Supporting Information

H^+–Assisted fluorescent differentiation of Cu^+ and Cu^{2+}: Effect of Al^{3+}–induced acidity on chemical sensing and generation of two novel and independent logic gating pathways

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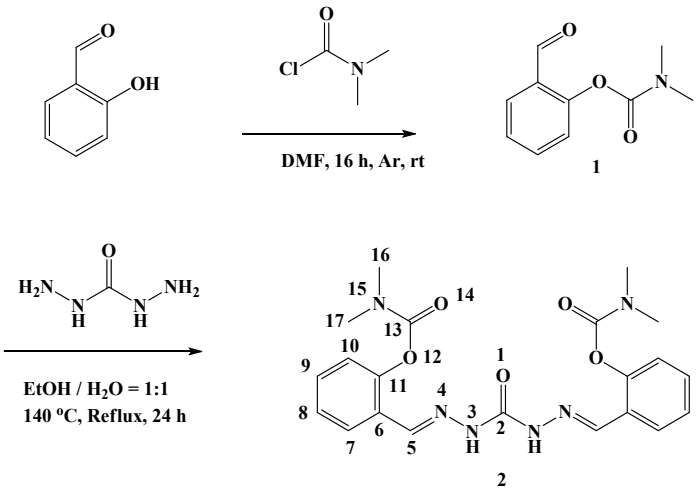
Experimental



Experimental Details

General remarks: All reagents used were purchased from commercial sources, like Sigma Aldrich, Junsei, TCI Companies without additional purification. For ^{1}H NMR and ^{13}C NMR spectroscopy, a Bruker Advance 400 MHz spectrometer was used. UV–visible analysis was performed with a Jasco V–530. Fluorescence was analyzed by RF–5301 pc Shimadzu Spectrophotometer. For checking molecular weight, a HR–LC/MS/MS (Bruker Daltonik, micro–TOF–Q model, Germany) was used.

Synthesis of Compound 1: Compound **1**, a known intermediate, was synthesized previously.[1] Specifically, dimethylcarbamoyl chloride (3.52 g, 32.8 mmol) was added into a salicylaldehyde (2.00 g, 16.4 mmol) in an anhydrous DMF solution (15 mL) in the presence of 1,4–diazabicyclo[2.2.2]octane (DABCO) (3.67 g, 32.8 mmol) and was stirred under argon for 16 h. H_2O (100 mL) was added so as to quench the reaction. The reaction mixture was stored at 4 °C for 3 h. The solution was extracted with ethyl acetate three times. The organic solvent portion was finally dried with anhydrous sodium sulfate, filtered and vacuum–dried to afford a pale yellow oil of **1**.

Synthesis of Compound 2: We followed the known procedure for **2**.[2, 3] **1** (2.00 g, 10.4 mmol) was dissolved in 15 mL EtOH. Carbohydrazide (0.466 g, 5.17 mmol) was dissolved in H_2O (15 mL). They were mixed together and refluxed at 140 °C for 24 h. After this time, the mixture was determined to have fully converted from the starting materials to the product etc.; the solution was then cooled to room temperature. A white powder was then precipitated upon

cooling and condensation of the solution, filtered and washed with EtOH and dried at room temperature to give **2** (1.4 g, 61 % yield). ^{1}H–NMR spectrum (400 MHz, DMSO) δ 10.8 (s, 2H, H_3), 8.25 (br, 2H, H_5), 8.03 (br, 2H, H_7), 7.40 – 7.35 (m, aromatic ring, 2H), 7.30 – 7.24 (m, aromatic ring, 2H), 7.14 – 7.11 (m, aromatic ring, 2H), 3.31 (s, 6H, H_{16}), 2.92 (s, 6H, H_{17}), ^{13}C–NMR (100 MHz, DMSO) δ 154.3 (C_2), 152.3 (C_{13}), 150.1 (C_{11}), 138.1 (C_6), 130.5 (C_5), 127.7 (C_{10}), 126.5 (C_7), 126.0 (C_9), 123.9 (C_8), 36.9 ($C_{16–17}$). HR–LC/MS/MS: calcd for $C_{21}H_{24}N_6O_5$ + Na: 463.1706, found: *m/z*, 463.1665 $(M + Na)^+$ (See Figures S1 – S4 for more clarification).

HR–LC/MS: The molecular mass of the probe was analyzed through High Resolution Mass spectrometry (HR–LC/MS, Bruker Daltonik instrument, micro–TOF–Q model, Germany). The ion source type was ESI, in which the ion polarity was in the positive mode, the nebulizer was 0.4 Bar, the capillary was 4,500 V, the dry Heater was set to 180 °C, the scan limit = 50 m/z, the End Plate Offset = –500 V, using a Dry Gas, at 4.0 L/min, with a Collision Cell RF of 250.0 Vpp, where the solvent was methanol.

UV–visible absorbance or Fluorescence measurements: UV–visible absorbance was measured with a *Jasco V–530* instrument. After a baseline correction with acetonitrile, each sample was analyzed through a wavelength range of 200 – 1100 nm. The fluorescence was measured with a Shimadzu fluorescence spectroscopy (RF–5301PC model). Both slit widths of excitation (EX) and emission (EM) were usually set as 5 nm. The quartz cuvette was used for both UV–visible and fluorescence analysis (cell path, 10 mm). The concentration of the probe was fixed at 10 μM in this study. The probe was dissolved in DMSO (5 mM) as a stock solution and subsequently diluted in acetonitrile (10 μM, 1.0 equiv). Solutions of 16 different metals (Ag^+, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Pb^{2+}, Zn^{2+} as their perchlorate salts, Cu^+ as an acetate salt, Al^{3+} as a chloride salt) were prepared in H_2O at 0.1 M were added into the probe solution. The final concentration of the metal ion was 100 μM (10 equiv) in acetonitrile. After 40 minutes of reaction time, UV–visible absorbance and fluorescence were analyzed. In particular, Cu^+, Co^{2+}, Fe^{2+} and Mn^{2+} solutions were prepared just before the reaction and used directly (less than 1 min) for the purpose of analyte screening or sensing to minimize its transformation into other oxidation states.

DFT calculations: Molecular structures and HOMO–LUMO were estimated using density functional theory (DFT) calculations using the Gausian 09 program. The B3LYP method with a 6–31g* basis set was used in which the 6–311g* basis set was used for Cu only. All calculations were performed in the gas phase.

Electron paramagnetic resonance (EPR) analysis: X–band CW–EPR (Bruker) was used for the detection and confirmation of spin multiplicity of Cu^+, Cu^{2+}, and Al^{3+}. Detection conditions were as follows: temperature = 20 K, microwave power = 0.92 mW, microwave frequency =

9.64 GHz, modulation frequency = 100 KHz, modulation Amp = 10 G. The source of Cu^{2+}, Cu^{+}, and Al^{3+} were $CuCl_2 \cdot 2H_2O$ (Sigma Aldrich), $CuCH_3COO$ (Sigma Aldrich), $AlCl_3$ (Sigma Aldrich). Cu^{+} solution was prepared and used immediately with a wait time of less than 1 min.

Measurement of Cu^{+} Lifetime under inert conditions via fluorescence: All solvents, acetonitrile and water, were purged with nitrogen gas (over 99.99 % purity) for 30 min before insertion into the Glove box (Korea Kiyon company, KK–01–AS model) to remove dissolved oxygen. During the manipulation of the sample into a Glove box, all materials and equipment containing pipettes, tips, and vials, etc, were placed under vacuum for 10 minutes and purged with argon (99.99 %), three times, to remove oxygen and moisture. In the glove box, Cu^{+} stock solution (100 mM) was prepared with pure H_2O and Cu(I)acetate (Sigma Aldrich). After preparing a Cu^{+} stock solution, $[Cu^{+}]$ from the Cu^{+} stock solution underwent reaction/coordination with compound **3** at various times. Time trials were taken for every 5 min over a 60 min period (total 13 samples) within the glove box. Then, each sample was taken out from the Glove box for measurement. Incubation time was 40 min; emission intensity was checked directly.

Cyclic voltammetry (CV): This experiment was carried out by using CHI 900B Potentiostat and employed Glassy carbon electrode (3 mm) as a working electrode, Pt wire as counter electrode and Ag/Ag^{+} non aqueous electrode as reference electrode. The supporting material is 0.1 M tetrabutylammonium perchlorate (TBAP) (Sigma Aldrich) in DMSO (Sigma Aldrich). The metal complex (Cu^{2+}-LH) was prepared by mixing copper(I) acetate(Sigma Aldrich) in DMSO and fluorescence probe ligand(LH) in DMSO. The metal complex was incubated in the electrochemical cell for more than 15 min. All CV measurements were performed under 50 mV/S scan rate and 0 s quiet time.

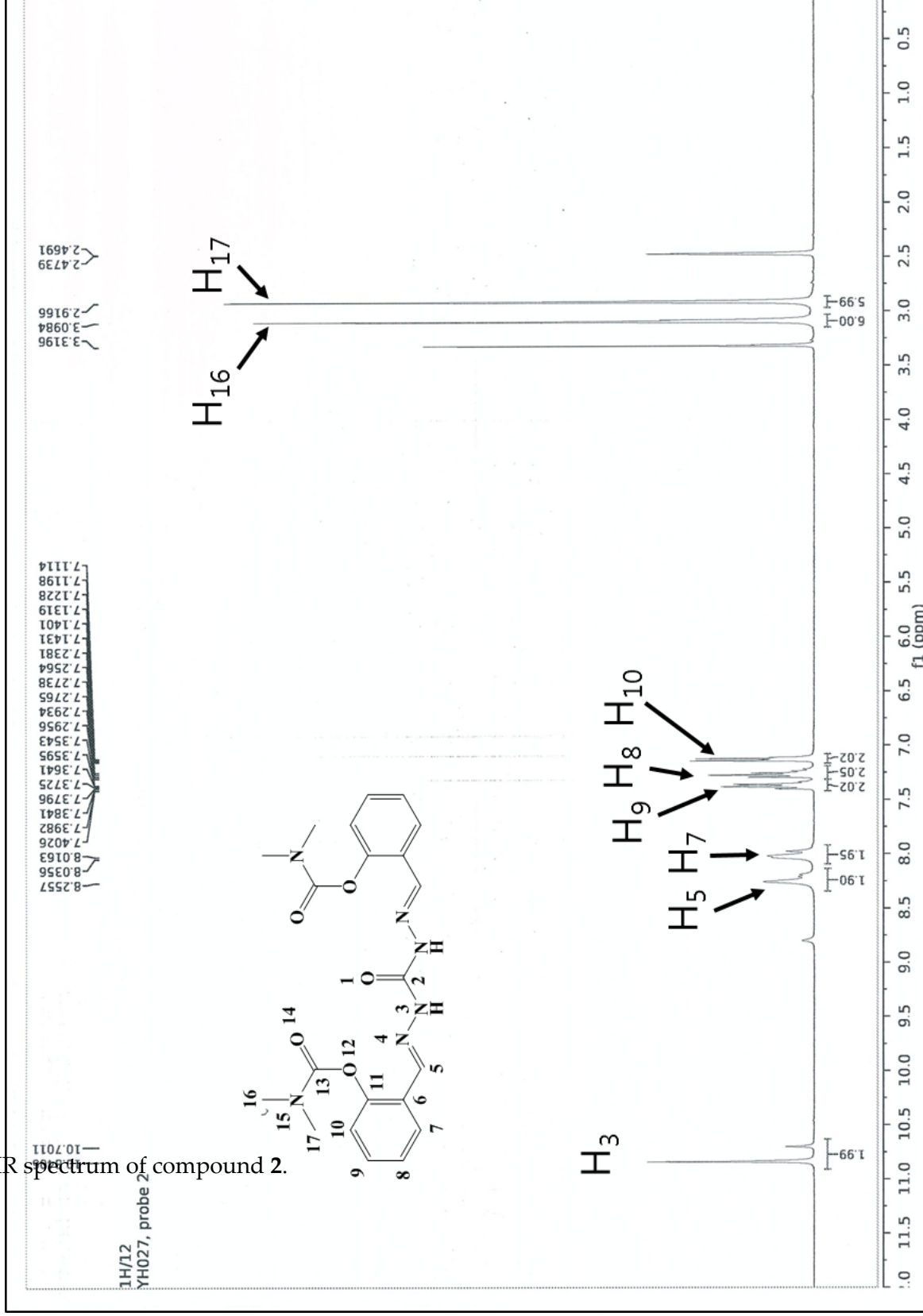


Figure S1. [1]H-NMR spectrum of compound **2**.

