Supporting Information

A regeneratable and highly selective fluorescent probe for fast detection of sulfide in aqueous solution

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Computational details.

The ground state geometry was optimized with the density functional theory (DFT) employing unrestricted M06L functional which is considered appropriate for studying transition metal bonding.[1] The 6-31G* basis set was used for the H, C, N, O and Cl atoms; the LANL2DZ effective core potential was employed was for the Cu atom. Vibrational frequencies have been analyzed at the optimized structures to confirm that the structure correspond to the local minimal on the energy surface. The excited states calculations using the time-dependent density functional theory (TD-DFT) method with B3LYP functional at same basis set level as the geometry optimization. All theoretical calculations were carried out using the Gaussian 09 programs.[2]

[1] Y. Zhao and D. G. Truhlar, "A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions," *J. Chem. Phys.*, **125** (2006), 194101: 1-18.

[2] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A. , J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09W, Revision A.02. Gaussian, Inc.: Wallingford CT, 2009.
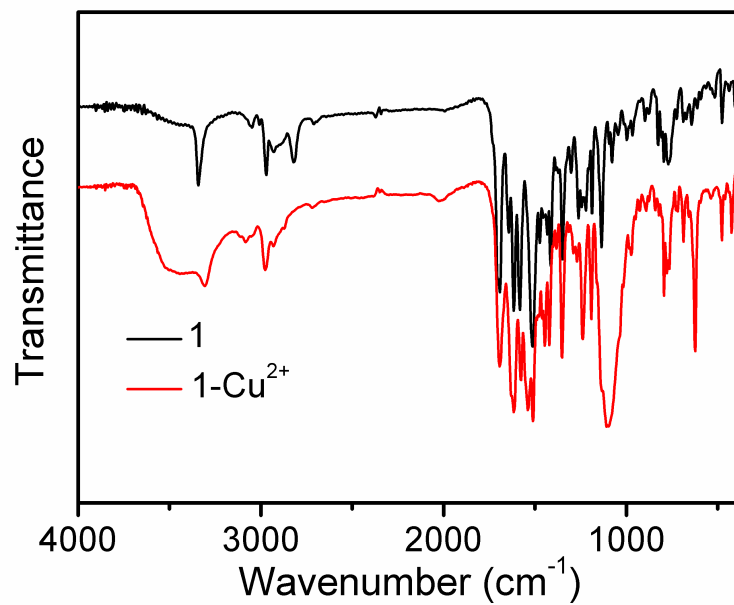
Supporting figures and tables

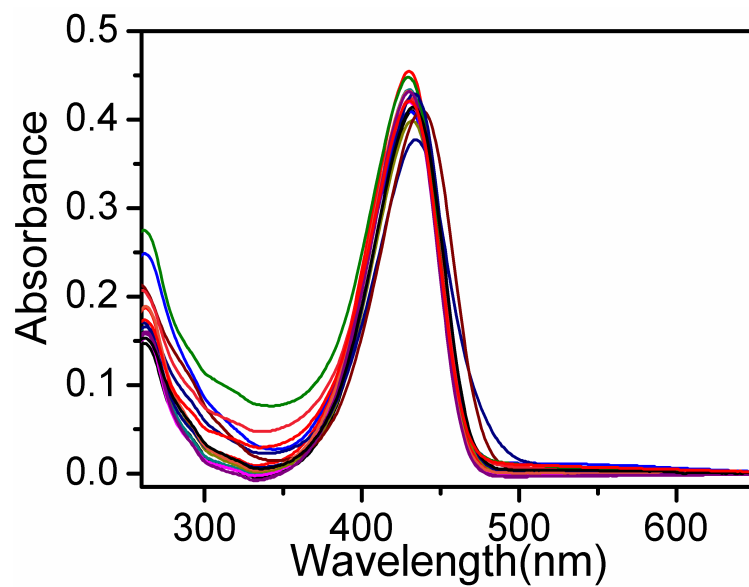**Figure S1.** IR spectra of Ligand **1** and **1-Cu^{2+}** complex.

