

Supporting Information

A fluorescence “turn-on” chemodosimeter for Cu²⁺ in aqueous solution based on the ion promoted oxidation

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Materials and measurements

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Solvents used were purified and dried by standard procedure prior to be used. The authentic sample of coumarin **6** was purchased from Tianjin Heowns Biochem LLC. The UV-vis absorption and fluorescence spectra were recorded on Hitachi 1601 spectrophotometer and Hitachi F-4500 spectrofluorometer, respectively. A 1.0cm quartz cuvette in a volume of 3.0 mL was used for all spectra collection. Thin-layer chromatography (TLC) was performed on glass plates coated with SiO₂ F254. The plates were inspected by UV light or in I₂ vapor. Column chromatography was performed on silica gel (160-200 mesh). ¹H and ¹³C NMR spectra were recorded on Bruker AV 400 (400 and 100 MHz, respectively) using tetramethylsilane (TMS) as an internal standard.

Spectral measurements

The stock solutions (0.1 mM) of the perchlorate salts of Fe³⁺, Cu²⁺, Ba²⁺, Ni²⁺, Mg²⁺, Na⁺, Ca²⁺, the nitrate salts of Pb²⁺, Mn²⁺, Ag⁺ and chloride salts of Co²⁺, Zn²⁺, Fe²⁺, Hg²⁺ in acetonitrile were prepared, respectively. A stock solution (1 mM) of compound **L** was prepared in acetonitrile; then 100 μL of this stock solution was added to the 100 mL volumetric flasks and diluted with HEPES (10 mM, pH = 7.4) buffer and acetonitrile to obtain the solution of **L** (1 μM). A solution of **L** (1 μM) was prepared in HEPES (10 mM, pH = 7.4) buffer containing 50% (v/v) water/CH₃CN; then 3.0 mL of the solution of **L** was placed in a quartz cell (10.0 mm width) and the fluorescence spectra were recorded after the addition of different metal ions to the solution of **L**, respectively. Unless otherwise noted, for all measurements, the

excitation wavelength was at 457 nm. The slit width of excitation was 2.5 nm and the slit width of emission was 5.0 nm. The solution of **L** was reserved in dark and stable in the above solvent system for at least one week.

Synthesis of chemodosimeter L: 2-Aminothiophenol (260 mg, 2 mmol) was dissolved in 10 mL methanol, then, the solution was added dropwise to 3-carbonyl-7-*N,N*-diethylaminocoumarin (490 mg, 2 mmol) in 50 mL methanol. The reaction mixture was refluxed for 4 h and the yellow solid was precipitated out. The crude product was collected and washed with CH₃OH to give **L** in a yield of 60%. ¹H NMR (400 MHz, CDCl₃) δ : 7.81 (s, 1H), 7.24 (t, 1H, J = 8.8 Hz), 7.09 (d, 1H, J = 7.56 Hz), 6.94 (t, 1H, J = 7.44 Hz), 6.78 (t, 2H, J = 7.36), 6.57 (d, 1H, J = 7.44 Hz), 6.49 (s, 1H), 6.31 (s, 1H), 4.72 (brs, 1H), 3.39 (q, 4H, J = 7.08 Hz), 1.22 (t, 6H, CH₃, J = 7.08 Hz). ¹³C NMR (100 MHz, CDCl₃) δ : 162.2, 156.0, 150.9, 146.0, 139.1, 129.4, 126.8, 125.5, 122.2, 121.4, 121.1, 111.0, 109.1, 108.3, 97.2, 64.3, 45.0, 12.5; EI-MS: [M]⁺ 352 (calculated: 352).

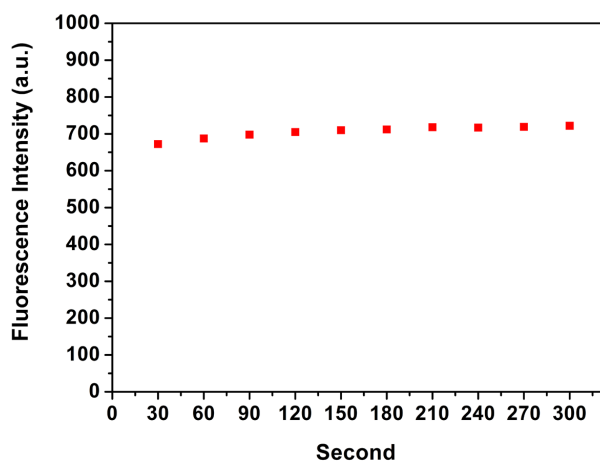


Figure S1. The variation of fluorescence intensity of compound **L** (1 μ M) + 1 equiv. Cu²⁺ in HEPPS (10 mM, pH = 7.4) buffer containing 50% (v/v) water/CH₃CN. within 300 seconds.

