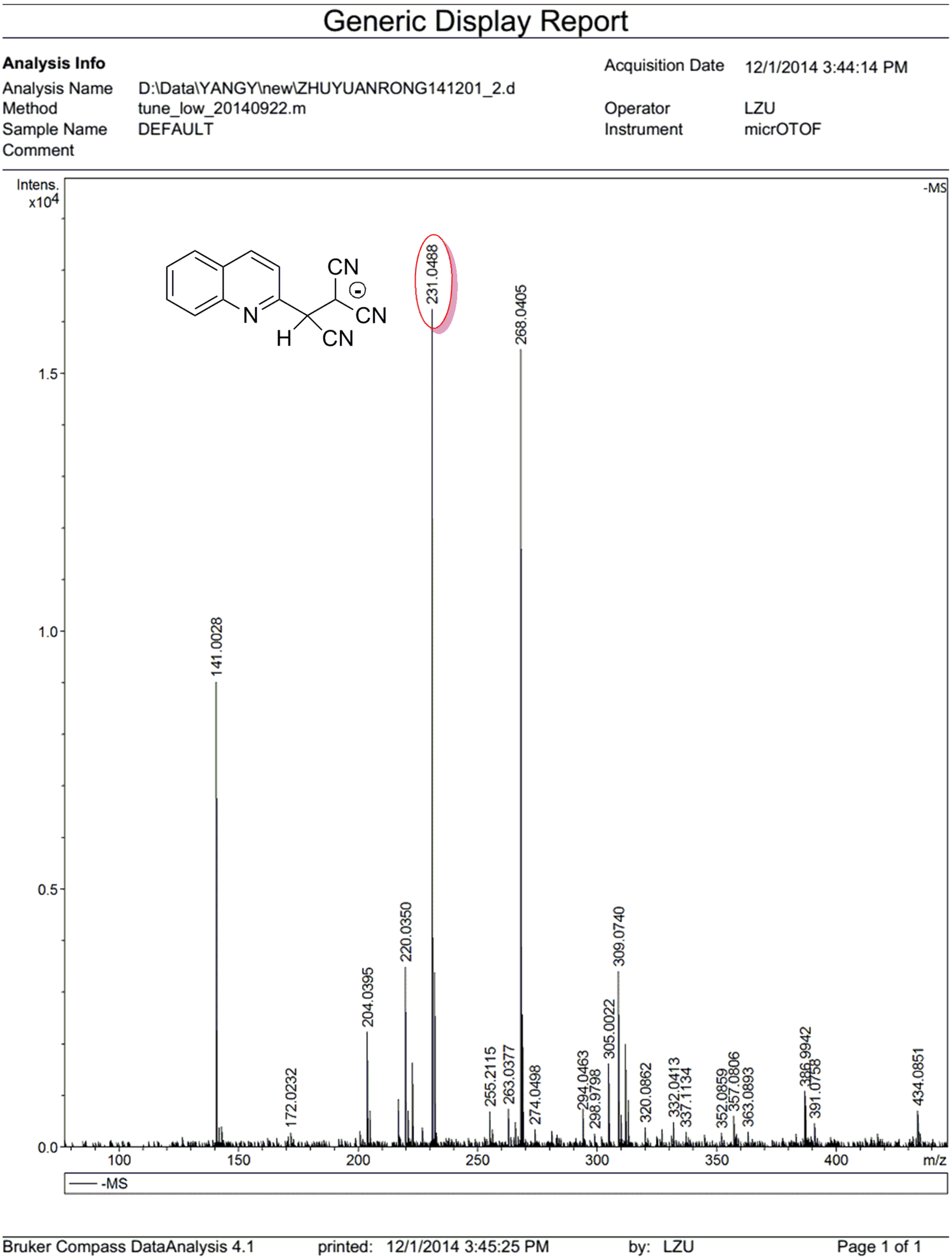
Figure S16 ESI-MS spectrum of **6**.

20. ESI-MS spectrum of 6+CN⁻ complex



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Operator LZU
Instrument micrOTOF

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Figure S17 ESI-MS spectrum of **6**+CN⁻ complex.