Figure S2. UV-vis spectra of ligand **1** (10 μM) in the presence of various metal cations.
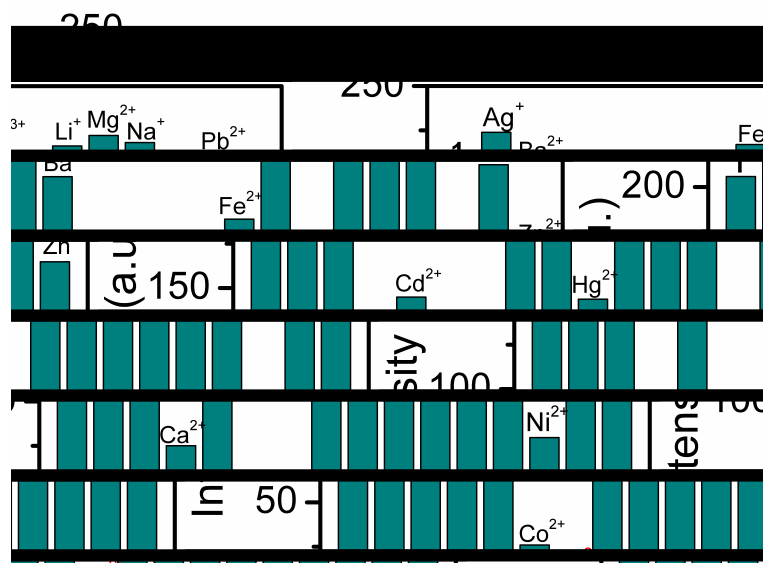
Figure S3. Fluorescence intensity changes of the **1** (10 μM) in the presence of various metal cations (2 equiv).
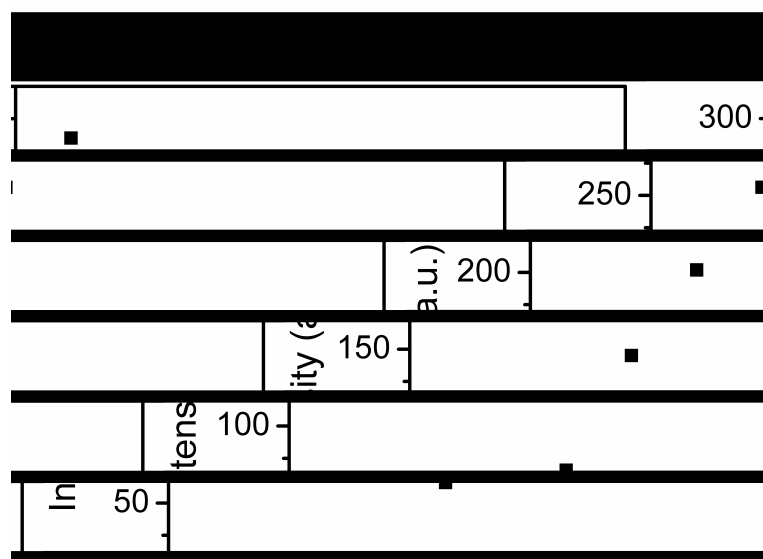
Figure S4. Job's plot of **1** with $\mathbf{Cu^{2+}}$ cations according to the method continuous variations. The fluorescent intensity was recorded at 483 nm. The total concentrations of 1 and Cu^{2+} were kept constant at 40 μM.