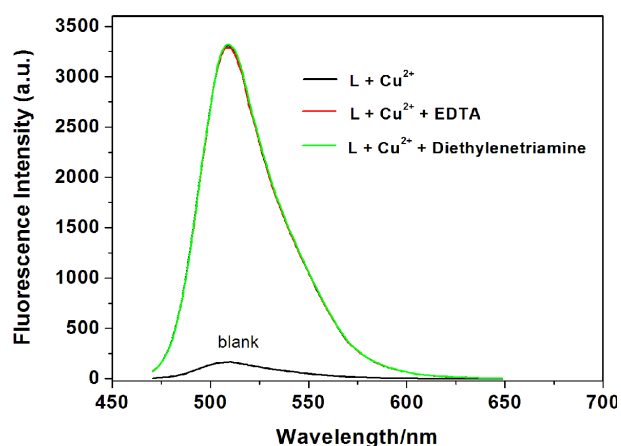


Figure S2. Fluorescence spectra of **L** ($1\ \mu\text{M}$) in the absence and presence of Cu^{2+} and the addition of EDTA and diethylenetriamine.

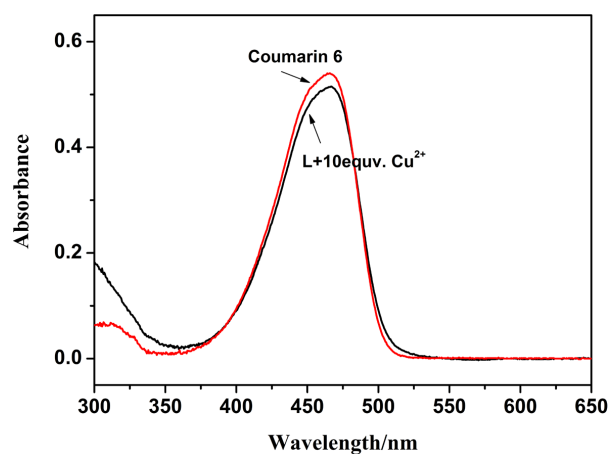


Figure S3. The UV-vis spectra of **L** ($10\ \mu\text{M}$) + 10 equiv. Cu^{2+} and authentic sample of coumarin **6** ($10\ \mu\text{M}$).

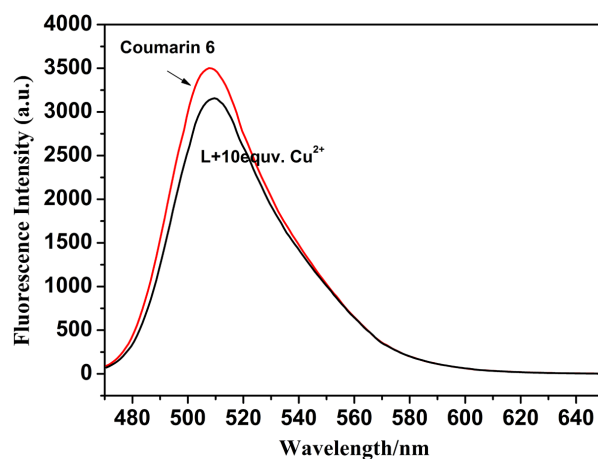


Figure S4. The Fluorescence spectra of **L** ($1\ \mu\text{M}$) + 10 equiv. Cu^{2+} and authentic sample of coumarin **6** ($1\ \mu\text{M}$).

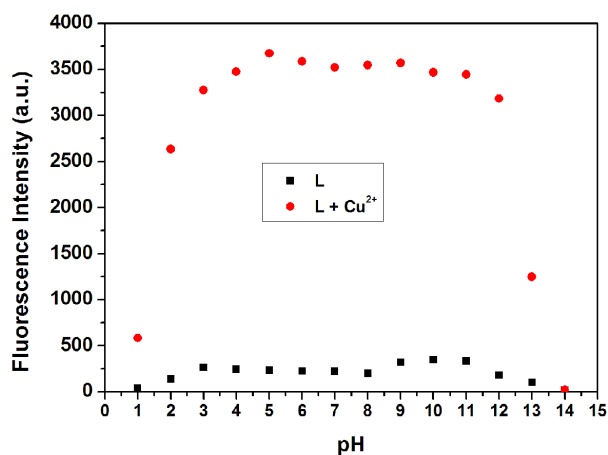


Figure S5. Variation of fluorescent intensity of **L** (1 μM) in aqueous solution (50% (v/v) water/ CH_3CN) with and without Cu^{2+} (10 μM) as a function of pH.

