Supporting Information

A Simple Quinoline-derived Fluorescent Sensor for Selective and Sequential Detection of Copper (II) and Sulfide Ions and Its Application in Living-cell Imaging

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1. ^{1}H NMR spectrum obtained for BMA

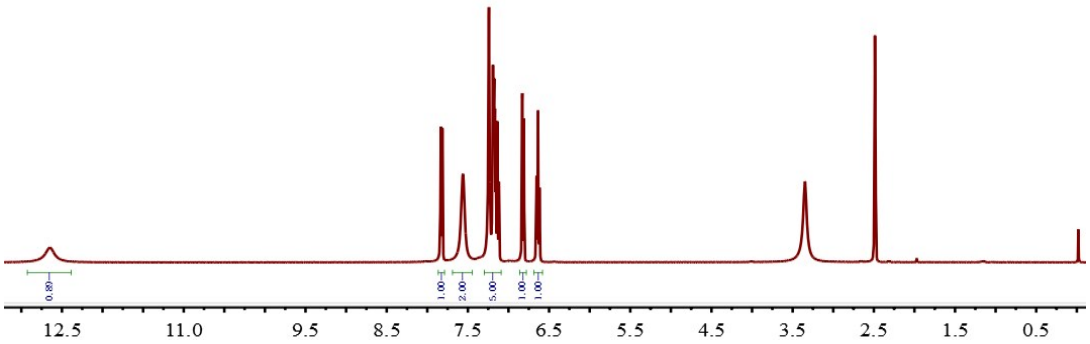

Figure S1. ^{1}H NMR of BMA (400 MHz, DMSO-*d6*) d (ppm): 12.65 (s, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.56 (s, 2H), 7.18 (m, *5*H), 6.82 (m, 1H), 6.64 (m, 1H).

2. ^{1}H NMR, ^{13}C NMR, and MS spectrum obtained for QLBA

^{1}H NMR of QLBA

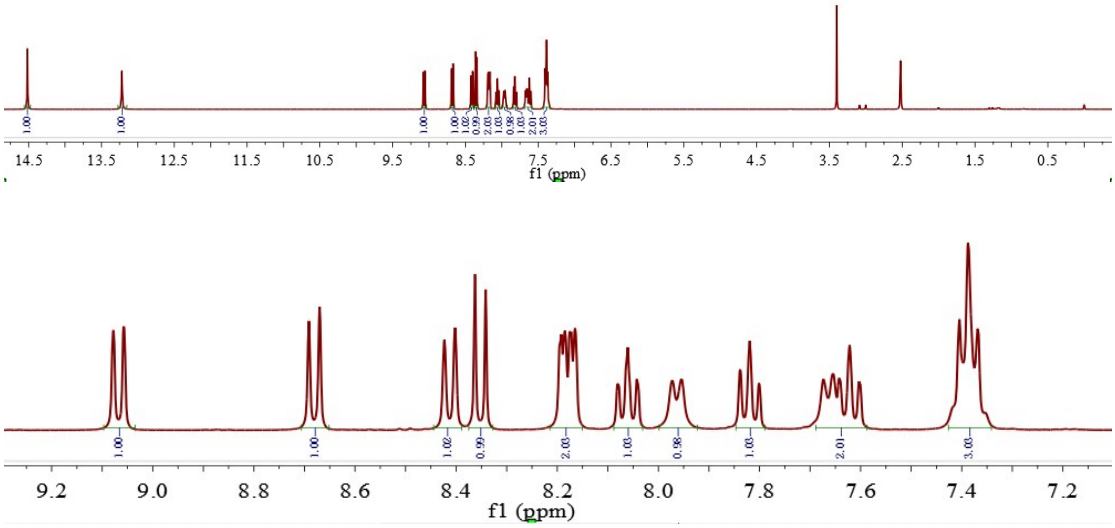

Figure S2. ^{1}H NMR (400 MHz, DMSO-*d6*) d (ppm): 14.52 (s, 1H), 13.22 (s, 1H), 9.07 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 8.0, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.18 (m, 2H), 8.06 (t, J = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.82 (t, *J* = 8.0, 1H), 7.64 (m, 2H), 7.39 (m, 3H). The above is the whole spectrum of ^{1}H NMR and the below is the partial spectrum.