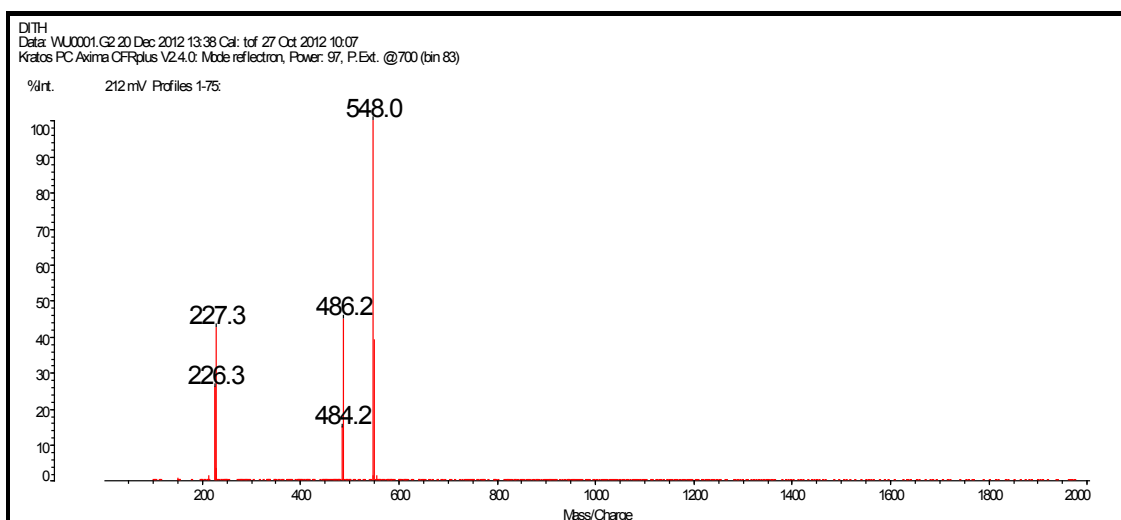
Figure S5. MALDI-TOF Mass spectrum of **1-Cu^{2+}** complex: m/z = 548 [**1+Cu^{2+}-H**]$^+$.
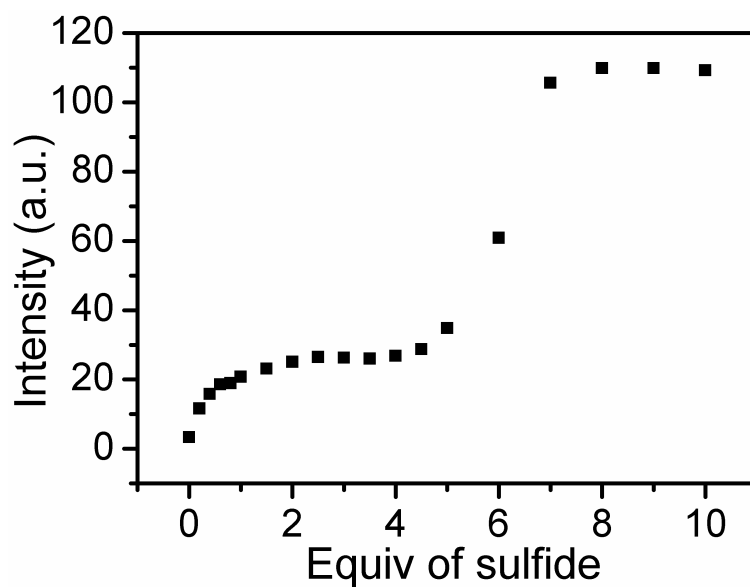
Figure S6. Fluorescence emission change of the *in situ* prepared **1-Cu^{2+}** (10 μM) vs sulfide equiv at 483 nm.
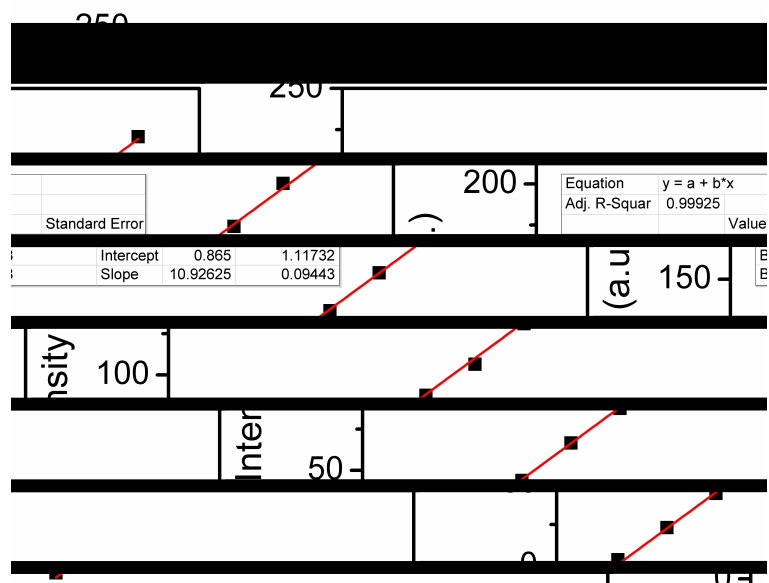
Figure S7. Fluorescence responses of **1-Cu^{2+}** (10 μM) in the presence of submicromolar level of sulfide.
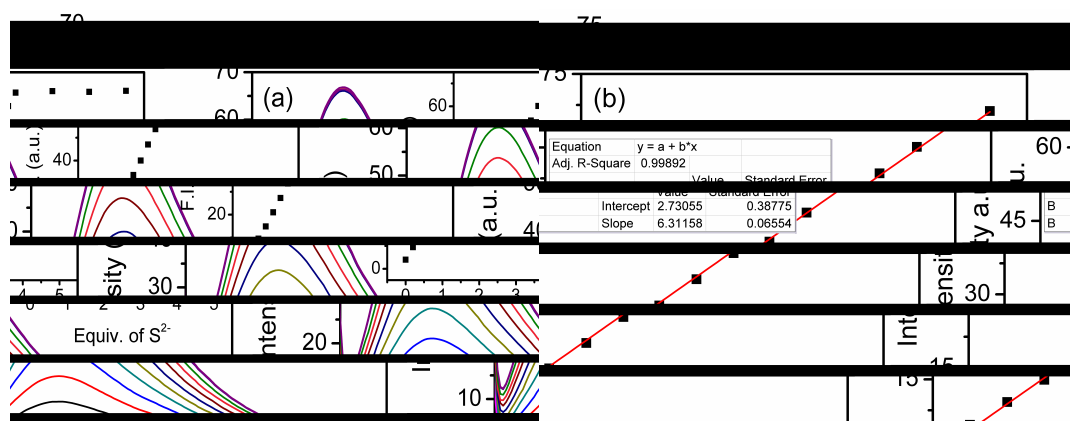