21. ESI-MS spectrum of 6+CN$^-$+Cu^{2+} complex

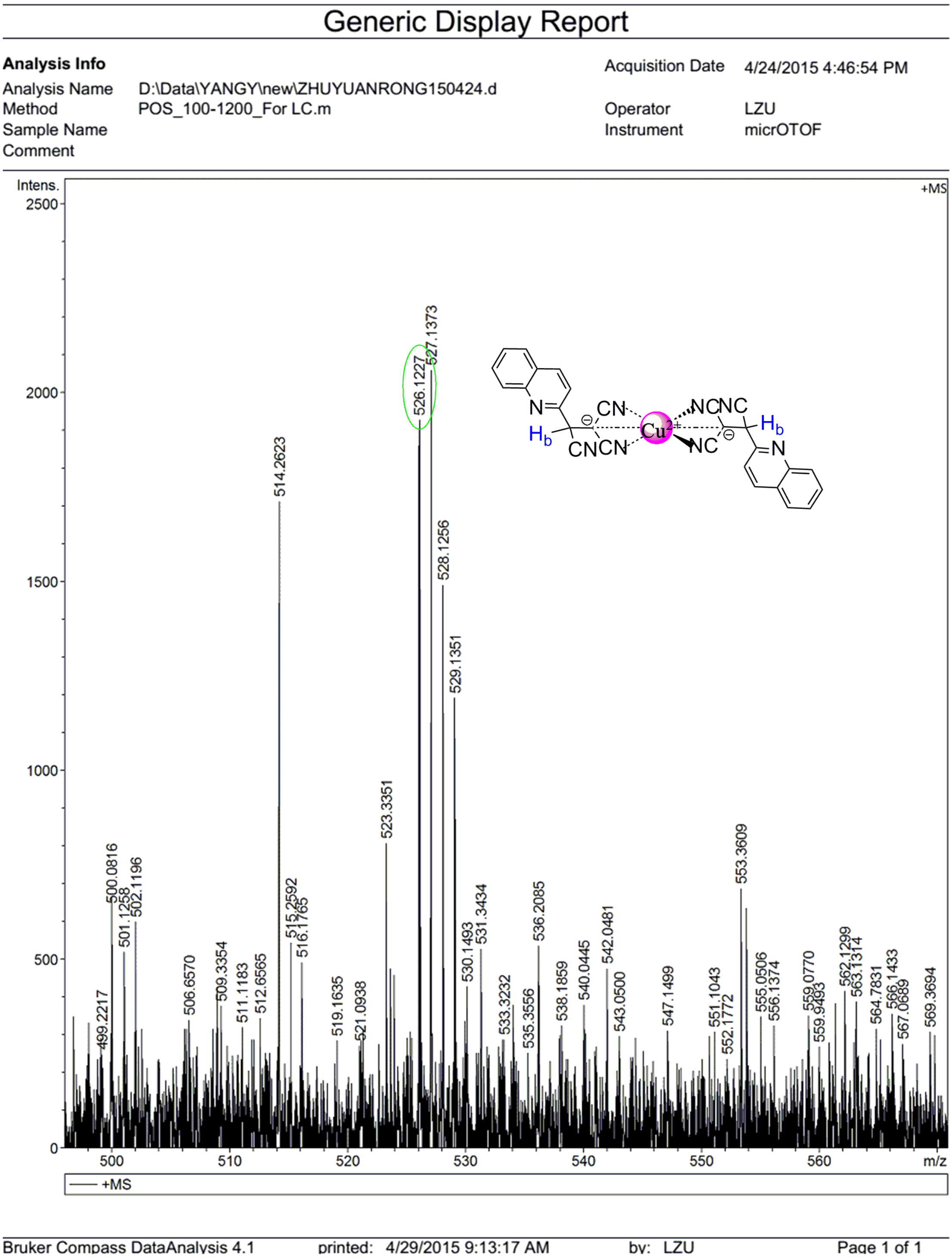

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Figure S18 ESI-MS spectrum of **6**+CN$^-$+Cu^{2+} complex.

