Electronic Supplementary Information

A hemicyanine-based 'turn-on' fluorescent probe for selective detection of Cu^{2+} and imaging in living cells

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Supplementary captions

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Experimental

General

Melting points were measured on a MEL-TEMPII apparatus. FT-IR spectra were recorded on a Nicolet 670 FT-IR spectrometer. High resolution mass spectra were recorded on a Thermo Scientific LTQ Orbitrap XL mass spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained at room temperature on a Bruker-AV-400 NMR spectrometer. UV–vis spectra were recorded with a Perkin Elmer Lambda-25 UV–vis spectrophotometer. The fluorescence quantum yield was evaluated with JY HORIBA FluoroLog-3 Steady-Transient fluorescence spectrometer. The fluorescence spectra were obtained on a F-7000 fluorescence spectrophotometer. All the measurements were taken at 25 °C. All the chemicals for synthesis and analysis were purchased from commercial sources and used as received without further purification. The metal ion salts in stock solutions used their nitrates and anions were used their tetrabutylammonium salts. The precursor compound 6-methoxy-2,3-dihydro-1H-xanthene-4-carbaldehyde was synthesized according to the reported procedures.[1]

Synthesis

6-Methoxy-2,3-dihydro-1H-xanthene-4-carbaldehyde (0.73 g, 3.00 mmol) was dissolved in methanol (25 mL). Then 2-aminophenol (0.33 g, 3.00 mmol) was added and the mixture was stirred for 10 h to obtain an orange-red precipitate. The solid was collected by filtration, then dissolved with 10.00 mL of methanol, and then 7.00 mL of methanol was removed by rotary evaporation under reduced pressure. The remaining solution was sealed and put into a refrigerator to cool and the dark red crystals was obtained. Yield: 63%.^{1}H NMR (DMSO-d_6) δ 8.90 (s, 1H), δ 8.48 (s, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.01 (t, J = 8.0, 1H), 6.86–6.80 (m, 3H), 6.67–6.64 (m, 2H), 3.78 (s, 3H), 2.66 (t, J = 6.0 Hz, 2H), 2.55 (t, J = 6.0 Hz, 2H), 1.71 (t, J = 6.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 160.93, 155.18, 153.78, 152.77, 137.42, 127.45, 127.21, 127.01, 123.88, 119.84, 115.60, 115.17, 114.27, 111.65, 110.02, 100.44, 55.61,

30.02, 23.60, 20.79. IR (KBr): 3390.69 cm^{-1} (υ_{OH}), 1562.04 cm^{-1} ($\upsilon_{C=N}$). HR-MS (ESI): m/z calcd for $C_{21}H_{20}NO_3^+$ $(M+H)^+$ 334.1438, found 334.1439.

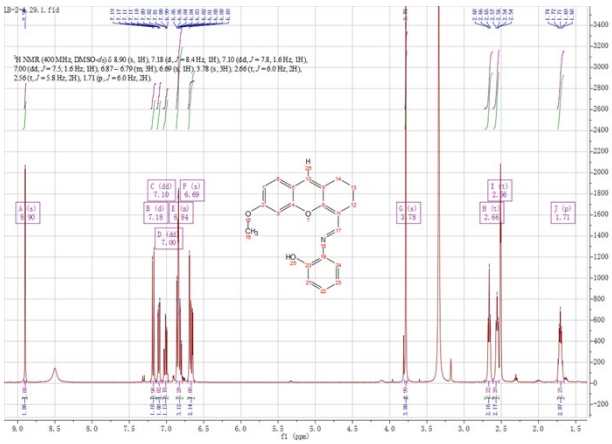

Fig. S1. ^1H NMR of probe L.