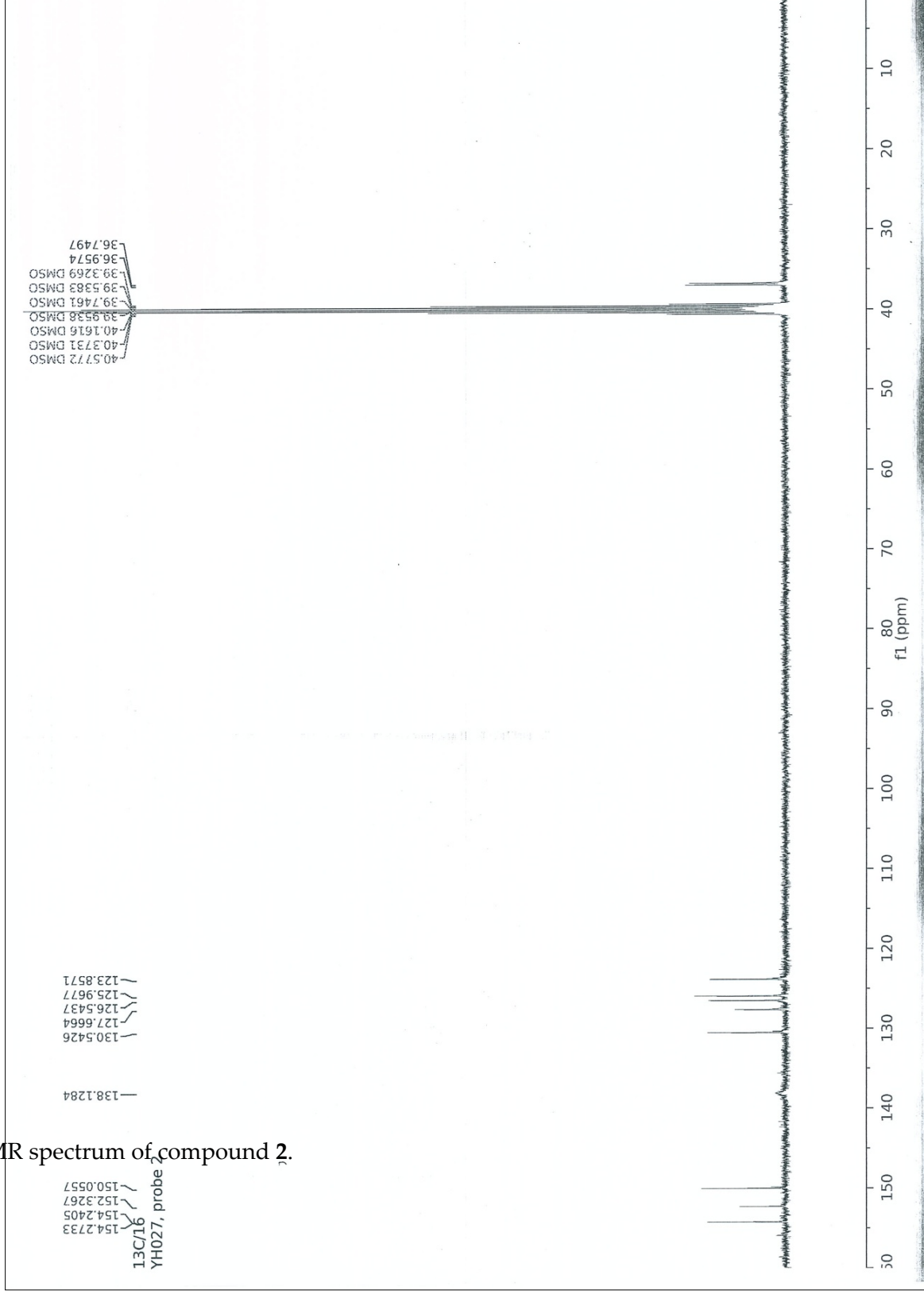
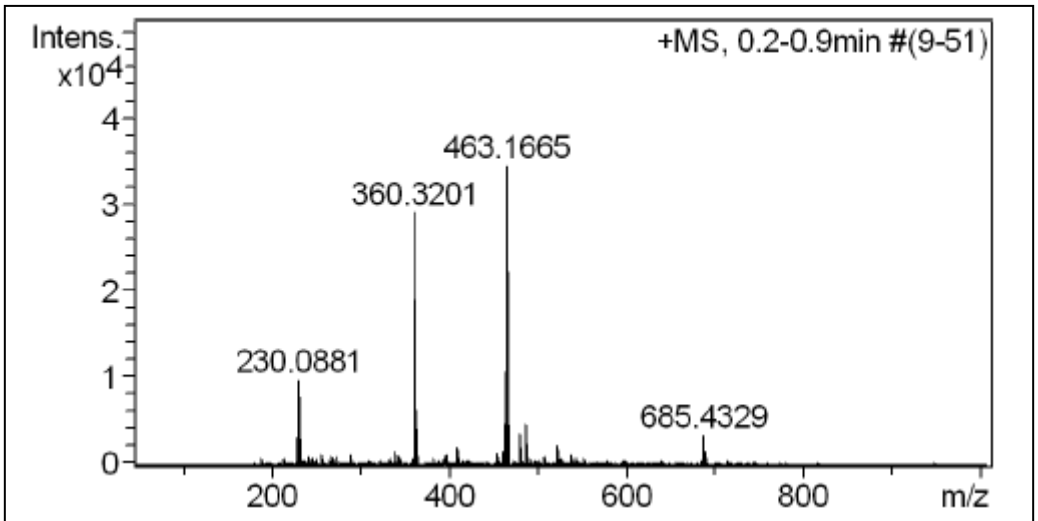


Figure S2. ^{13}C-NMR spectrum of compound **2**.



#	m/z	I
1	227.6516	2956
2	230.0881	9734
3	360.3201	28974
4	361.3236	6359
5	463.1665	34489
6	464.1692	7294
7	479.1359	3424
8	485.1491	4675
9	521.1828	2201
10	685.4329	3309

Figure S3. HR-LC/MS result of compound **2**. Product peak = 463.1665 $(M + Na)^+$

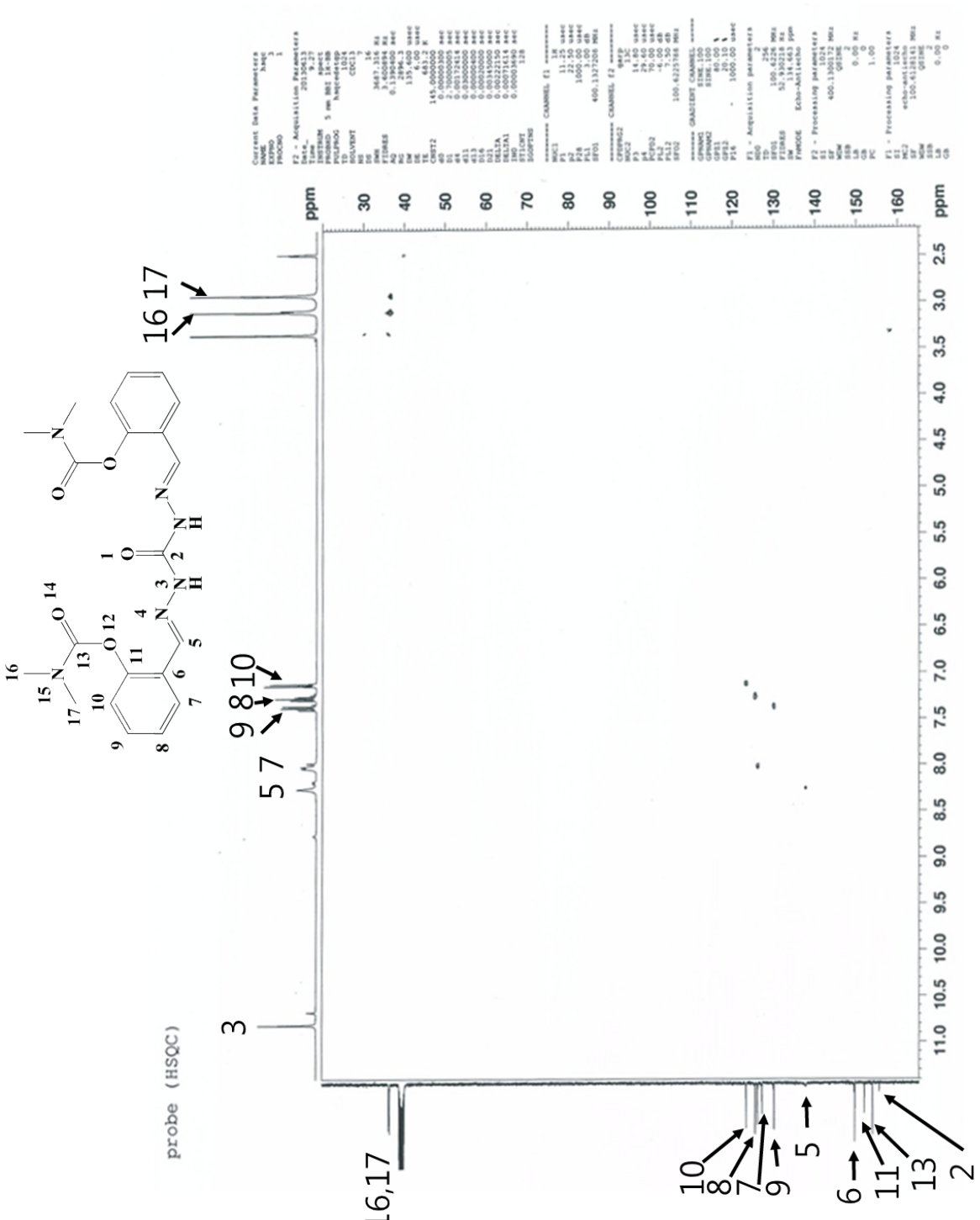


Figure S4. ^{1}H-^{1}H HSQC-NMR spectroscopic result (solvent – DMSO-d_6) of compound **2**.