22. The Job's plot examined between 6-CN$^-$ and Cu^{2+}

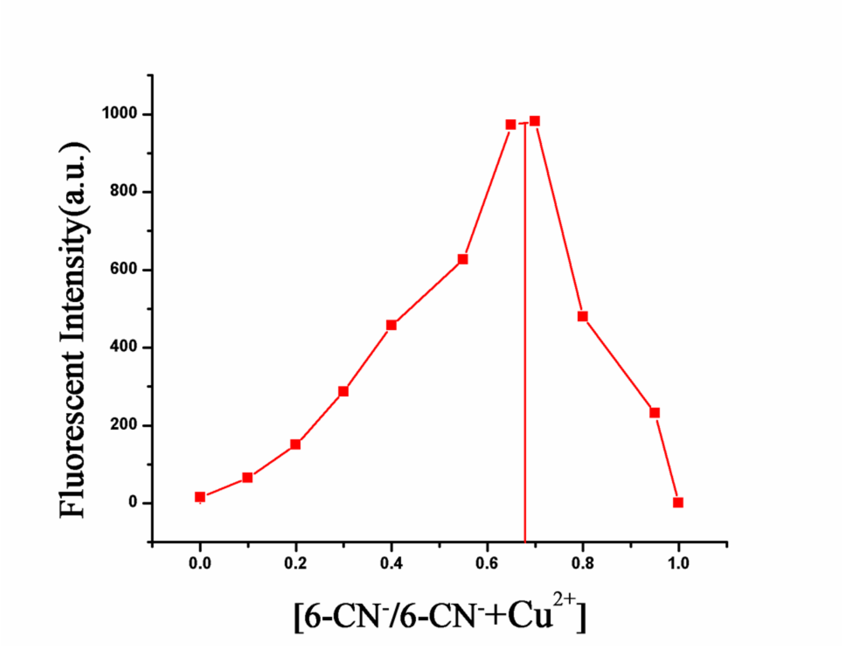


Figure S19 The Job's plot examined between **6**-CN$^-$ and Cu^{2+}, indicating the 2:1 stoichiometry.