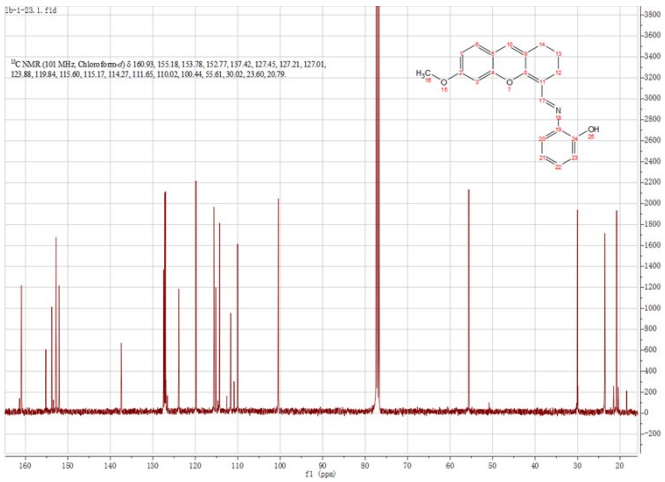

Fig. S2. ^{13}C NMR of probe L

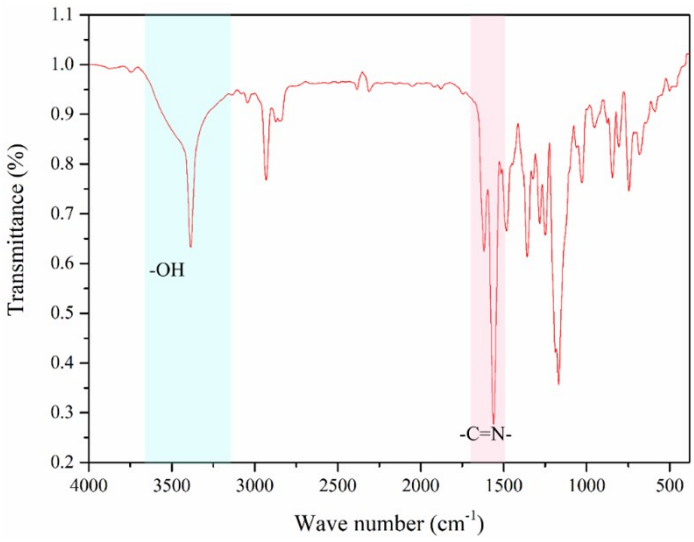

Fig. S3. IR of probe L.

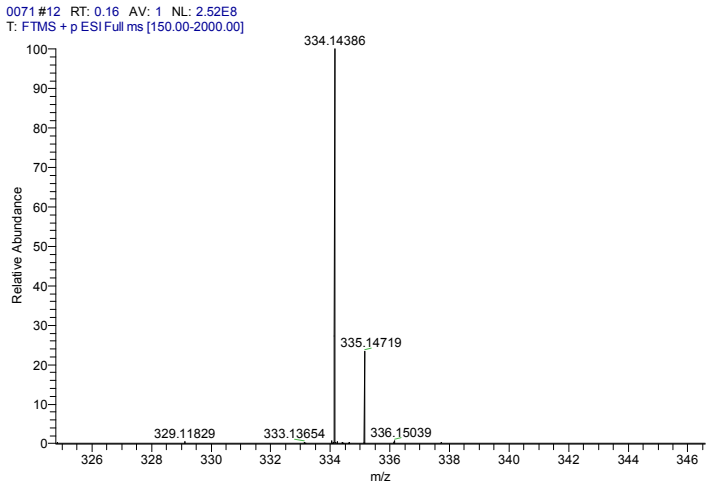

Fig. S4. HRMS (ESI) m/z calcd for $C_{21}H_{20}NO_3^+$ $(L+H)^+$ 334.14377, found 334.14386.

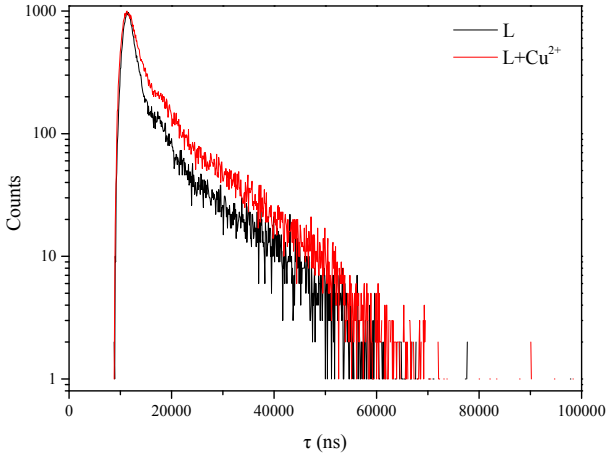

Fig. S5. Fluorescence lifetime of L and the complex of probe Lwith Cu^{2+} in MeCN-HEPES (v/v, 4:1, 10 mM, pH 7.3) solution. And the fluorescence lifetime of probe L is 7322.83 ns, the fluorescence lifetime of the complex of probe Lwith Cu^{2+} is 8237.62 ns.