^{13}C NMR of QLBA

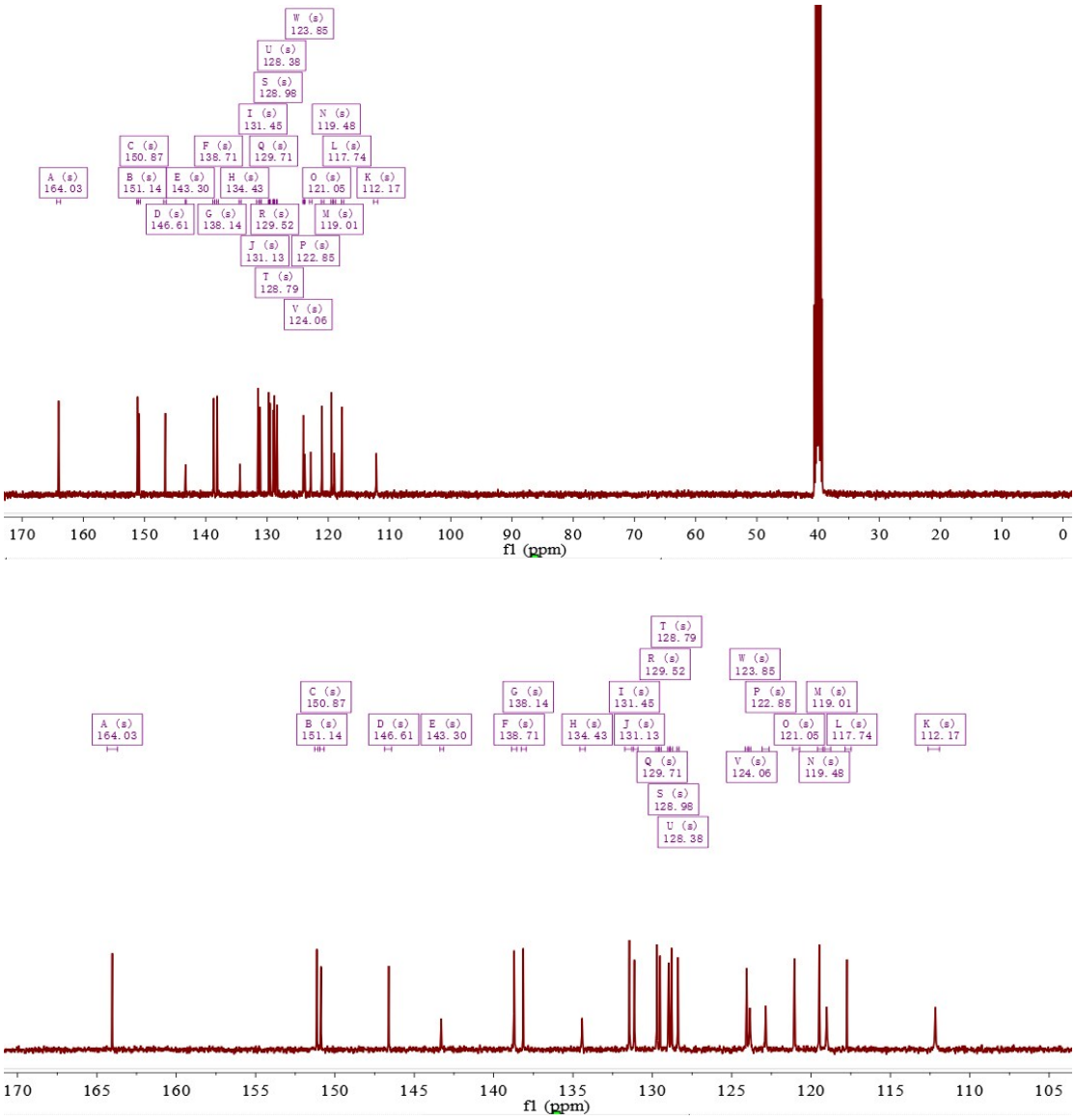

Figure S3. ^{13}C NMR (100 MHz, DMSO-*d6*) d (ppm): 164.03, 151.14, 150.87, 146.61, 143.30, 138.71, 138.14, 134.43, 131.45, 131.13, 129.71, 129.52, 128.98, 128.79, 128.38, 124.06, 123.85, 122.84, 121.08, 119.48, 119.01, 117.74, 112.17 (Fig. S2). The above is the whole spectrum of ^{13}C NMR and the below is the partial spectrum.