23. Influence of pH on 6, CN⁻ and Cu²⁺

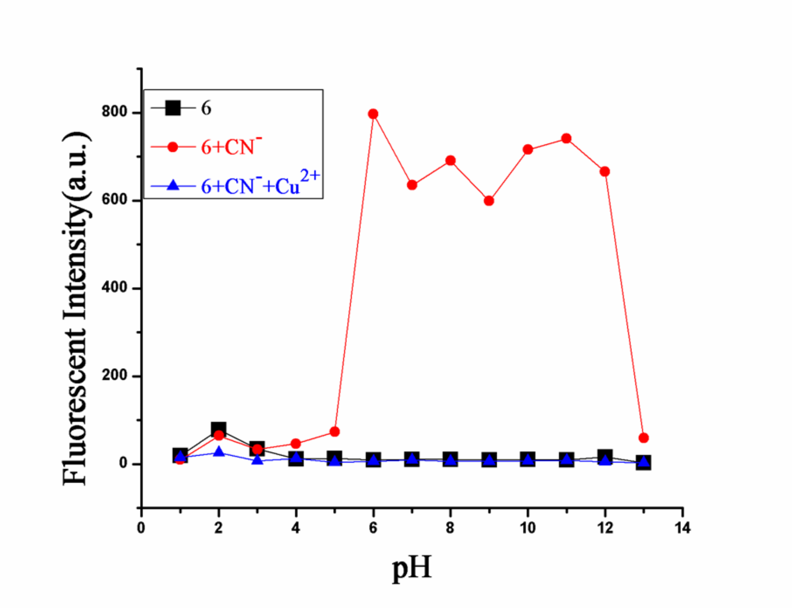
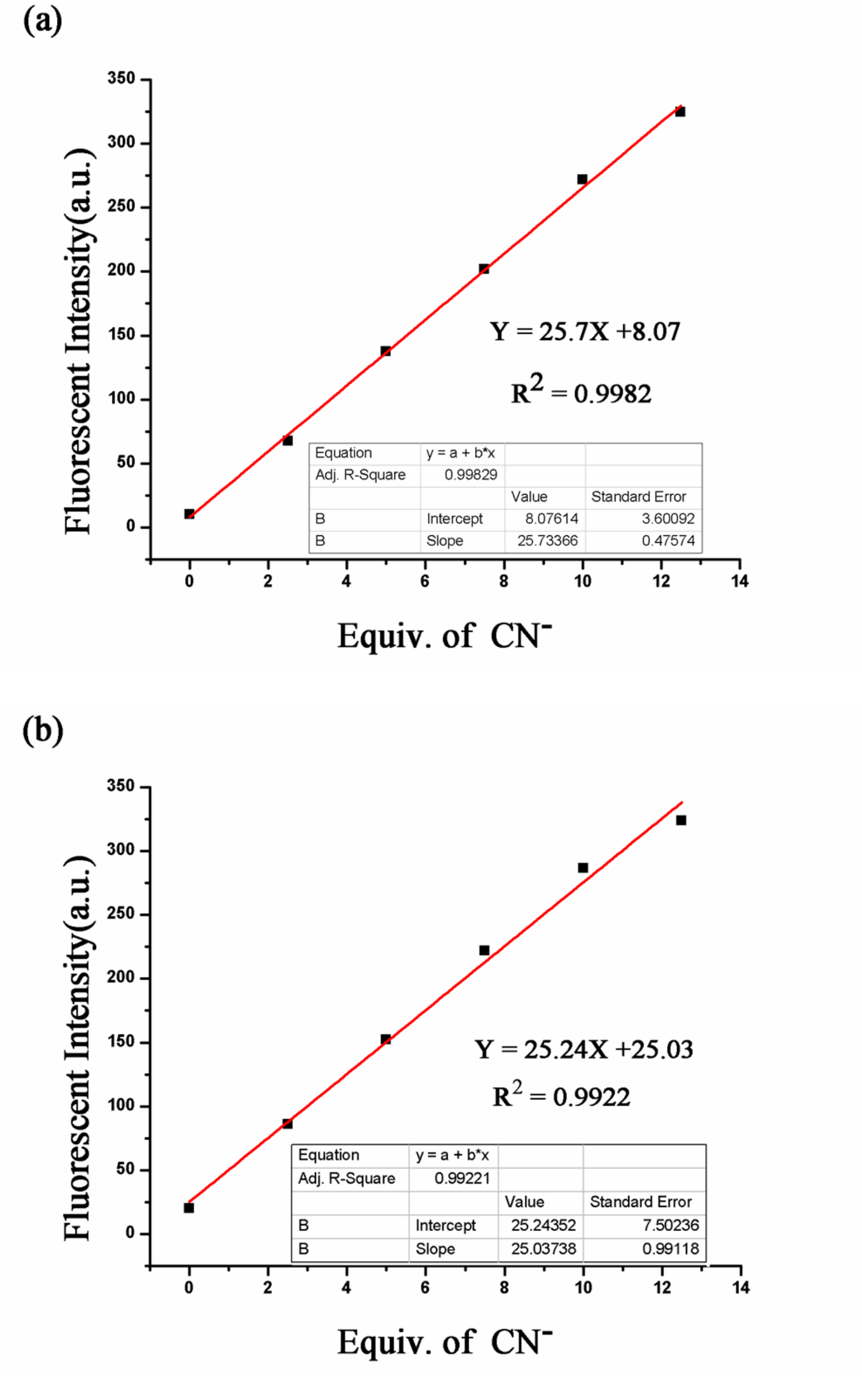


Figure S20 Influence of pH on the fluorescence of **6, 6**+CN⁻ and **6**+CN⁻+Cu²⁺ in HEPES buffered solution in DMSO/H_2O (1:9, v/v).

24. A linear relationship between the fluorescent intensity with the cyanide concentration.



Equation	y = a + b*x		
Adj. R-Square	0.99829		
		Value	Standard Error
B	Intercept	8.07614	3.60092
B	Slope	25.73366	0.47574

Equation	y = a + b*x		
Adj. R-Square	0.99221		
		Value	Standard Error
B	Intercept	25.24352	7.50236
B	Slope	25.03738	0.99118

Figure S21 A linear relationship between the fluorescent intensity with the cyanide from 0 to 12.5 equivalents in real water sample: (a) Tap water, (b) Yellow River water.