Figure S8. (a) Fluorescence titration spectra of the independently prepared **1-Cu^{2+}** (5 μM) in the presence of various concentrations of Na$_2$S (0–10 μM). Inset: Fluorescence intensity of the **1-Cu^{2+}** at 483 nm as a function of S^{2-} concentration. (b) Fluorescence responses of **1-Cu^{2+}** (5.0 μM) in the presence of submicromolar level of sulfide 1~10 μM).
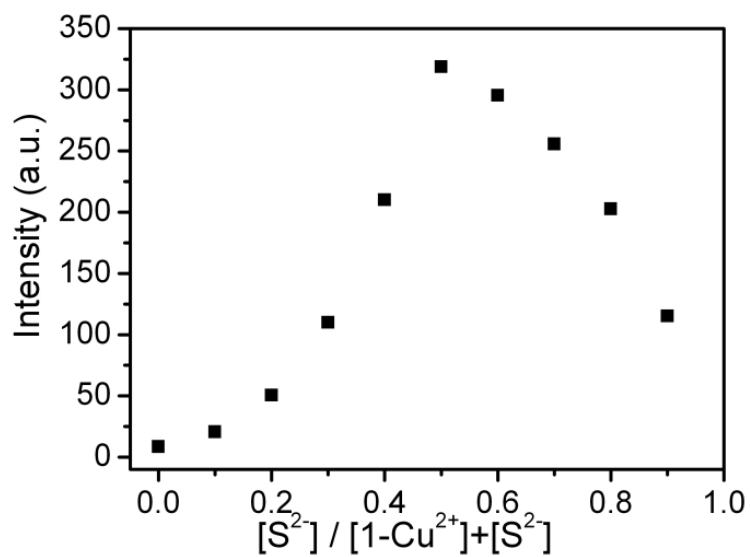
Figure S9. Job's plot of Probe **1-Cu^{2+}** with S^{2-} according to the method continuous variations. The fluorescent intensity was recorded at 483 nm. The total concentrations of **1-Cu^{2+}** and S^{2-} were kept constant at 40 μM.
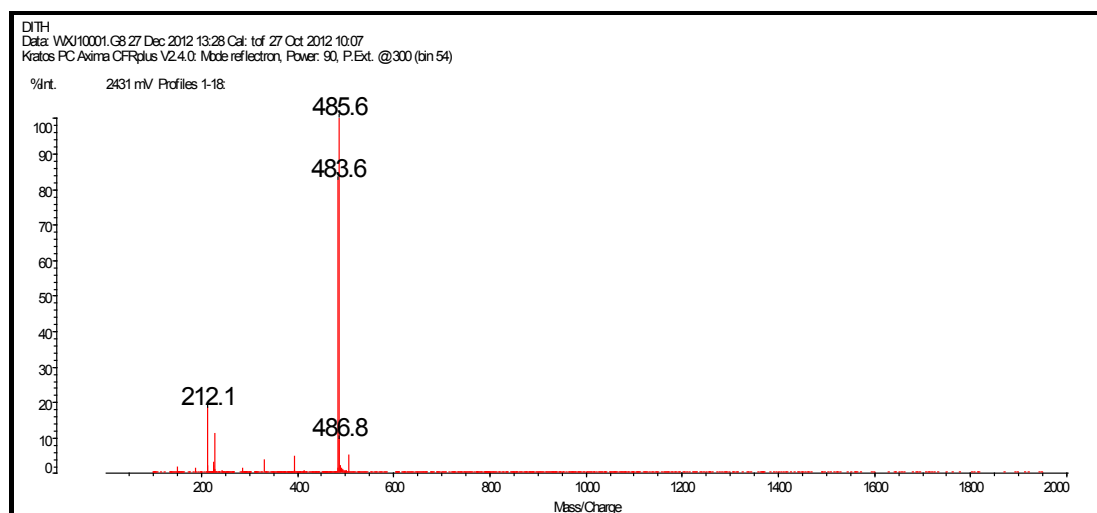