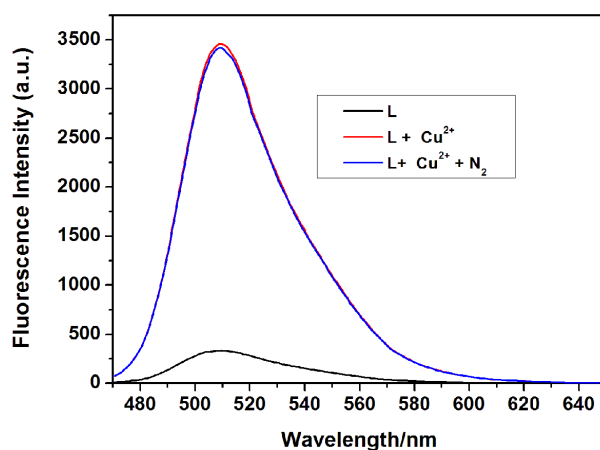


Figure S6. Fluorescence spectra of **L** (1 μM) + Cu^{2+} in the presence and absence of N_2 .

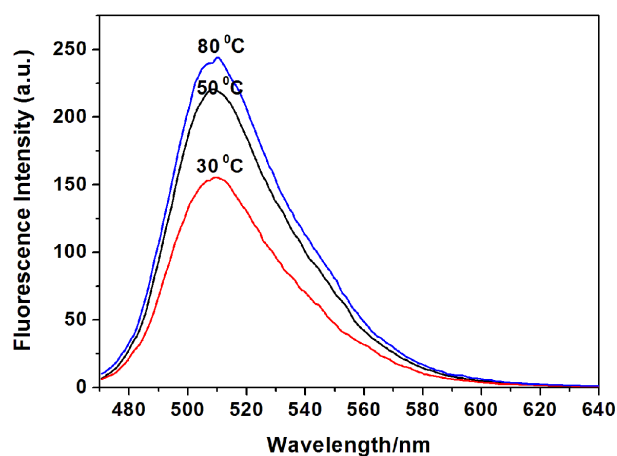


Figure S7. Fluorescence spectra of **L** (1 μM) + Fe^{3+} (10 eq.) at 30 °C, 50 °C, 80 °C, respectively.

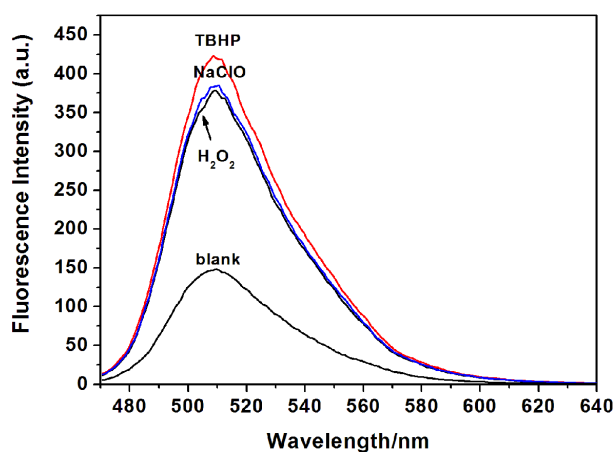


Figure S8. Fluorescence responses of **L** ($1\ \mu\text{M}$) with different oxidants.

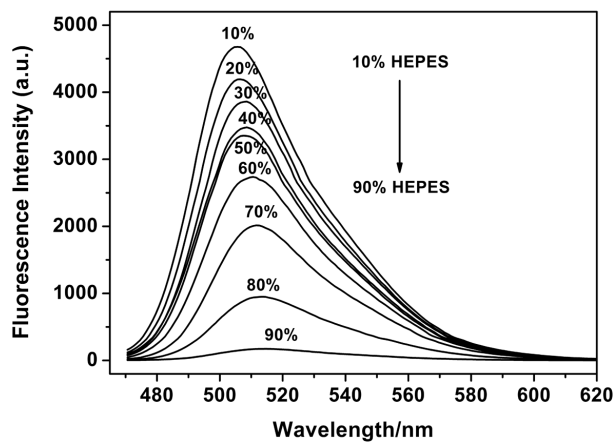


Figure S9. Fluorescence spectra as the ratio of solvent ($V_{\text{CH}_3\text{CN}}/V_{\text{HEPES}}$) was changed from 1:9 to 9:1.