ESI mass spectra of QLBA

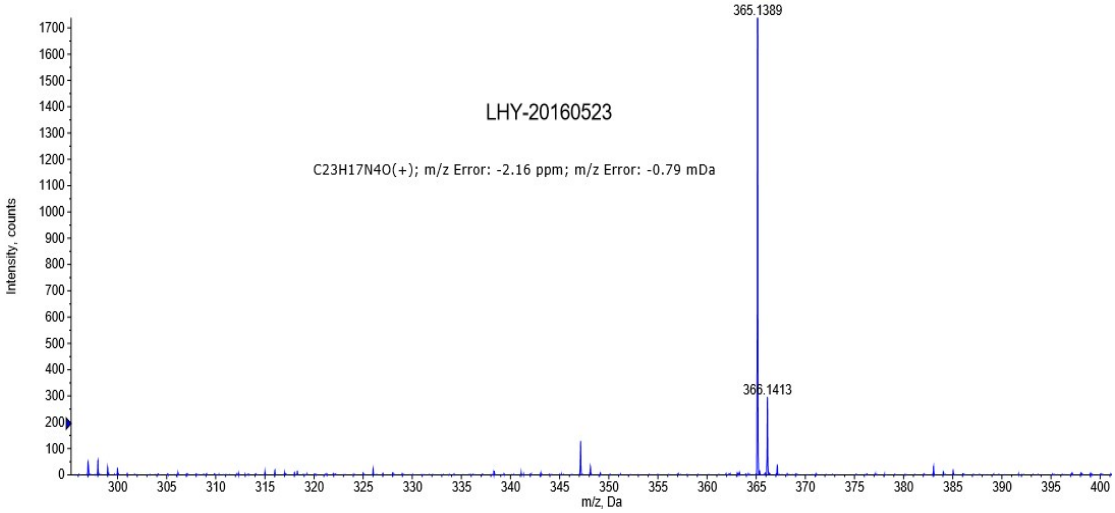

Figure S4, ESI mass spectra of QLBA. HRMS calcd for $C_{23}H_{16}N_4O$ $[QLBA+H]^+$: 365.1397, Found: 365.1389.

3. The selectivity of QLBA

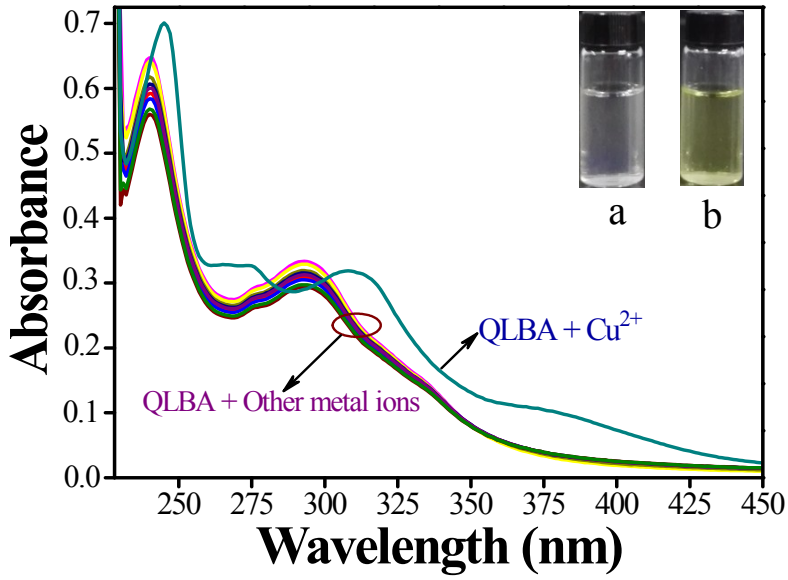

Figure S5, Absorption spectra obtained for QLBA (10 μM) in MeOH–HEPES buffer (1/9, v/v, pH 7.2) after the addition of 3.0 equiv. of Cu^{2+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Pb^{2+}, Hg^{2+}, and Cd^{2+}; Inset: Optical photographs (visible light) for QLBA (20 μM) after addition of (a) 3.0 equiv. of other metal ions and (b) 3.0 equiv. of Cu^{2+}.