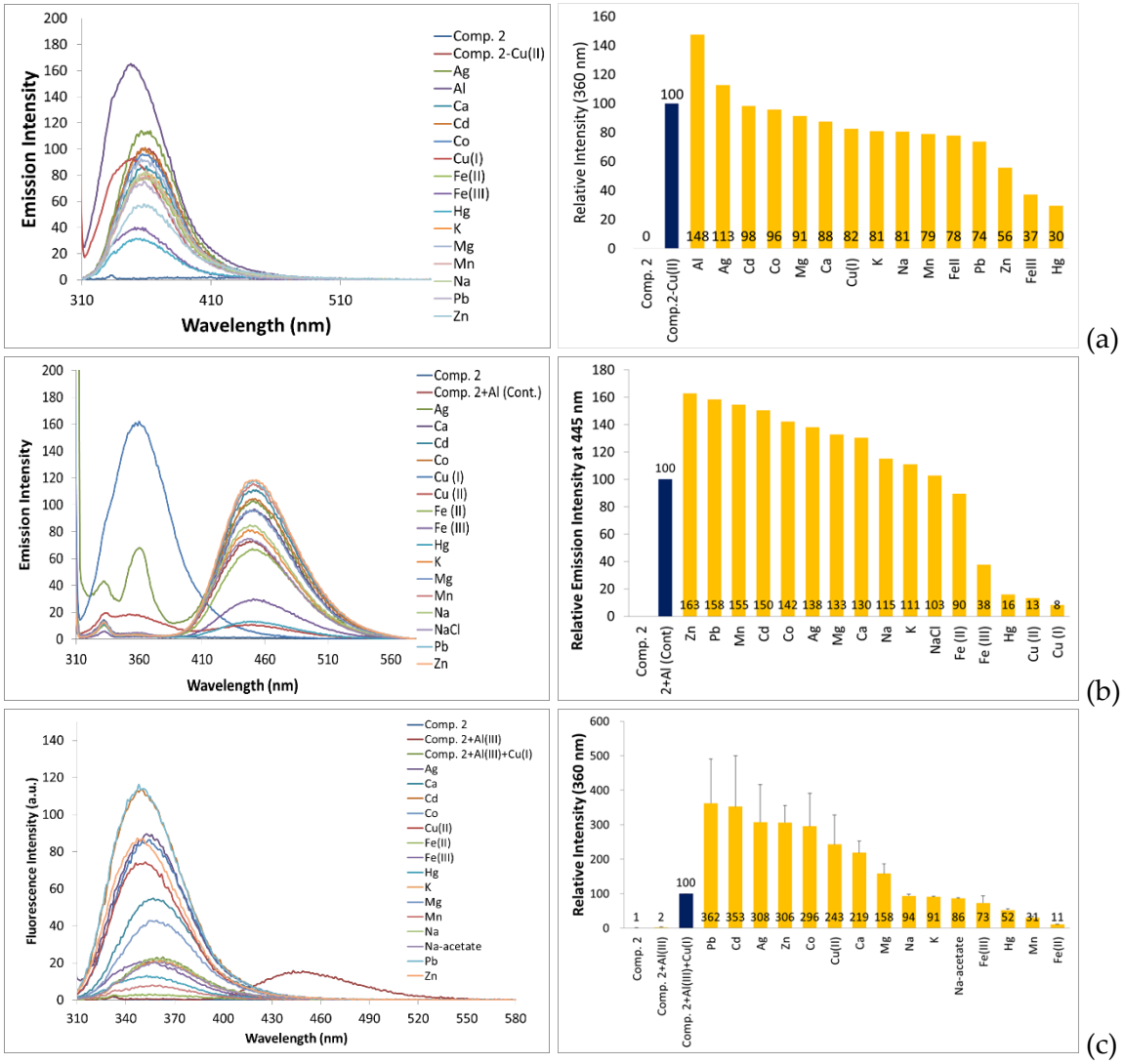


Figure S5. Emission spectrum and relative fluorescence emission intensity of **2** within interference experiments with Cu^{2+} or Al^{3+} against other metal ions. Emission spectra and relative emission intensities of the probe with other metal ions in the presence of Cu^{2+} (a), Al^{3+} (b), or Cu^{+}/Al^{3+} (c). Error bars indicate standard deviation. Experiments were repeated 3 times. Solvent: acetonitrile, λ_{ex} = 300 nm, Slit width (EX: 5 nm, EM: 5 nm).

Note: Sensing of Cu^{2+} with **2** was found to be slightly in competition with Hg^{2+} and Fe^{3+}. When the Al^{3+}-based emission signal was measured for the interference with other 15 metal ions, Cu^{+}, Cu^{2+} Fe^{3+}, and Hg^{2+} revealed quenching effects, respectively, implying that the Al^{3+} probing has some limitations in selectivity with the presence of these particular metal ions. Cu^{+} showed a 17 % quenching effect on the **2** + Cu^{2+} emission. However, Al^{3+} + Cu^{+} was activated by Cu^{2+},

meaning that Cu^{+} binding with the ligand in the presence Al^{3+} is strong and Cu^{2+} cannot displace Cu^{+}.

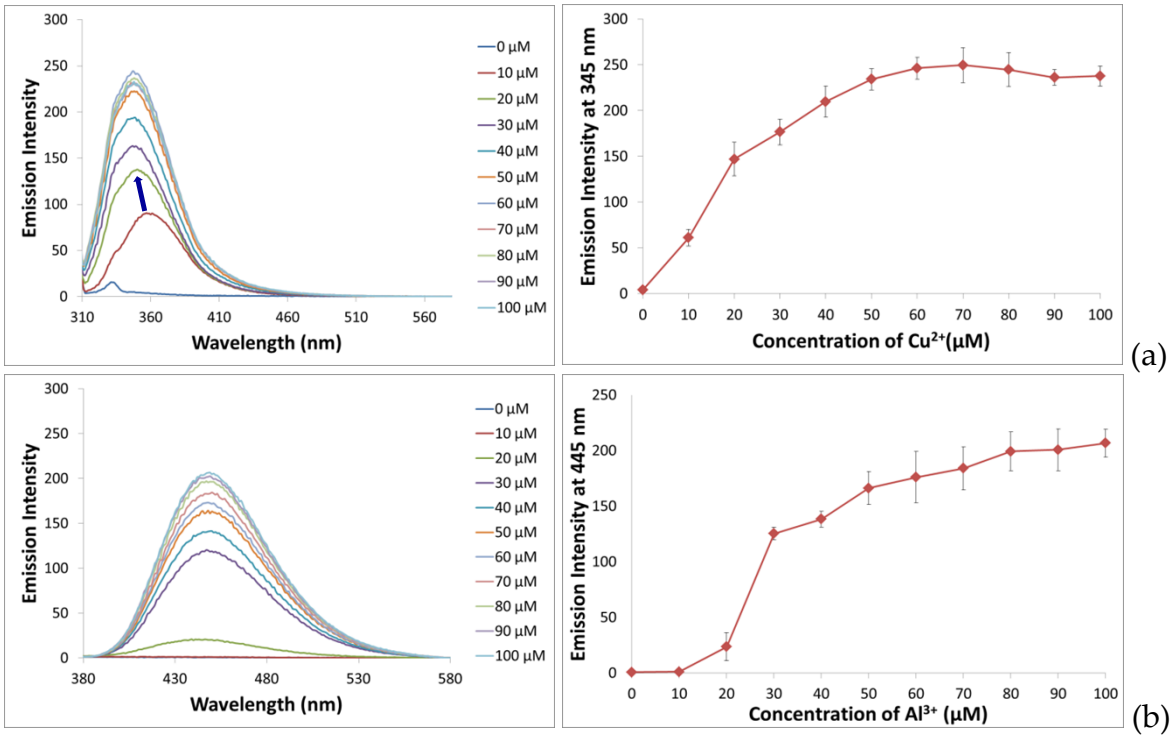
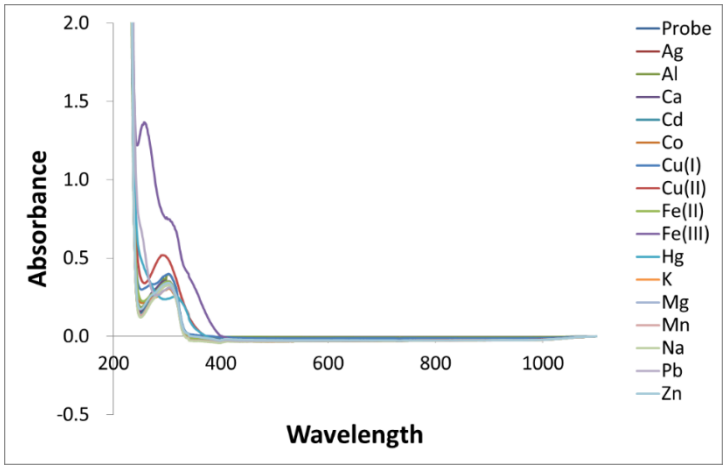
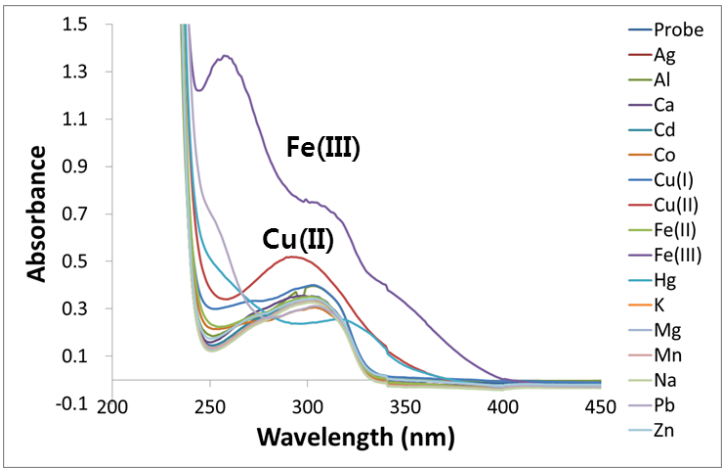


Figure S6. (a) Emission spectrum of **2** (10 μM, 1 equiv) via the titration (1 – 10 equiv) of Cu^{2+} and emission intensity at 345 nm. Blue shift, ~ 15 nm (blue arrow), (b) Emission spectrum of **2** (10 μM, 1 equiv) by the titration of Al^{3+} and emission intensity at 445 nm. λ_{ex} = 300 nm, Slit width (EM: 5 nm, EX: 5 nm). Solvent: acetonitrile.

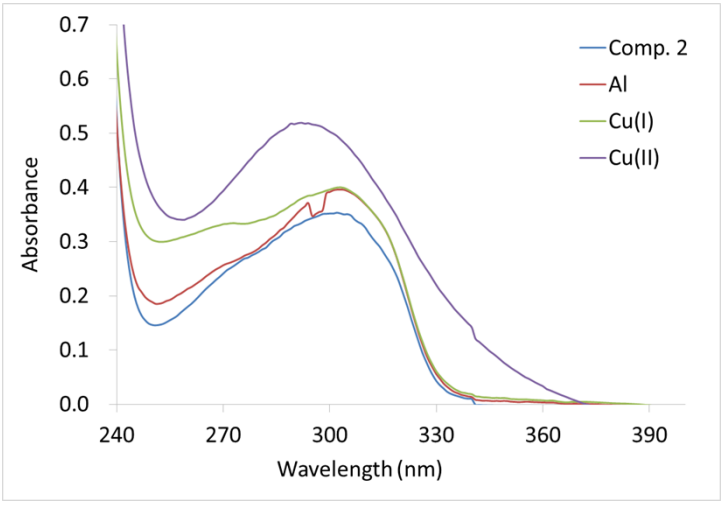
Note: In fluorescence titrations, when Cu^{2+} was titrated into **2**, a blue shift near 15 nm was observed from 360 nm to 345 nm. This phenomenon may arise from *intramolecular charge transfer* (ICT) in which a secondary copper ion is ionophore–bound [**2**·2Cu^{2+}**]**. When the second copper ion binds, the structure of the molecule may change to induce torsional strain which will change the orbital distribution and energy level to induce an emission shift. During aluminum titration, the emission intensity increased at 445 nm without a concomitant shift in wavelength shifting. Interestingly, a large fluorescence increase was shown between 2 and 3 equiv, implying a critical ratio for the interaction by Al^{3+} to the probe to be at least 3 equiv. Al^{3+} titration showed a sigmoidal curve which implies a complication of factors where at least two equiv of Al^{3+} are necessary for fluorescence enhancement.