Figure S10. MALDI-TOF MS spectrum of compound **1**: m/z = 485.6[M]$^{+}$
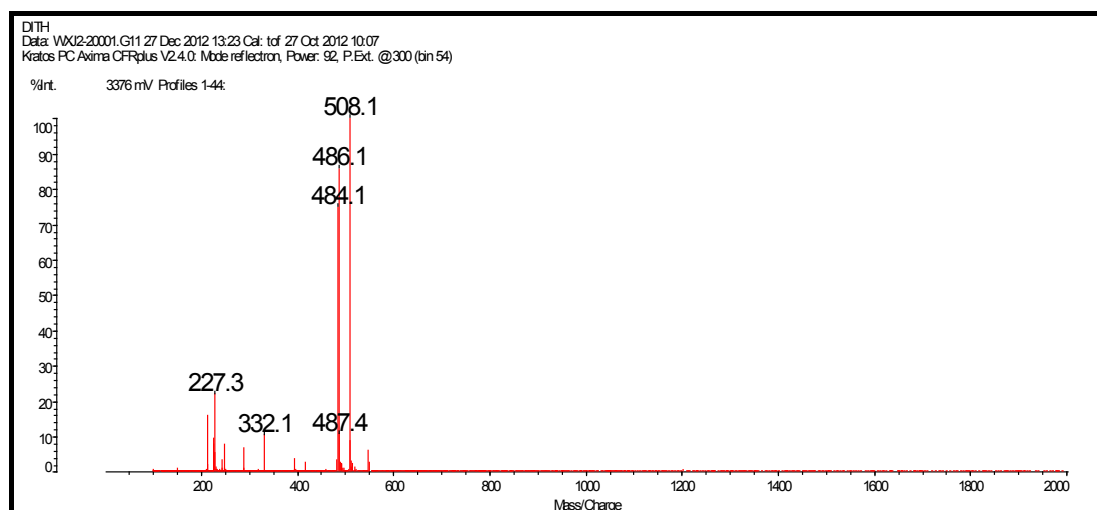
Figure S11. MALDI-TOF Mass spectrum of probe **1-Cu^{2+}** after addition of 2 equiv of sulfide anion: m/z = 508.1 [**1**+Na]$^{+}$.
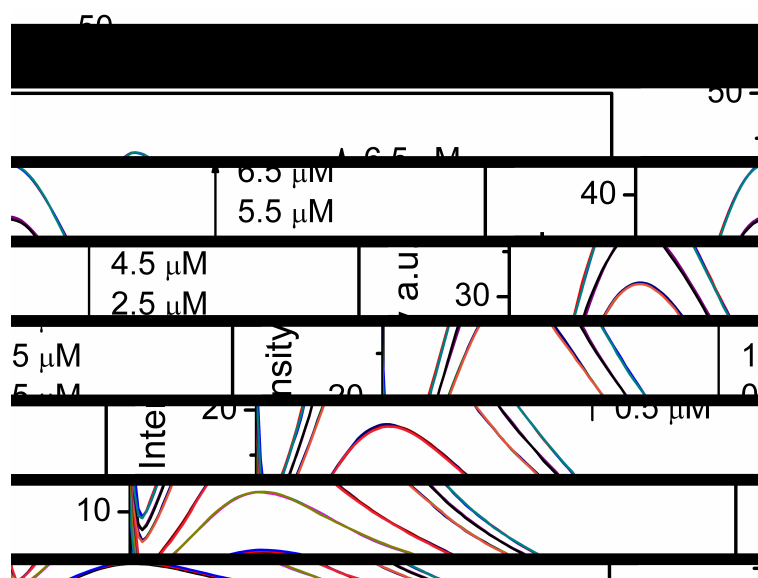