4. Competitive experiments for QLBA

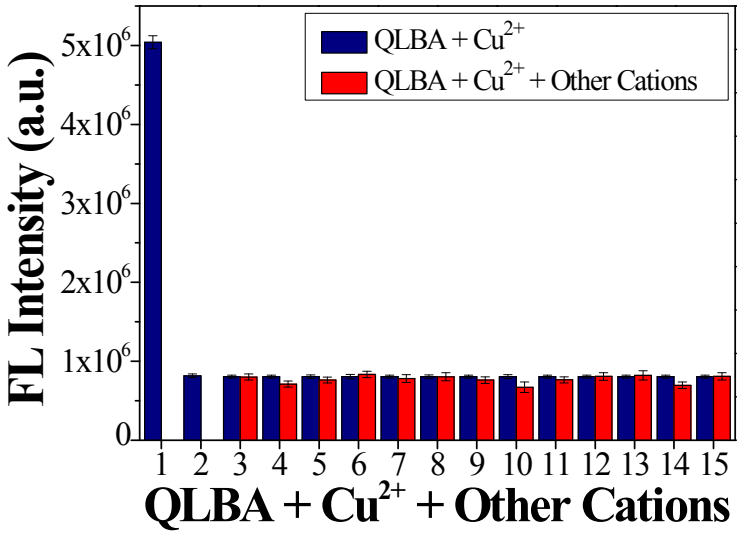

Figure S6. The fluorescence intensity at 435 nm of QLBA (10 μM) with 30 μM of Cu^{2+} in CH_3OH-HEPES buffer (1/9, v/v, pH 7.2), and then added 30 μM of various metal ions. 1, QLBA; 2, Cu^{2+}; 3, Cu^{2+}+Na^{+}; 4, Cu^{2+}+K^{+}; 5, Cu^{2+}+Mg^{2+}; 6, Cu^{2+}+Ca^{2+}; 7, Cu^{2+}+Co^{2+}; 8, Cu^{2+}+Zn^{2+}; 9, Cu^{2+}+Mn^{2+}; 10, Cu^{2+}+Fe^{3+}; 11, Cu^{2+}+Al^{3+}; 12, Cu^{2+}+Cr^{3+}; 13, Cu^{2+}+Pb^{2+}; 14, Cu^{2+}+Hg^{2+}; 15, Cu^{2+}+Cd^{2+} (λex= 370 nm).

5. pH analysis

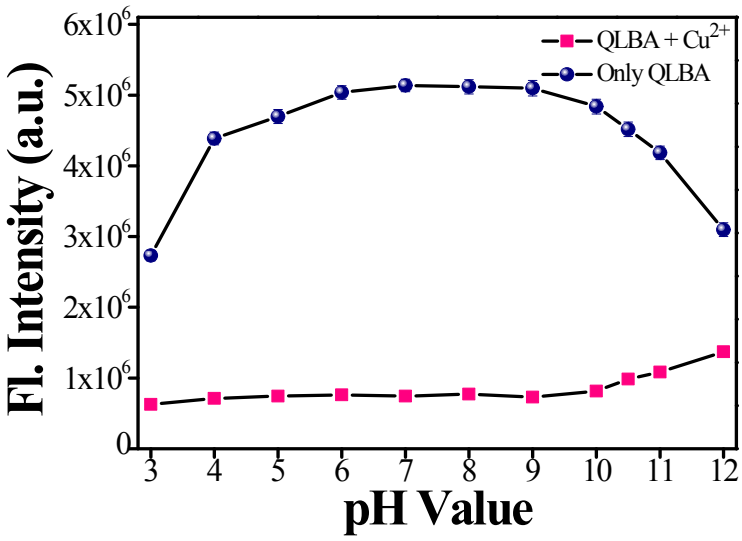

Figure S7. Fluorescence intensity recorded for QLBA (10 μM) at various pH values in the absence and presence of 3 equiv. Cu^{2+} (λex= 370 nm, λem= 435 nm).