(a)

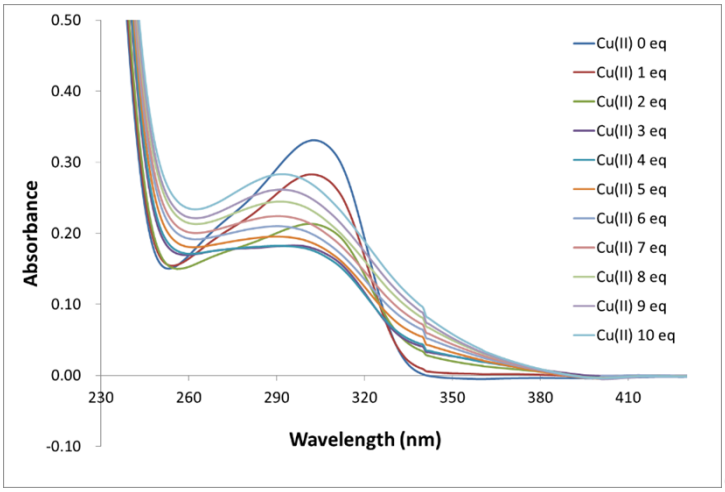


(b)

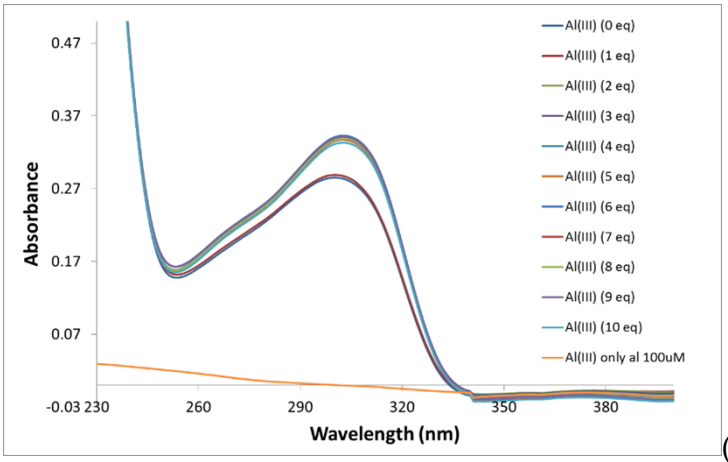


(c)

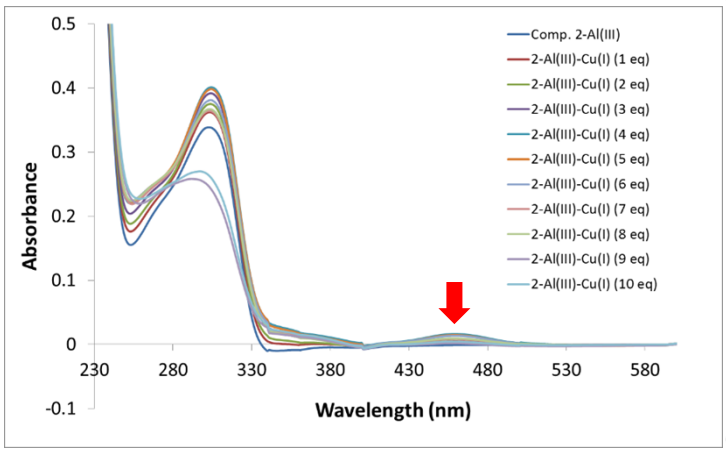
Figure S7. UV-visible absorbance in the region of (a) 200 nm – 1100 nm, (b) 200 nm – 450 nm for the probe (Comp. **2)** with 16 metal ions; (c) same as (b) but spectra for only **2**, Cu^{+}, Cu^{2+} and Al^{3+} spectra are shown. Solvent: acetonitrile.



(a)



(b)



(c)

Figure S8. UV titration of Cu^{2+} (a), Al^{3+} (b), and Cu^{+} (c) with Comp. **2**. Solvent: acetonitrile.

Note: There were no isosbestic points found in the UV titration experiments of Cu^{2+}, Al^{3+}, Cu^{+}, which imply binding ratios are not 1: 1, but rather multi-binding modes. A new long wavelength peak at 460 nm (c, red arrow) was shown, which implies the strong binding between the ligand and Cu^{+}.

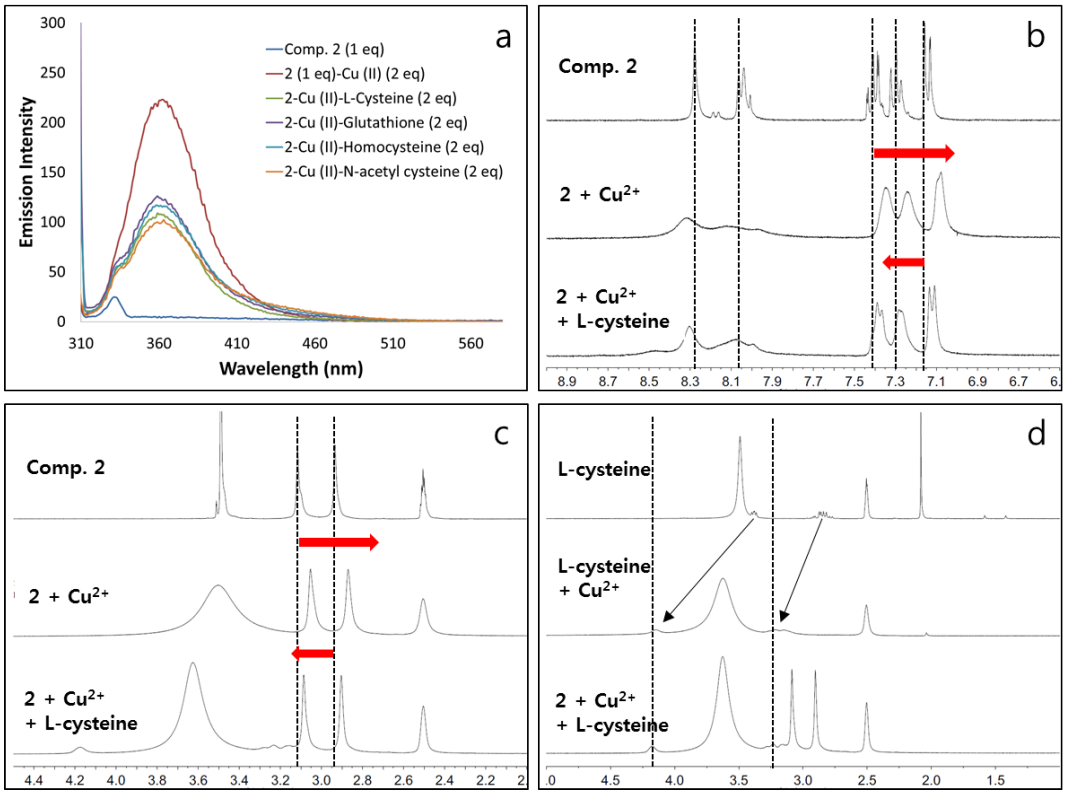


Figure S9. (a) Partial reversibility of **2** (1 equiv) induced by four kinds of biothiols monitored by fluorescence measurements, (b) ^{1}H–NMR verification on reversibility **2**, **2** with Cu^{2+} ions (2 equiv), and **2** with Cu^{2+} and L–cysteine in the region of 6.5 ppm ~ 9.0 ppm, (c) ^{1}H–NMR at the region of 2.0 ppm ~ 4.5 ppm, (d) *L*–cysteine, *L*–cysteine with Cu^{2+} ions (2 equiv), and **2** with Cu^{2+} and L–cysteine at the region of 1.0 ppm ~ 5.0 ppm. Fluorescence (λ_{ex} = 300 nm, slit width: EX: 5 nm, EM: 5 nm, solvent: acetonitrile), NMR Solvent: DMSO–d_6.

Note: Analyte binding reversibility is vital in contemporary metal ion sensing applications and requires an external substrate with greater binding power than the receptor. Several previous studies showed that there are strong interactions between metal ions and thiols (–*SH*).[4-6] Reversibility of probing of Cu^{2+} was thus expected to be effected in the presence of biological thiols (*L*–cysteine, Glutathione, Homocysteine, *N*–acetyl cysteine). '*ON–OFF*' fluorescence was exhibited, which may arise from the interactions among thiol, probe and Cu^{2+}. However, the fluorescence '*turn–OFF*' was not complete. More specifically, reversibility

by various biological thiol compounds was inspected through ^{1}H–NMR spectroscopy. Comparison of emission intensity between **2**, **2** + Cu^{2+}, and **2** + Cu^{2+} + *L*–cysteine was achieved.

For these three cases, the proton signal number and integration matched well, suggesting the probe functionalities were not cleaved or lost during reversibility testing. When the copper ions were added, protons based in the aromatic region (7.11 – 8.06 ppm) and Schiff base region (8.28 ppm) became broad, likely arising not from fluxionality, but from a paramagnetic effect expected from the presence of Cu^{2+}. Small peak shifting (more up–field, 0.06 ppm different from that for the probe) was evident for the *N*–dimethyl region. When *L*–cysteine was added into the solution of the probe with Cu^{2+}, shifting in the *reverse* direction was shown (0.03 ppm, downfield); splitting was shown again in the aromatic region (7.11–7.41 ppm). In addition, peaks from *L*–cysteine in the presence of **2** and Cu^{2+} ions matched well with *L*–cysteine in the presence of Cu^{2+}, which means *L*–cysteine may undergo reaction with Cu^{2+} and block, or help detach, one Cu^{2+} ion from binding to the ligand.