Figure S12. Detection of sulfide anions in six synthetic tap water samples using **1-Cu^{2+}** (5 μM) as a fluorescent probe (n=3).
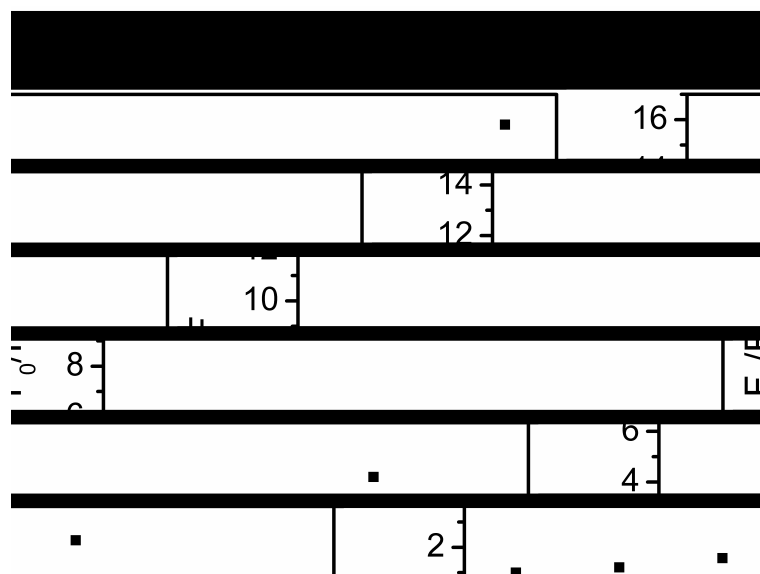
Figure S13. Stern–Volmer plots for Cu^{2+}, $[Cu^{2+}] = 0\sim10\ \mu M$.