6. ^{1}H NMR of QLBA under different pH.

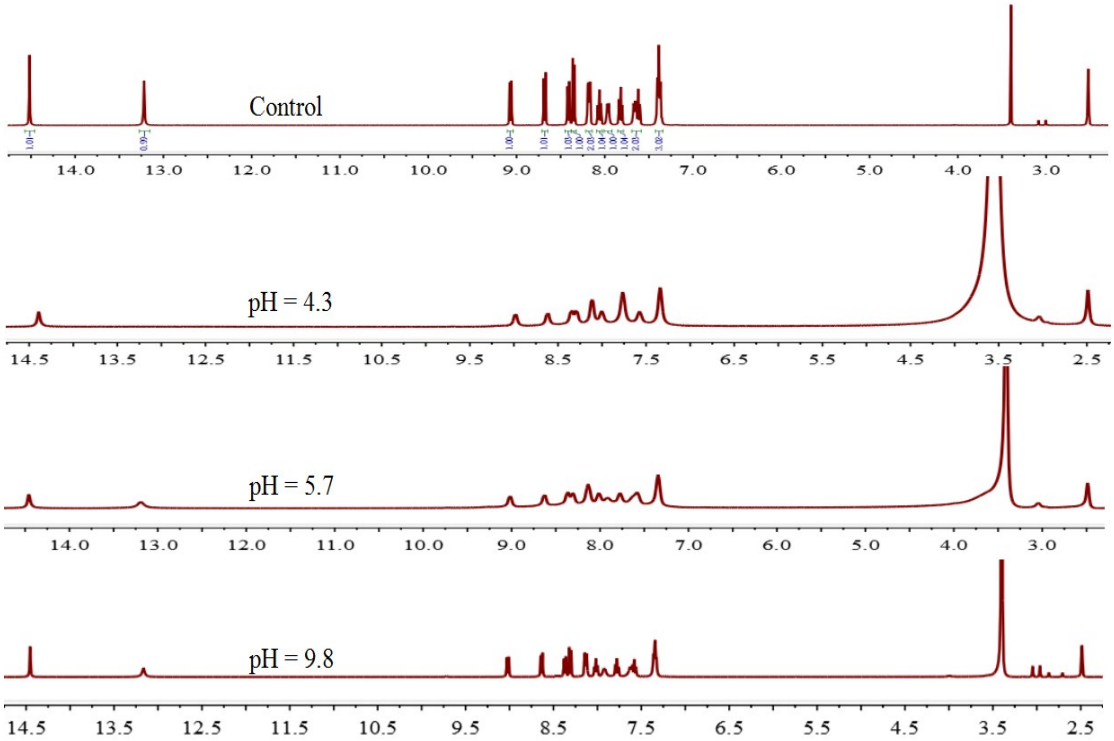

Figure S8. ^{1}H NMR of QLBA under different pH conditions. Control: QLBA in d_6-DMSO.