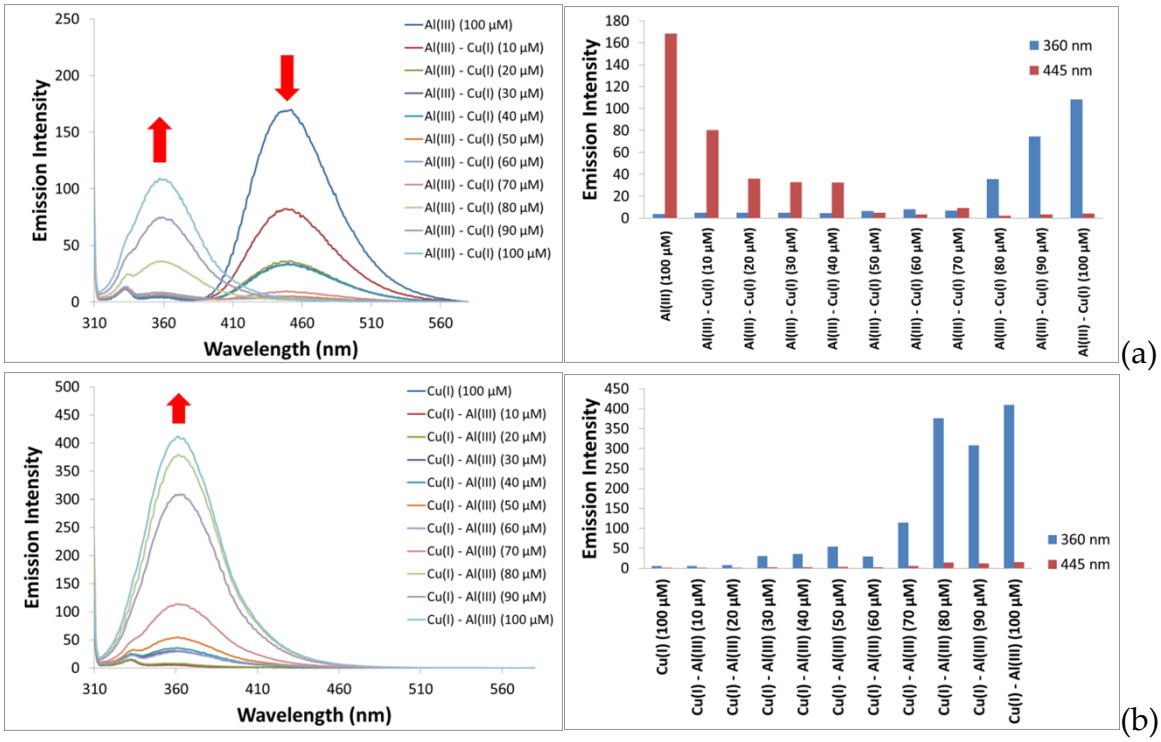
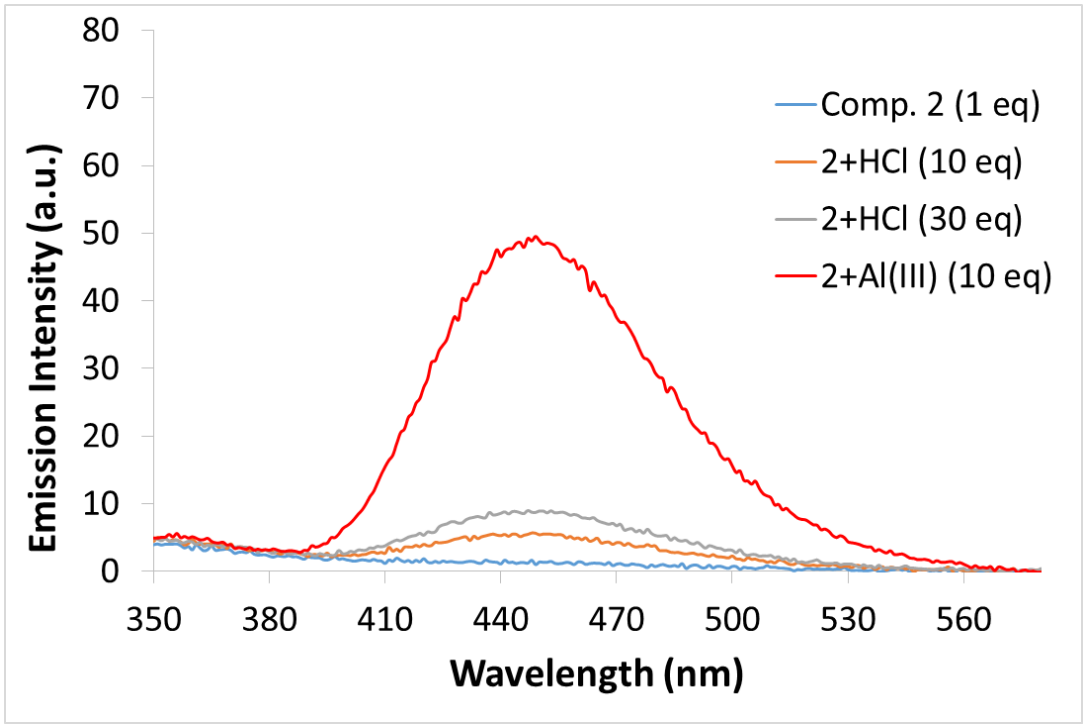
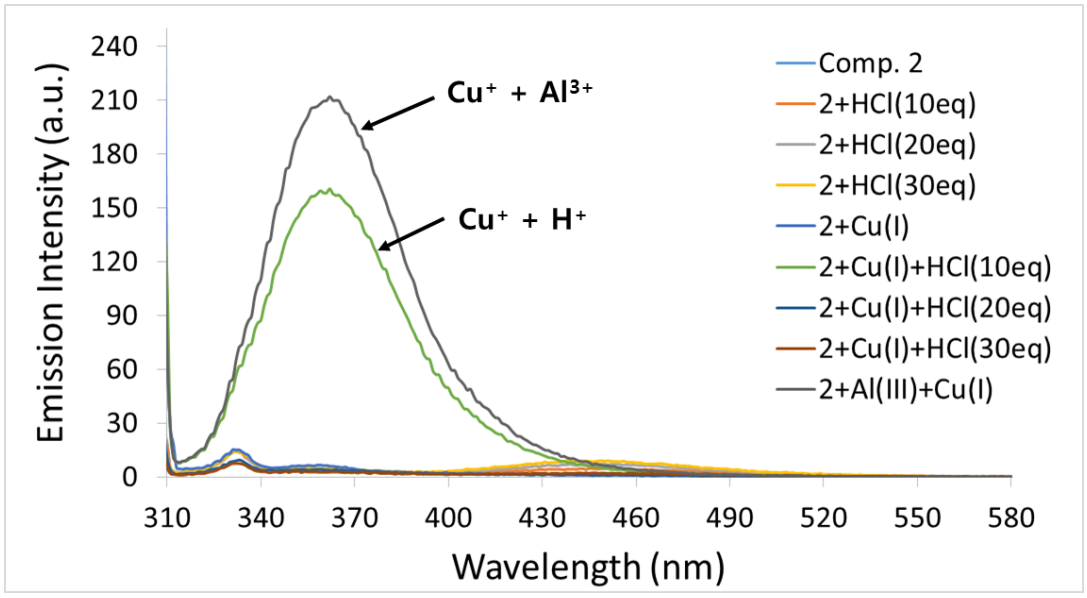


Figure S10. Data reflecting Al^{3+}–assisted Cu^{+} fluorescence "turn–ON" for the probe system. (a) Titration of Cu^{+} to the probe in the presence of Al^{3+}; (b) Titration of Al^{3+} to the probe in the presence of Cu^{+}. Excitation: 300 nm, Slit width (EX: 5 nm, EM: 5 nm), Solvent: acetonitrile.

Note: Two types of titrations were performed; Cu^{+} titration in the presence of Al^{3+}, and Al^{3+} titration in the presence of Cu^{+}. Interestingly, both cases showed fluorescence "*turn–ON*" signaling at ~360 nm, suggesting Cu^{+} undergoes a "*turn–ON*" event regardless of the insertion order. When Cu^{+} was titrated in the presence of Al^{3+}, Cu^{+} fluorescence "turned–ON" at ~360 nm after first demonstrating a "*turning–OFF*" of the signal which arose from Al^{3+} at ~445 nm. On the other hand, an Al^{3+} titration in the presence of Cu^{+} showed a rising fluorescence "*turn–ON*" at 360 nm which is the same wavelength as that found at low concentrations of Cu^{2+} without emission at 445 nm. As a result, a Cu^{+} fluorescence signal was not perturbed by Al^{3+} addition, which strongly suggests that Cu^{+} affinity with the ligand is stronger than Al^{3+}.

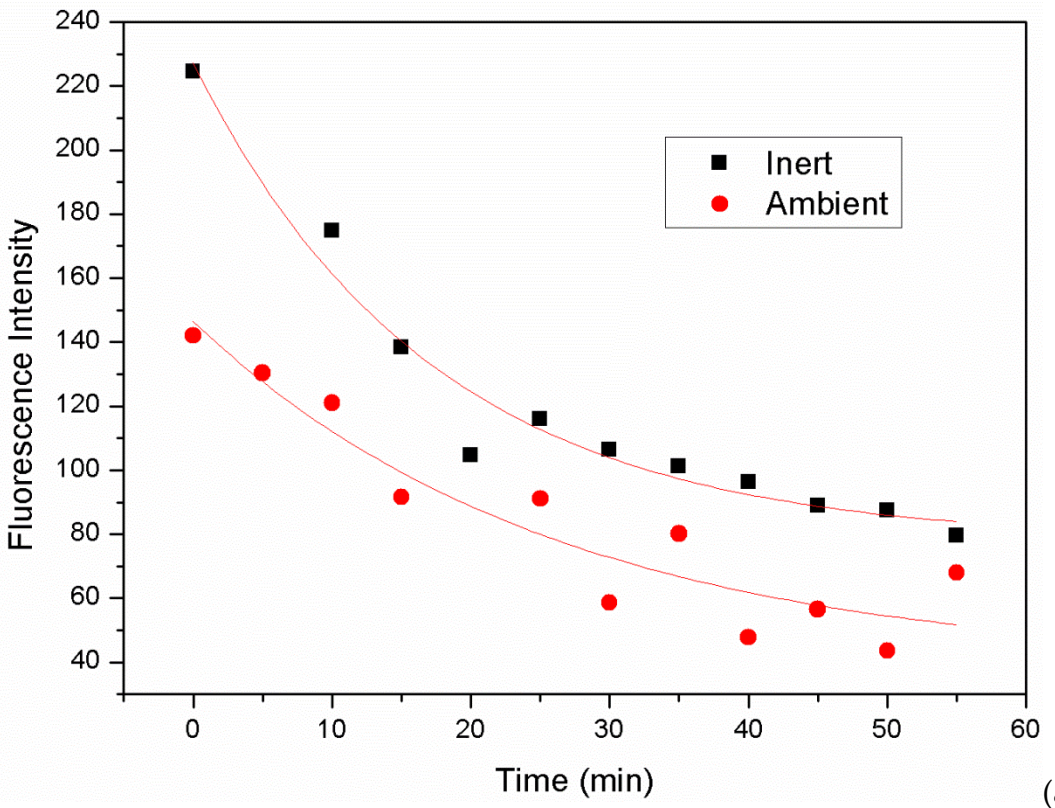


(a)



(b)

Figure S11. Effect of H^+ or OH^- on the fluorescence of Comp. **2** with Al^+ (a), and with Cu^+. λ_{ex} = 300 nm, Slit–width (EX: 5 nm, EM: 5 nm), Solvent: acetonitrile.



(a)

Equation	y = A1*exp(-x/t1) + y0		
Adj. R-Square	Inert : 0.95769 Ambient : 0.8655		
		Value	Standard Error
Inert	y0	77.82	8.02
Inert	A1	149.42	10.24
Inert	t1	**17.19**	2.97
Ambient	y0	38.63	22.34
Ambient	A1	107.84	19.95
Ambient	t1	**26.05**	13.21

(b)

Figure S12. Decay curves (a) and exponential equations fitted (b) from emission data of Cu(I) acetate under inert or ambient conditions. Solvent for Cu^{+} stock solution: H_2O, Solvent for emission measurements: acetonitrile, Excitation: 300 nm, Slit width (EX: 5 nm, EM: 5 nm)

Note: Cu^{+} can disproportionate into Cu^{2+} or Cu^{0} spontaneously under ambient conditions. For the stability of Cu^{+} in this probing system, lifetimes of Cu^{+} in ambient and inert conditions were measured. As a result, lifetimes of Cu^{+} under ambient conditions and inert conditions were calculated as 26 and 17 min, respectively, via exponential fitting. This result means that less than 5 min of delay time (between preparation to reaction) does not severely influence the probing ability of **2** for Cu^{+} in this system. Interestingly, Cu^{+} also changed into Cu^{2+} and Cu^{0} under inert conditions. A mixture of the characteristic red–colored reduced copper metal precipitate and blue–colored Cu^{2+} concentration (slurry), and green–colored Cu^{+} was found after 1 h under these inert conditions, as well as under ambient conditions.

The emission intensity of the probe at initial time (0 min) under inert conditions was higher than that under ambient conditions which may arise from the removal of dissolved oxygen present in solvent. Molecular oxygen is usually known as a fluorescence quencher,[7] which means that the removal of dissolved oxygen from the solvent under inert conditions may enhance initial emission intensity.

Additionally, the decay time of the inert condition was faster than for the ambient case, which suggests that the fluorescence under ambient conditions was already quenched to induce a relatively slow decay trend yielding lower emission intensity.