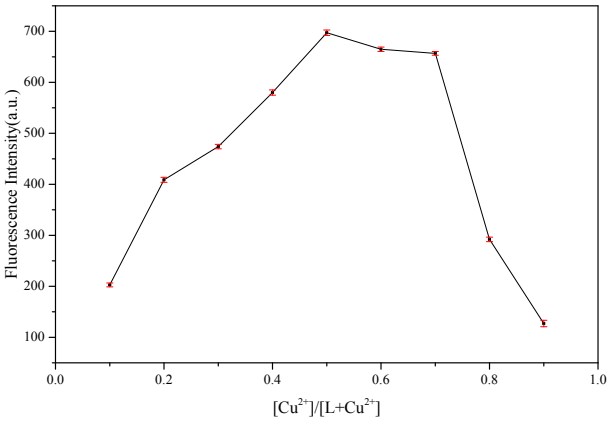

Fig. S6. Job's plots of the complexation between L and Cu^{2+} ([L] + [Cu^{2+}]) in MeCN-HEPES (v/v, 4:1, 10 mM, pH 7.3) solution.

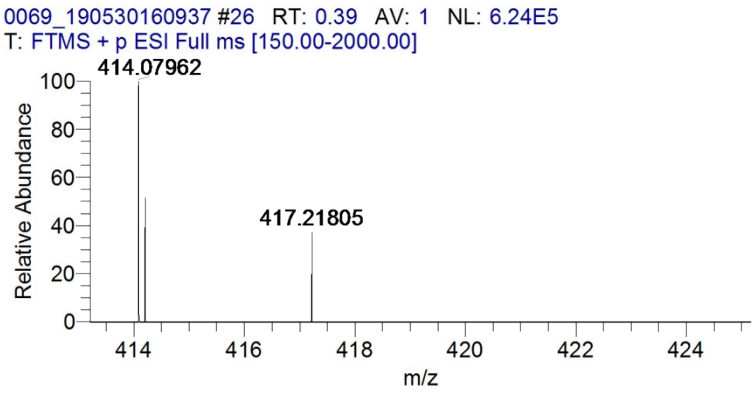

Fig. S7. HRMS (ESI) m/z calcd for [L+Cu^{2+}+H_2O] 414.0756, found 414.07962.

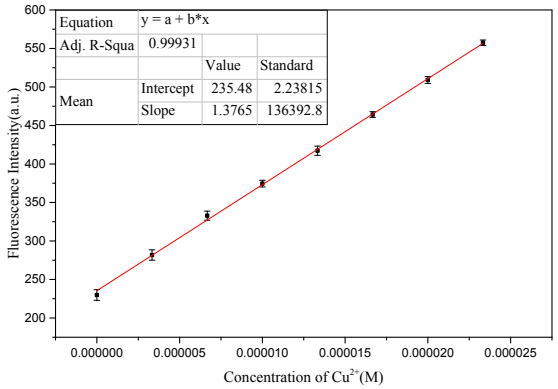

Fig. S8. The linear relation of fluorescence intensities of L to the low concentration of Cu^{2+} ions (3.33×10^{-6}—2.33×10^{-5} M) in MeCN-HEPES (v/v, 4:1, 10 mM, pH 7.3) solution. And the detection limit of L to Cu^{2+} is 3.3079×10^{-5} M.

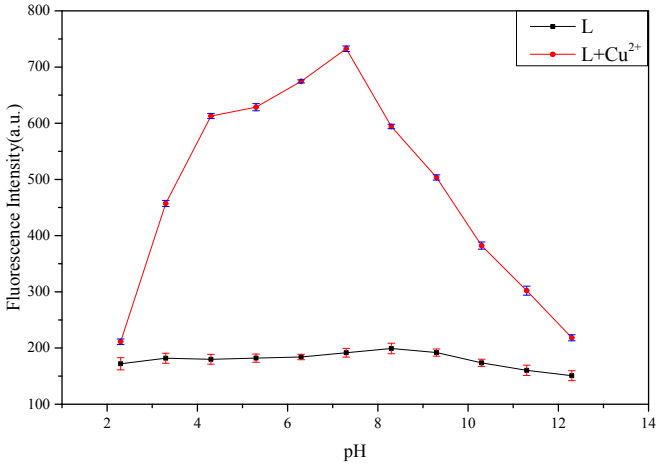

Fig. S9. The black and red lines indicate the fluorescence intensity change of free probe L and the complex with Cu^{2+} at 520 nm in the MeCN-HEPES system.