7. HRMS for QLBA and QLBA-Cu under different pH.

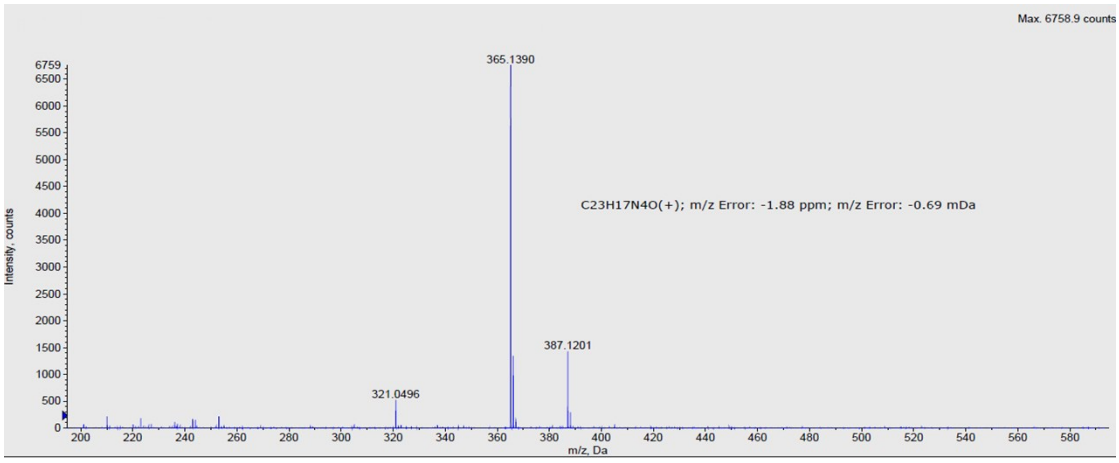

Figure S9a. ESI mass spectra of QLBA under pH=4.3 condition. Calcd for $C_{23}H_{16}N_4O$ $[QLBA+H]^+$: 365.1397, Found: 365.1390; Calcd for $C_{23}H_{15}N_4ONa$ $[QLBA+Na]^+$: 386.1144, Found: 386.1201.

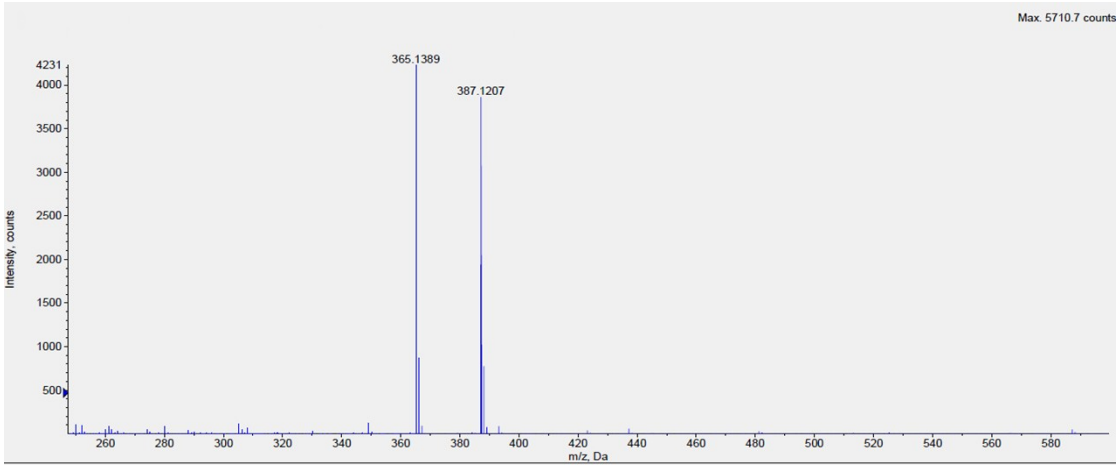

Figure S9b. ESI mass spectra of QLBA under pH=9.8 condition. Calcd for $C_{23}H_{16}N_4O$ $[QLBA+H]^+$: 365.1397, Found: 365.1389; Calcd for $C_{23}H_{15}N_4ONa$ $[QLBA+Na]^+$: 386.1144, Found:386.1207.