We suggest related mechanisms below, regardless of the presence of molecular oxygen.

$$Cu^{+} \rightarrow Cu^{2+} + e^{-} \qquad E° = -0.158\ V$$

$$Cu^{+} + e^{-} \rightarrow Cu^{0} \qquad E° = 0.522\ V$$

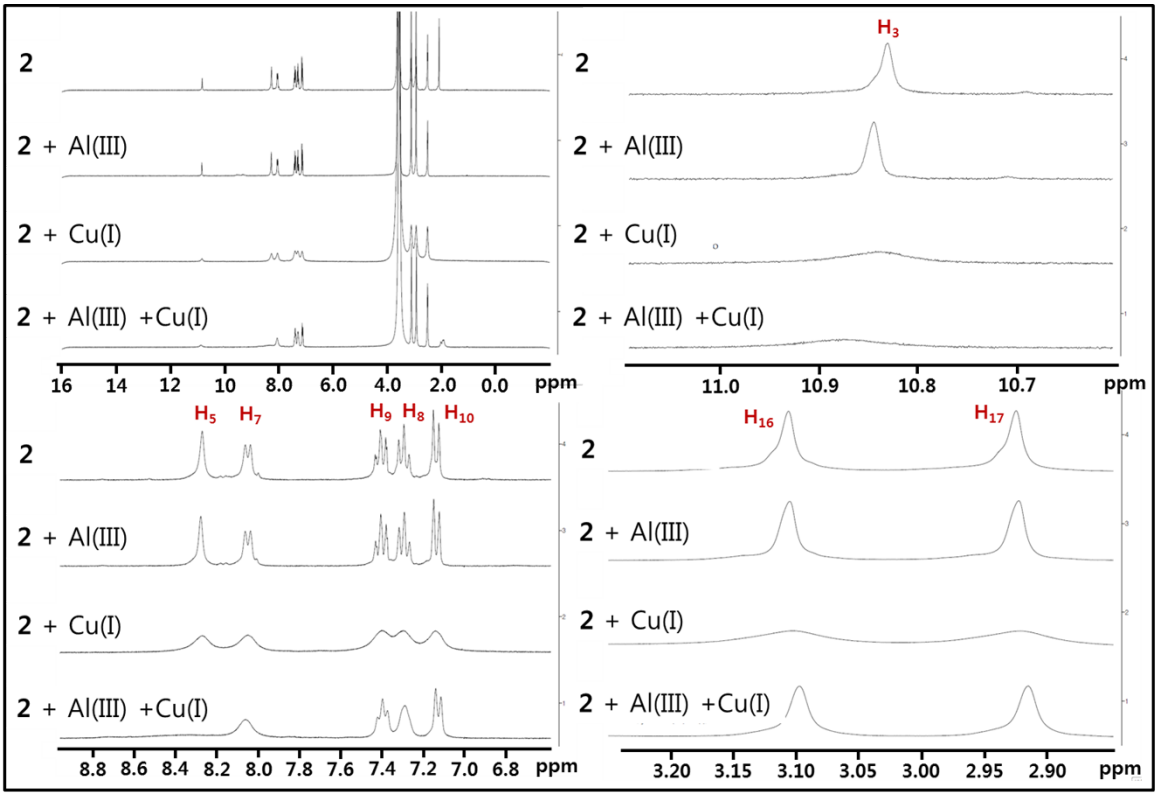


Figure S13. ^{1}H-NMR analysis of **2** (1 equiv) with Al^{3+} (1 equiv), Cu^{+} (1 equiv), or Al^{3+} (1 equiv) + Cu^{+} (1 equiv) for the estimation of binding sites. Solvent: DMSO-d_6 (95.5 v/v %) + D_2O (4.3 v/v %).

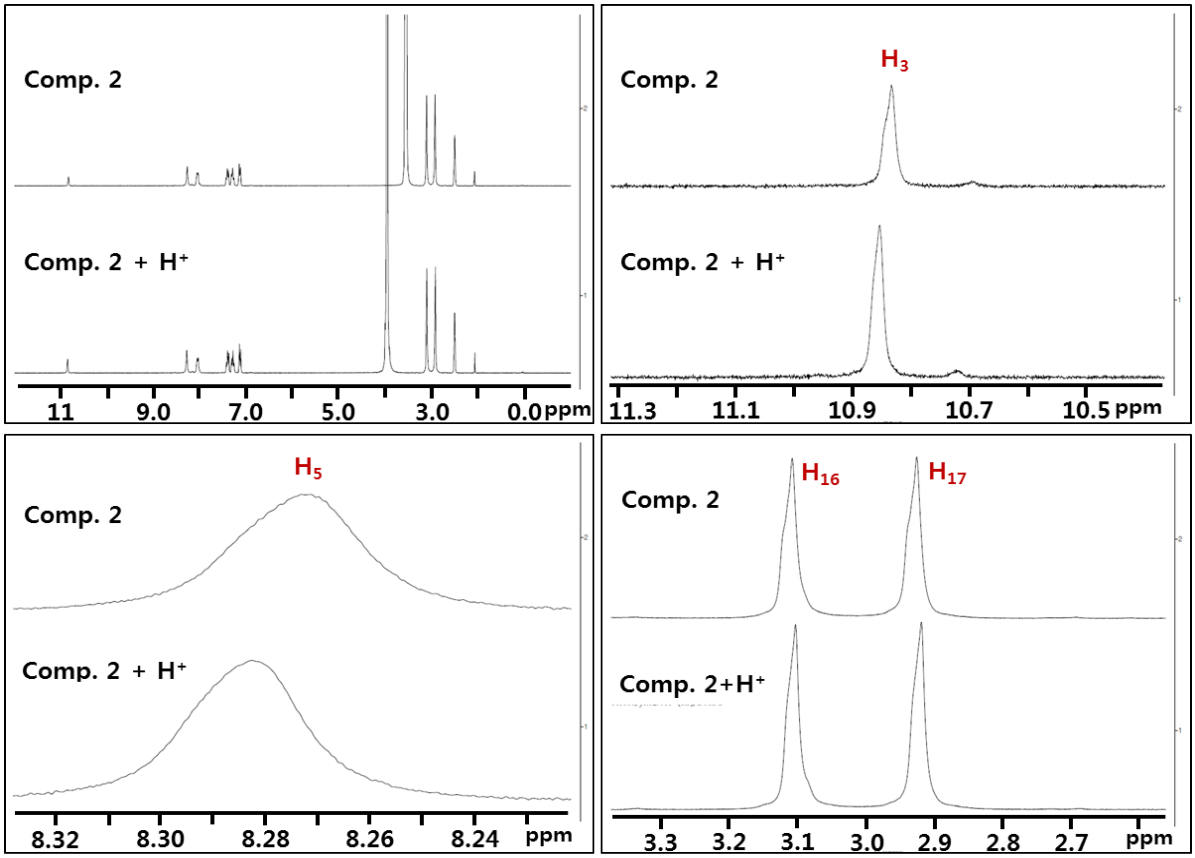


Figure S14. ^{1}H-NMR analysis of **2** (1 equiv) with HCl (1 equiv). Solvent: DMSO-d_6 (95.5 v/v %) + D_2O (4.3 v/v %).

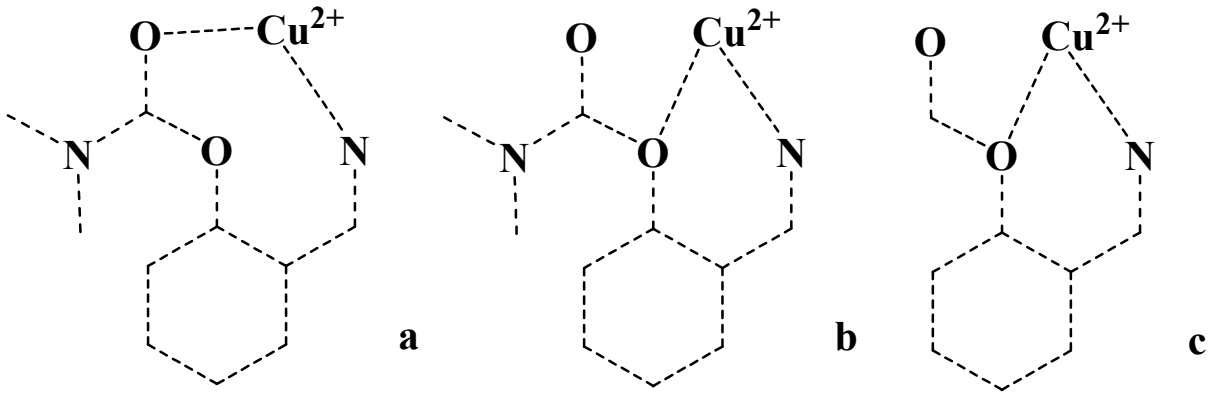


Figure S15. Result from a serach using the Cambridge Structural Database (CSD). **a** and **b**: no references, **c**: one reference (Inorganic chemistry, 2000, 39, 620).[8]

Note: A crystal structure of the probe was not obtained. This may be due to its intrinsic high flexibility and use of only DMSO solubility. When CCDC data was checked, only one similar structure was revealed.

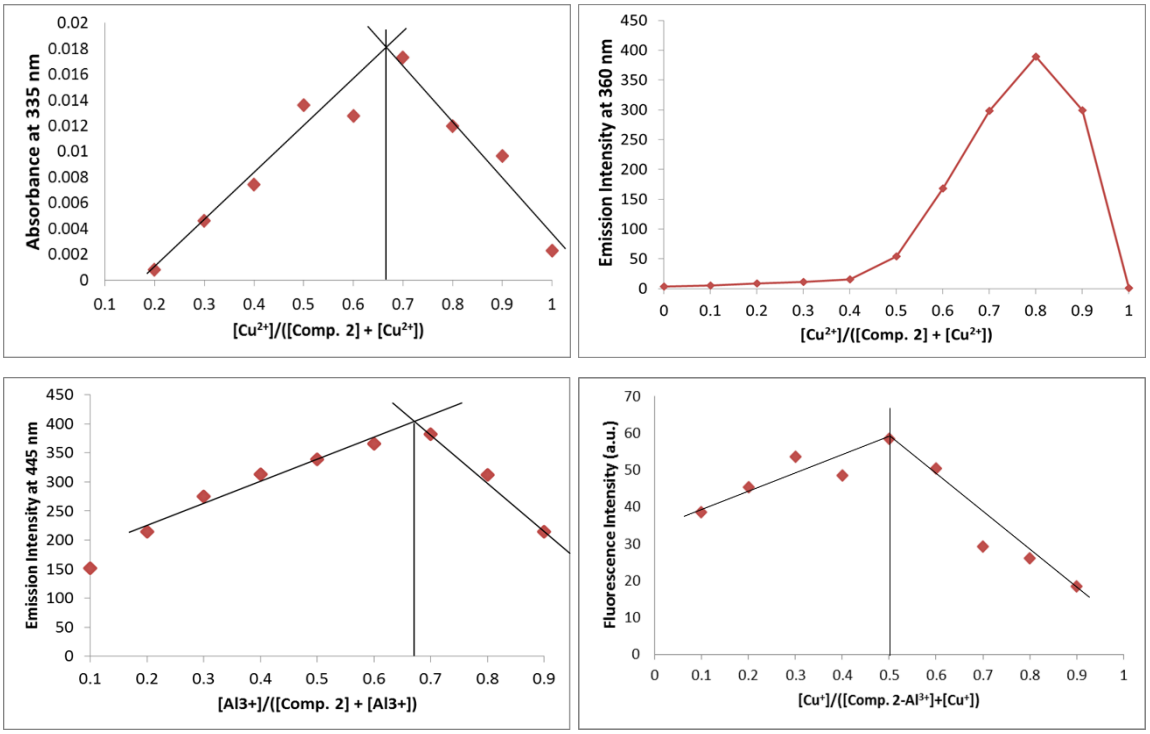


Figure S16. Job analysis for between Cu^{2+} (*top*), Al^{3+} (*bottom-left*), and Cu^{+} in the presence of Al^{3+} (*bottom-right*) with Comp. **2**. Total concentrations for Cu^{2+}, Al^{3+}, and Cu^{+} were the same (16.7 μM). For Cu^{+}, Al^{3+}, the equivalency was fixed as 10 equiv to Comp. **2**. Solvent; acetonitrile, Excitation wavelength; 300 nm, slit width (EX: 5 nm, EM: 5 nm). ※Al^{3+} was added first with Comp. **2** for 10 min; Cu^{+} was then added and incubated for 30 min after which time the emission was checked.