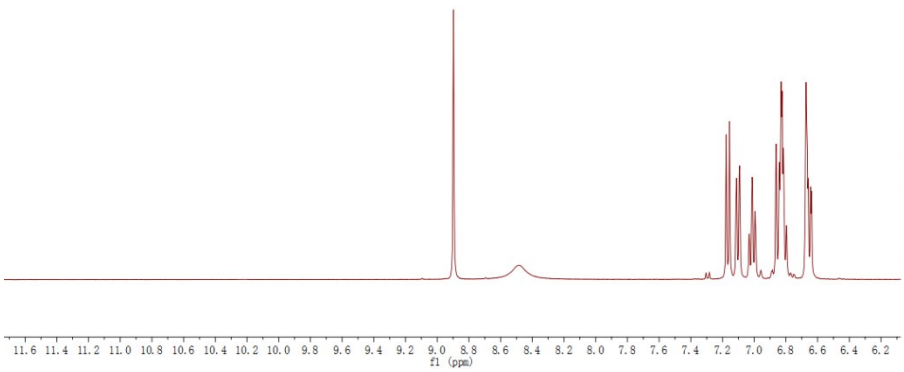

Fig. S10. The NMR spectrum of the aromatic region of probe L.

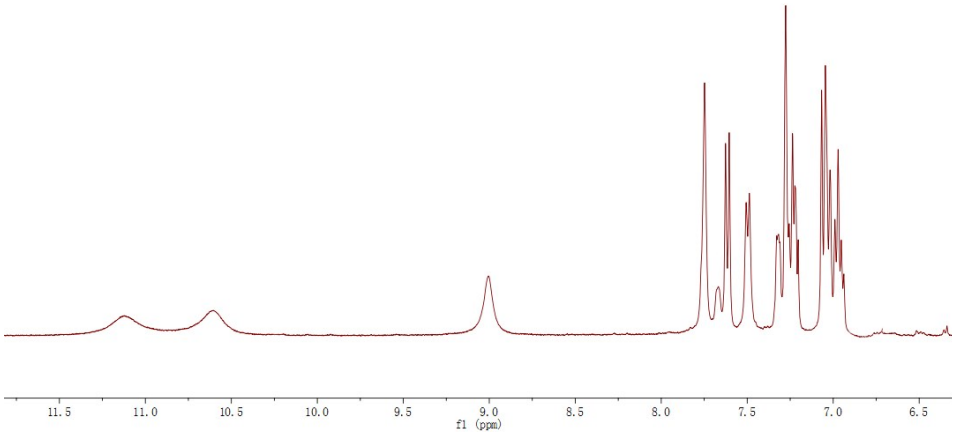

Fig. S11. The NMR spectrum of the aromatic region of complex of probe L with Cu^{2+}.

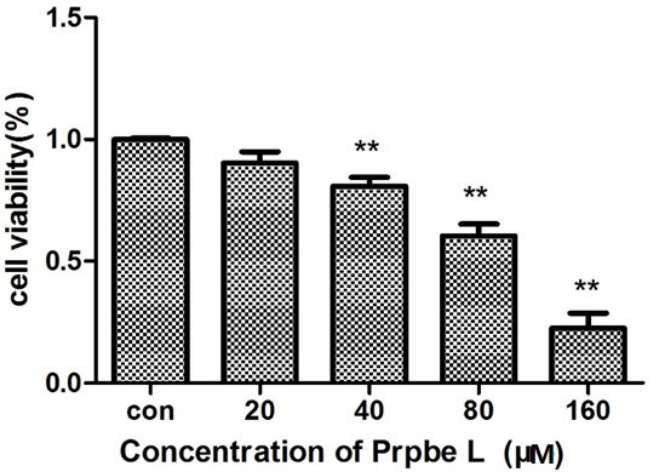

Fig. S12. The toxicity experiment of HepG2 cells. The cell survival rate is above 80% (81.3 %) when the probe concentration reaches 40 μM.

References

1 Y. Qi, Y. Huang, B. Li and S. Wu, *Anal. Chem.*, 2018, **90**, 1014–1020.