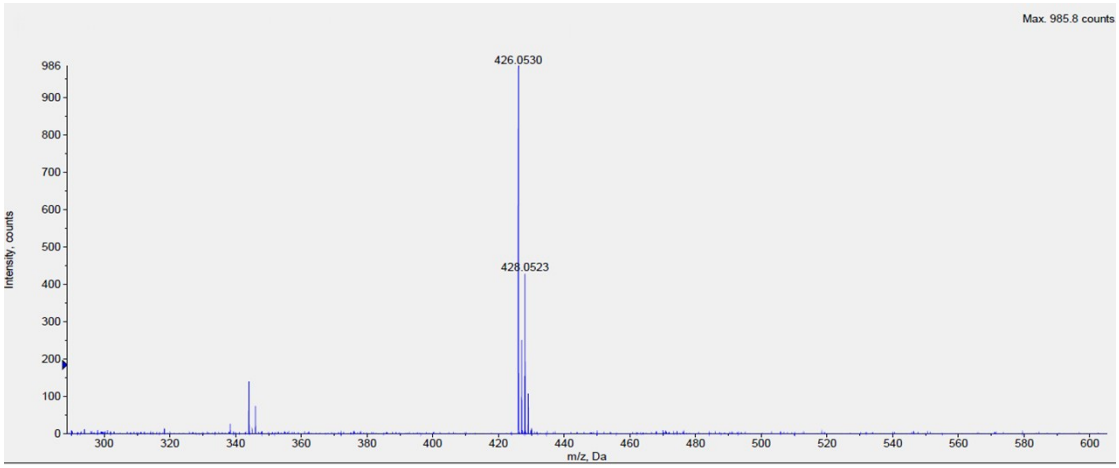

Figure S9c. ESI mass spectra of QLBA in the presence of $CuCl_2$ (2 equiv.) under pH=4.3 condition. Calcd for $[QLBA + Cu - H]^+$: 426.0536, found: 426.0530.

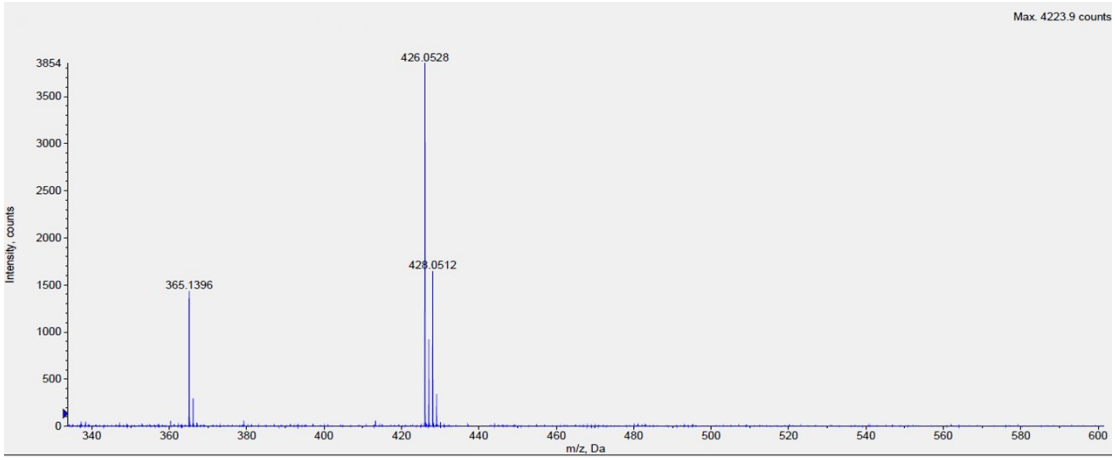

Figure S9d. ESI mass spectra of QLBA in the presence of $CuCl_2$ (2 equiv.) under pH=9.8 condition. Calcd for $[QLBA + Cu - H]^+$: 426.0536, found: 426.0528.

8. Fluorescence titration analysis

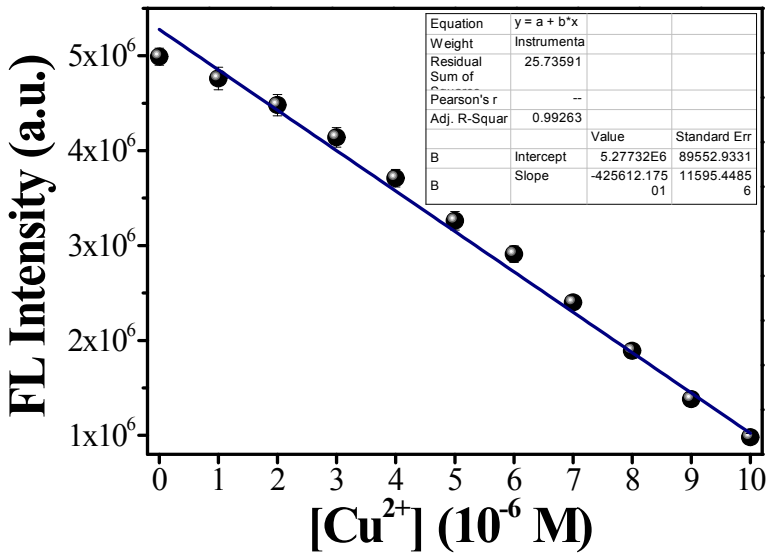

Figure S10. Calibration curve obtained for fluorescence intensity of QLBA (10 μM) versus the concentration changes of Cu^{2+} ions in MeOH–HEPES buffer (1/9, v/v, pH 7.2). The spectra were obtained 10 min after Cu^{2+} addition (λex= 370 nm, λem= 435 nm).