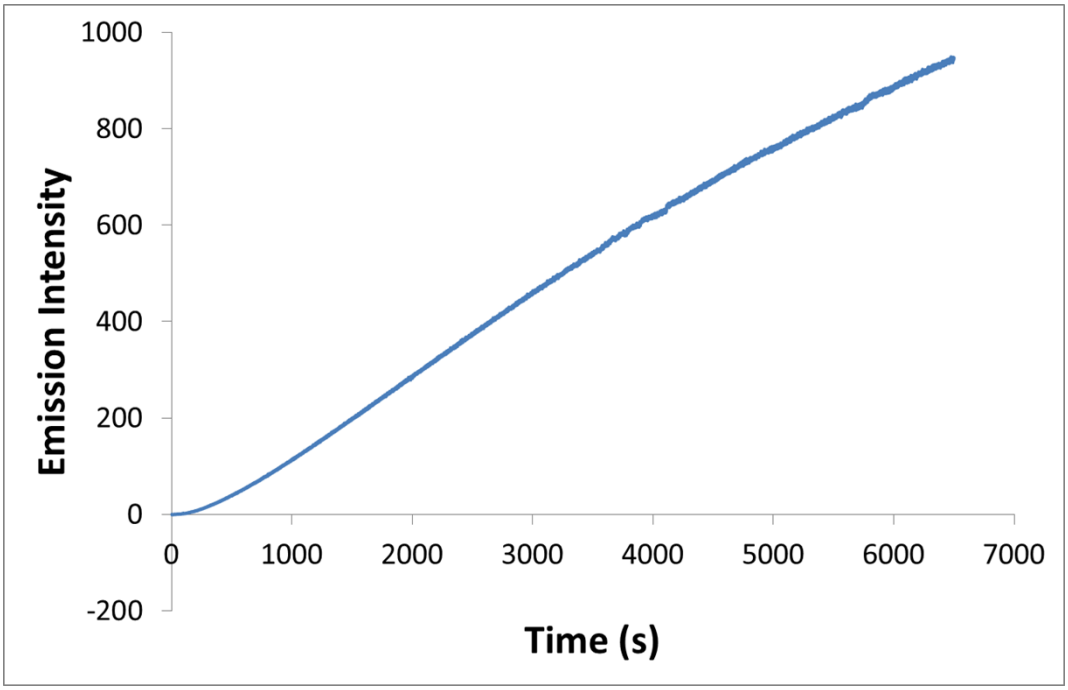


Figure S17. Time-dependent emission intensity of the Comp. **2** (10 μM, 1 equiv) with Cu^{+} (10 equiv) in the presence of Al^{3+} (10 equiv). Solvent: acetonitrile, Excitation: 300 nm, Emission: 360 nm, Slit width (EX: 5 nm, EM: 5 nm).

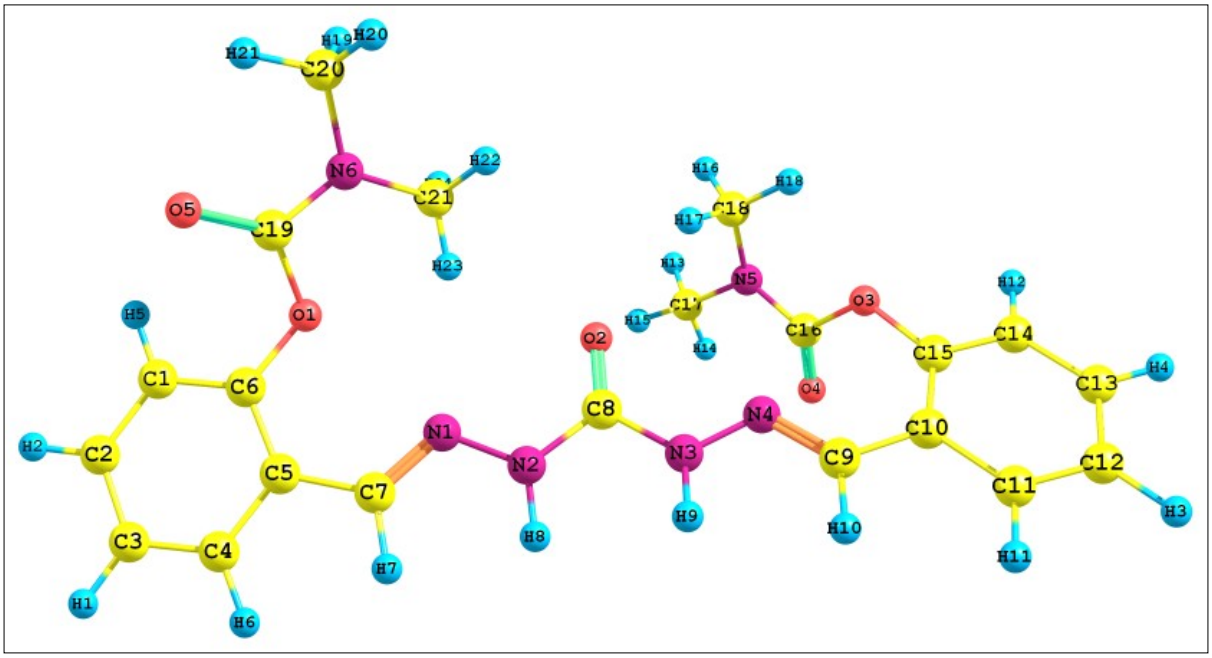
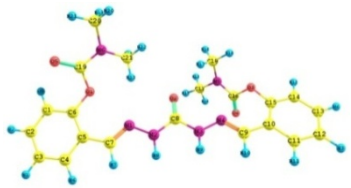
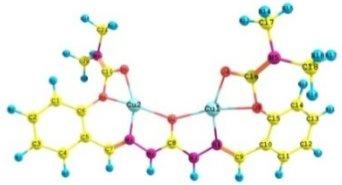
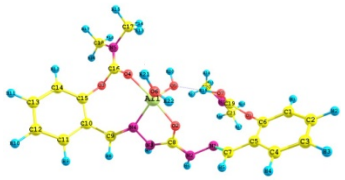
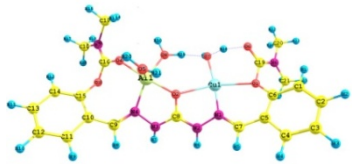
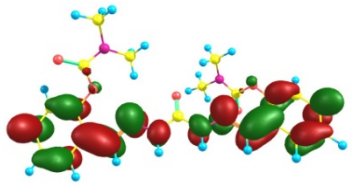
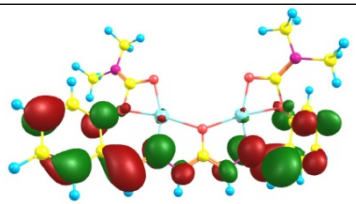
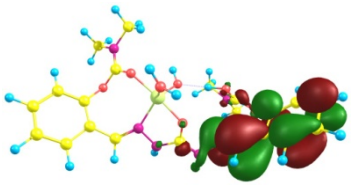
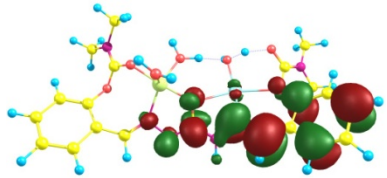
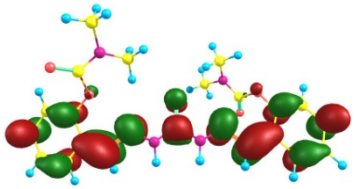
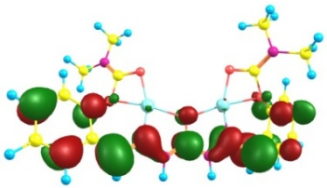
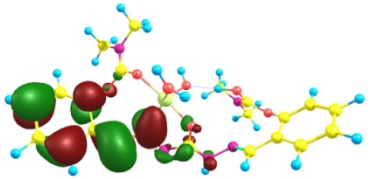
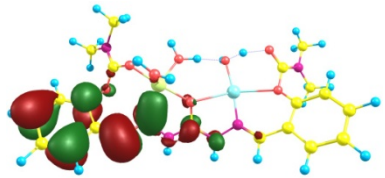
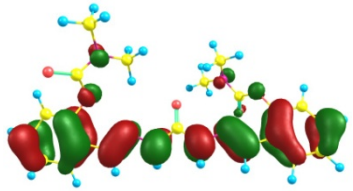
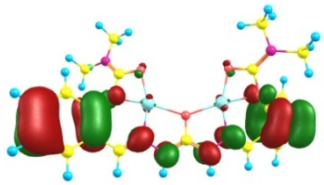
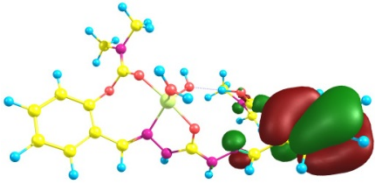
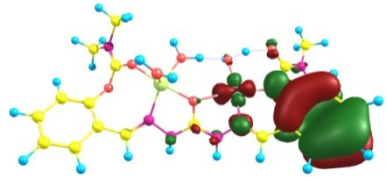
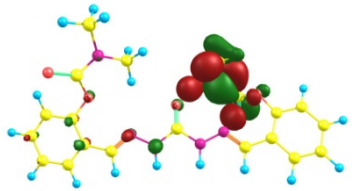
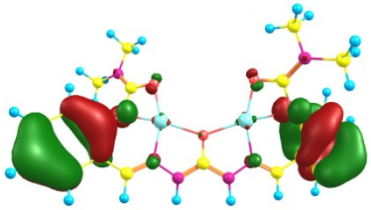
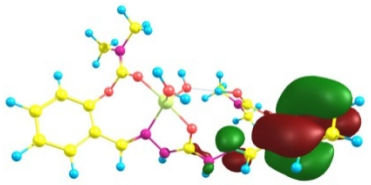
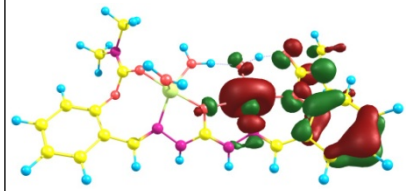
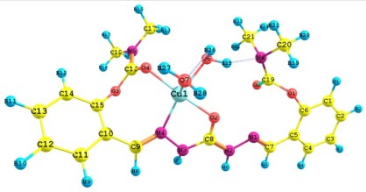
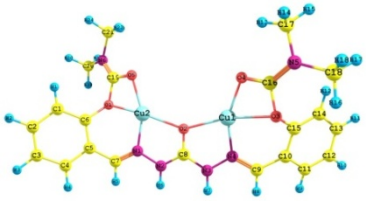
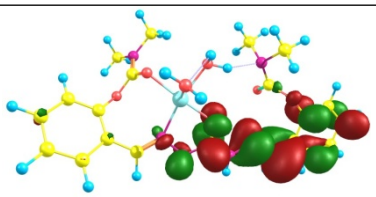
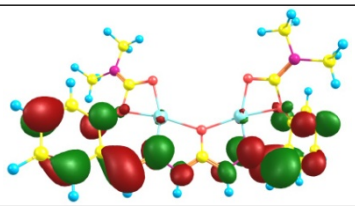
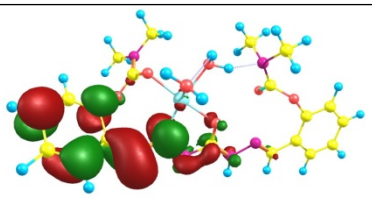
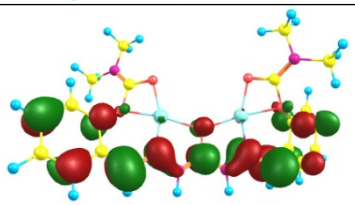
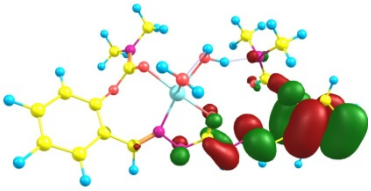
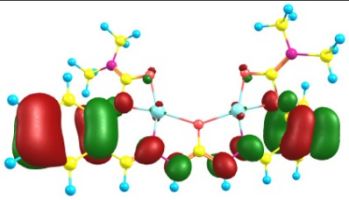
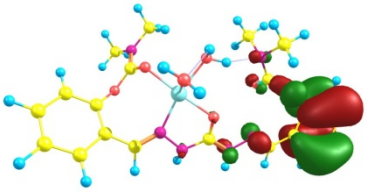
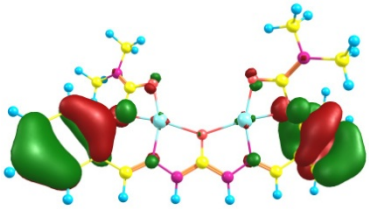