Table S1.   Selected Bond Lengths (Å) and Bond Angles (deg) of complex **1-Cu.**

Bond Lengths (Å)	Bond Angles (deg)
Cl1-Cu1 2.2423(17)	N1-Cu1- N3 164.2
Cu1-N1 1.988(4)	N1-Cu1-N2 83.3
Cu1-N2 2.032(4)	N1-Cu1-N4 88.0
Cu1-N3 1.990(4)	N2-Cu1-N4 79.7
Cu1-N4 2.660(4)	N3-Cu1-N2 81.9
	N3-Cu1-N4 94.8
	N1-Cu1-Cl1 97.6
	N3-Cu1-Cl1 97.1
	N2-Cu1-Cl1 179.0
	N4-Cu1-Cl1 100.7

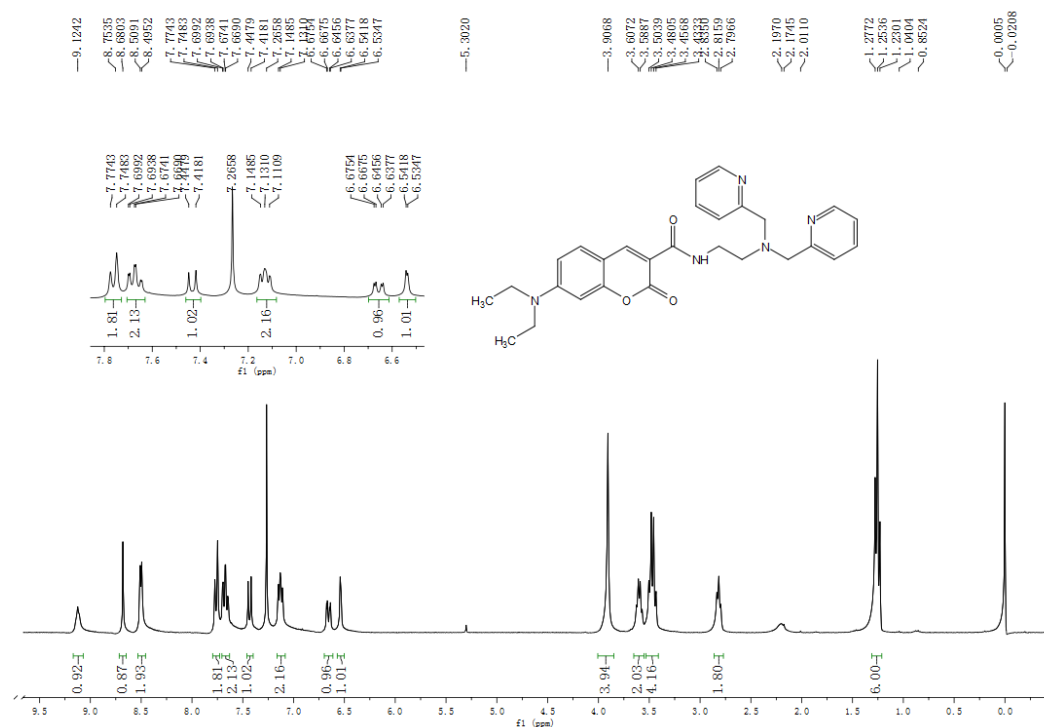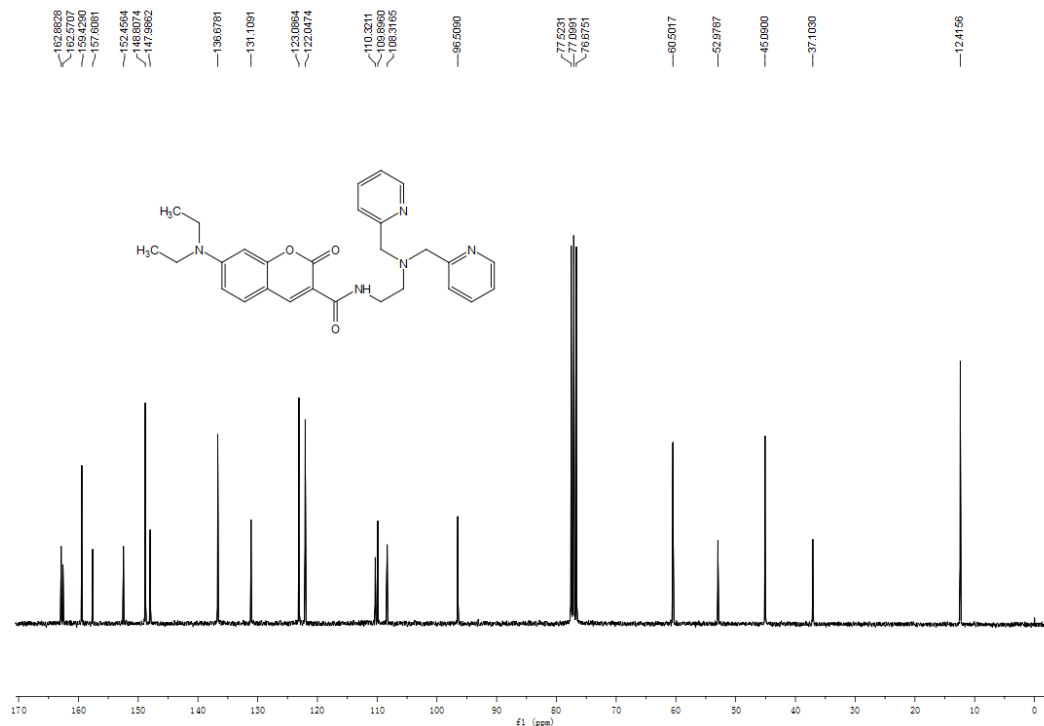# Characterization

Figure S14. ^{1}H NMR spectrum of compound **1** in CDCl$_3$

Figure S15. ^{13}C NMR spectrum of compound **1** in CDCl$_3$