9. Fluorescence titration analysis in tap-water

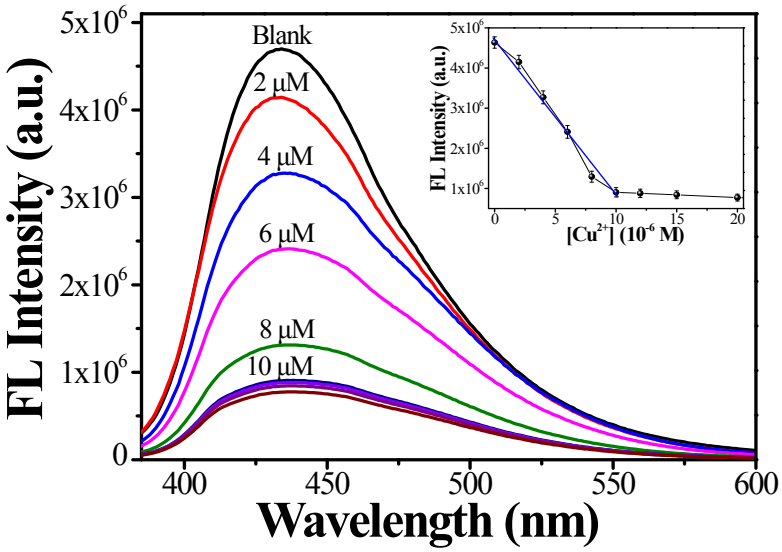

Figure S11. (a) Fluorescence emission spectra and (b) variation of fluorescence intensity recorded for QLBA (10 μM) upon gradual addition of Cu^{2+} (0, 2, 4, 6, 8, 10, 12, 15, 20 μM) in tap water-MeOH (v/v, 9/1). (λ_{ex} = 370 nm, λem= 435 nm).

10. MTT analysis

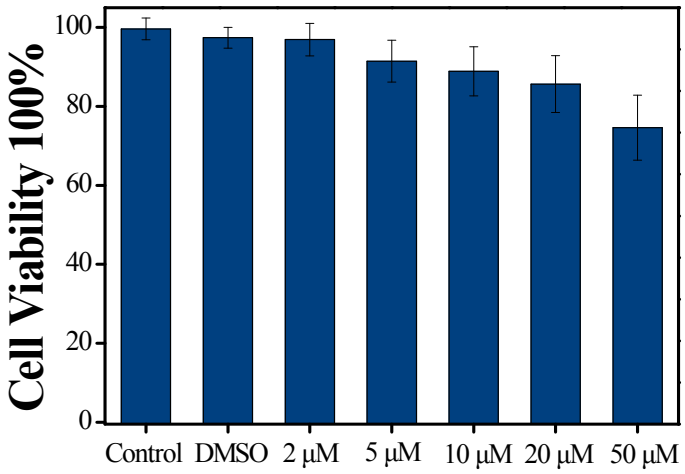

Figure S12. MTT assay of QLBA on HeLa cells (with QLBA 0, 2, 5, 10, 20, 50 μM) for 24h (DMSO denotes: Only 0.5% DMSO).

11. Calculation of the limit of detection

The limit of detection (*LOD*) was calculated based on the fluorescence titration according to the following equation (Eq. S1) [1,2], where Sb_1 is the standard deviation of the blank solution and S is the slope of the calibration curve in Figure S6. To determine Sb_1, the emission intensity of QLBA in MeOH–HEPES buffer (1/9, v/v, pH 7.2) without any metal ions was measured 10 times, respectively.

$$DL = 3 \times Sb_1 / S \qquad \textbf{(Eq. S1)}$$

12. References

[1] Barba-Bon, A., Costero, A.M., Gil, S., Parra, M., Soto, J., Martínez-Máñez, R. et al., **2012**. *Chem. Commun.* 48, 3000-3002.

[2] T. Mistri, R. Alam, M. Dolai, S. K. Mandal, A. R. Khuda-Bukhshb, M. Ali, *Org. Biomol. Chem*., 2013, 11, 1563-1569.