Figure S18. Structure of Comp. **2** optimized through DFT calculations. (B3LYP functional and 6–31G* basis set for light atoms).

	Probe	Probe·2Cu^{2+}	Probe·Al^{3+}·2H$_2$O	Probe·Al^{3+}·Cu^{+}·3H$_2$O
Structure				
LUMO+1				
LUMO				
HOMO				
HOMO-1				

(a)

	Probe·1Cu^{2+}	Probe·2Cu^{2+}
Structure		
UMO+1		
LUMO		
HOMO		
HOMO-1		

(b)

Figure S19. (a) Top view of molecular structure and HOMO-LUMO of DFT-optimized geometry of probe only (Comp. **2**) (first column), the probe with two Cu^{2+} ions (second column), probe with one Al^{3+} ion (third column), and the probe with one Al^{3+} ion and Cu^{+} (fourth column) in the gas phase. (b) Orbital distribution between binding of 1 and 2 Cu^{2+} ions associated with the probe. (B3LYP functional and 6-31G* basis set for light atoms; 6-311G* basis set for Cu and Al).

Table S1. Information of the probe calculated through 'molinspiration property engine v2011.04' at the website, http://www.molinspiration.com.

Properties (NOTE: abbreviations same as on website)	Value
LogP	2.836
PSA	124.939
natoms	32.0
MW	440.46
nON	11
nOHNH	2
nviolations	1
nrotb	8
volume	393.509

※ LogP: Octanol-water partition coefficient, PSA: molecular polar surface area, n atoms: number of atoms without hydrogen, MW: molecular weight, n ON: number of O atoms and N atoms, n OHNH: number of OHNH functional groups, n violations: number of violations against 'Rule of 5', n rotb: number of rotatable bonds, volume; molecular volume.

※ Rule of 5: Lipinski suggested 4 properties about 'drug-like' molecules; log P value should be less than 5, molecular weight should be less than 500, number of hydrogen bond acceptors should be less than 10, number of hydrogen bond donors should be less than 5.[9]

※ **Estimation of the probe pharmacological properties:** Considering the importance of biological drug properties, we calculated the Log P (octanol-water partition coefficient), PSA (molecular polar surface area), n atoms (number of atoms without hydrogen) n ON (number of O atoms and N atoms), n OHNH (number of OHNH functional groups), n violations (number of violations against 'Rule of 5'), n rotb (number of rotatable bonds), and molecular volume through through 'molinspiration property engine v2011.04' at the website, http://www.molinspiration.com.[10]

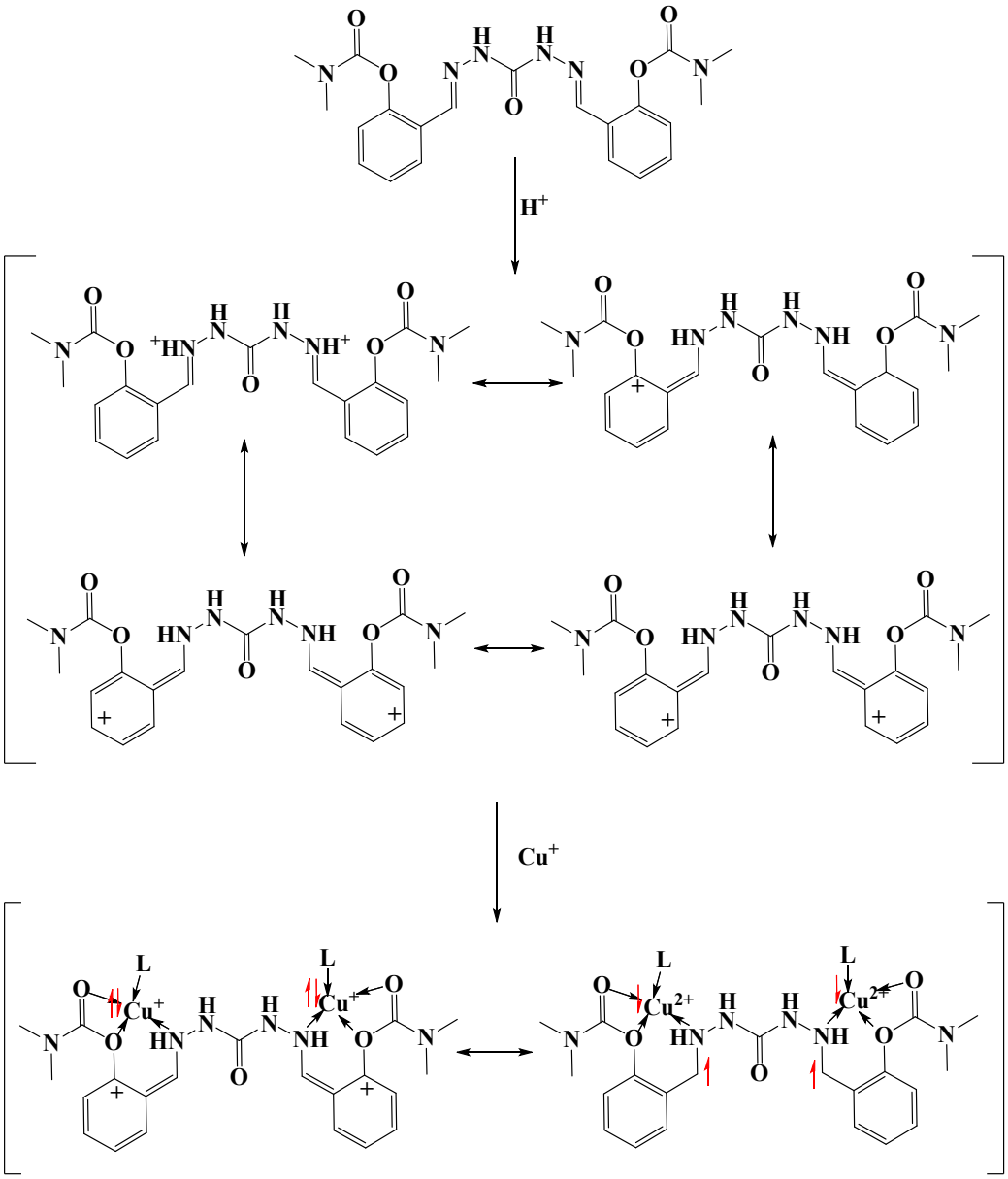


Figure S20. Proposed redox non–innocence mechanism for fluorescence "*turn-ON*" of Cu^{+} in the presence of H^{+}.

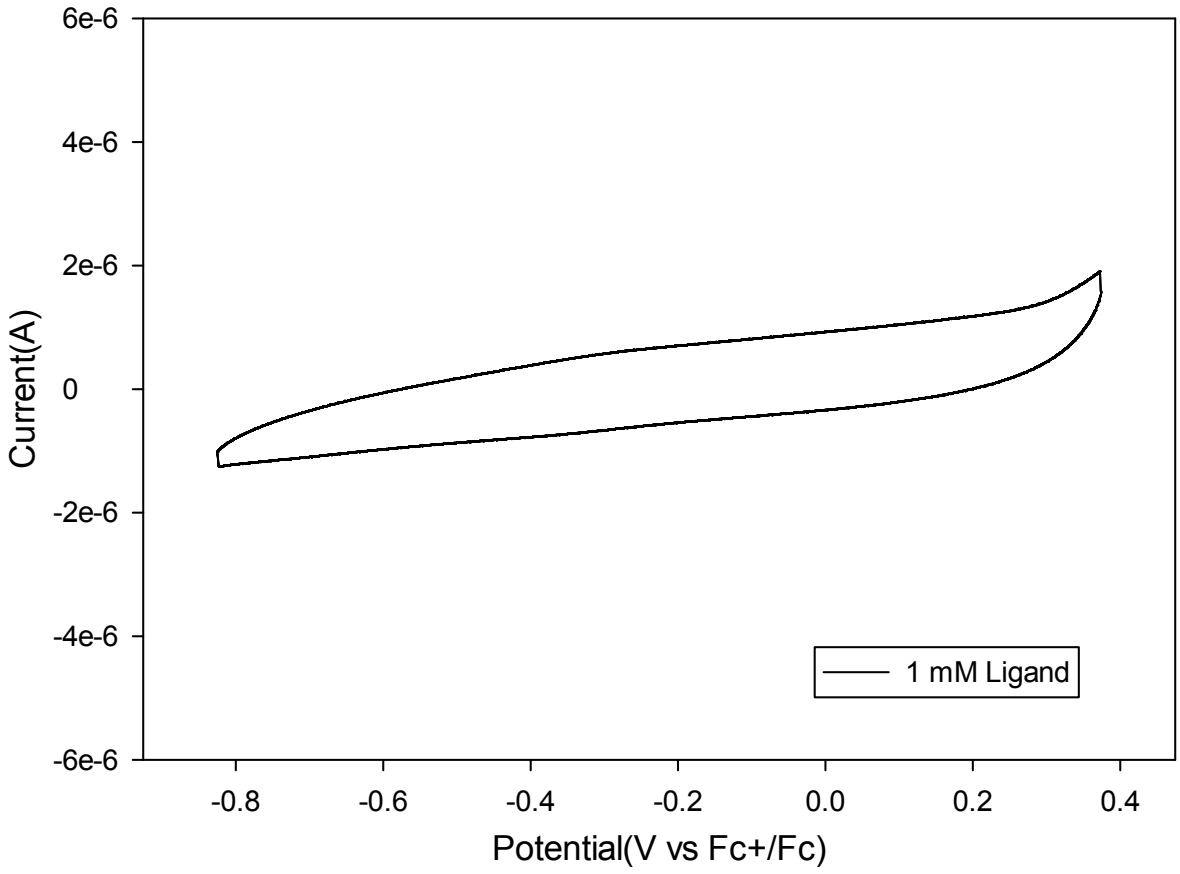


Figure S21. Cyclic voltammetry of ligand (Comp. **2**)

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