Schiff Base Functionalized 1,2,4-Triazole and Pyrene Derivatives for Selective and Sensitive Detection of Cu^{2+} in the Mixed Organic- Aqueous Media

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Research Article

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Abstract

We have prepared Schiff base functionalized 1,2,4-Triazole and Pyrene derivatives for selective, sensitive, and naked eye colorimetric detection of Cu^{2+} in the mixed organic- aqueous media. Amongst the 18 different metal ions studied for absorption and fluorescence titration, only Cu^{2+} ion encourages the modification in spectral properties of Schiff base functionalized 1,2,4-Triazole and Pyrene Probe. The stoichiometric ratio of the Probe-Cu^{2+} complex was determined to be 2:1 according to Job's plot. The lower detection limit estimated for Cu^{2+} is 0.234 nM which shows excellent sensitivity and selectivity of the present analytical method towards detection of Cu^{2+} ion in the mixed organic-aqueous media. The present approach has been successfully utilized for the quantitative determination of Cu^{2+} ion from environmental aqueous solution.

1. Introduction

Recently, studies on environmentally or biologically important metal ions have been continuously conducted. Many metal ions exist in nature and the human body, but not all metal ions have harmful effects. Some substances cause diseases, such as arsenic, cadmium, mercury, and lead[1], but there are also metal ions that are essential components of living things such as selenium, zinc, iron, and copper[2]. Of course, it is not good if there are many, but among them, copper is one of the metals used in the industry as a bronze alloy with tin since ancient times. It is also used in the general manufacturing industry and it is known as a corrosion-resistant metal. Due to this property, it is a metal mainly used as an electric wire. In biochemistry, it is used as a copper protein that plays a role in electron transport and oxygen movement[3]. The human body contains about 1.4 mg of copper per kilogram of body weight, and it is abundant in the brain, kidneys, and blood. It is also an essential component of hemoglobin, which carries oxygen. Besides, it is related to the behaving of p-type ATP and is necessary for promoting antioxidant function and for the action of some enzymes[4][5]. When a person's body is deficient in copper, copper deficiency creates or affects risk factors such as hypercholesterolemia and glucose tolerance, and can upsurge chronic irritation and oxidative stress, which are considered important triggers of cardiovascular disease[6]. However, on the contrary, copper toxicity is rare in humans but causes abdominal pain, liver and kidney failure, and death[7]. As such, copper is more important in industrially and environmentally.

Investigation for specific ions may be performed in various ways, such as electrically identifying ions[8] or using a membrane[9]. Among them, in this study, a chemosensor probe was used to observe the fluorescence intensity, that changes due to the photophysical properties that change through the reaction of an atom with an unshared electron pair in a molecule and a specific ion. Besides, many experiments for detecting specific ions of a chemical sensor using a change in the fluorescence spectrum, which are efficient in terms of cost, sensitivity, and selectivity, have been conducted[10][11][12]. Many compounds are being synthesized with chemistry-sensors, among the heterocyclic compounds, the 5 membered ring compound 4-Amino-1,2,4-Triazole-3-thiol derivative has an amine group and thiol group, so the amine

group reacts easily with aldehyde to become a Schiff base (Imine) group and can be used as a chemosensor. Schiff base is synthesized by simple experiments under simple conditions and is a good functional group for use in chemical sensors because of the simple structure of the double bond between nitrogen and carbon and the unshared electron pair of nitrogen[13]. In addition, there are more opportunities to bind with ions due to the sulfur in the thiol group. Pyrene is a generally well-known fluorophore, and as a remarkable feature, it is well known as a p-type quenching fluorophores, and due to its characteristic, many experiments have been conducted in the field of photophysical properties[14]. In this study, a Schiff Base derivative chemosensor probe **TP** or Cu^{2+} based on pyrene and imine was developed. However, the chemical sensor developed in this study was not a quenching type sensor, which is the main characteristics of pyrene, but an Off-On type sensor.

In summary, in this study, a Schiff base derivative (E)-5-(4-bromophenyl)-4-((pyren-1-ylmethylene)amino)-4H-1,2, 4-triazole-3-thiol (**TP**) (Scheme 1) was synthesized, the structure was identified through nuclear magnetic resonance, infrared, and mass spectrometry, and various ions (Na^{+}, K^{+}, Cs^{+}, Cu^{+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Cd^{2+}, Ba^{2+}, Fe^{3+}, Y^{3+}) were analyzed using the photophysical properties analyzed with an ultraviolet-visible spectrophotometer and a fluorescence spectrophotometer in the mixed organic-aqueous media. The selectivity of the probe **TP** for detecting Cu^{2+} was confirmed, predicted how Cu^{2+} and the probe **TP** were bound, the binding ratio was checked, and the experiment in pH conditions carried out well and the lower detection limit of Cu^{2+} ion was confirmed through fluorescence measurement.

2. Synthesis

2.1 Reagents and instruments

Reagents, solvents, and metal cationic samples (Na^{+}, K^{+}, Cs^{+}, Cu^{+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Cd^{2+}, Ba^{2+}, Fe^{3+}, Y^{3+}) used for synthesis and binding experiment. It was prepared with chloride, nitrate, and sulfate salts, and each reagent was purchased from Alfa Aesar (UK), Sigma-Aldrich (Munich, Germany), Samjeon Pure Chemical Industries (Daejeon, Korea), and Daejeonghwageum (Siheung, Korea). These reagents used without further purification. ^{13}C and ^{1}H NMR were measured at 126 MHz, 500 MHz, and 400 MHz with a Bruker Avance (Germany) NMR Spectrophotometer using DMSO-d_6. Mass spectrometry (LC-MS) was measured using a 2975/ZQ2000 (waters) spectrometer. Infrared analysis was measured using a Frontier IR spectrophotometer (Perkin Elmer, USA). The process of the reaction was judged using TLC, and ultraviolet-visible absorption analysis was studied using a UV-2600 UV-Vis spectrophotometer of Shimadzu Corporation (Kyoto, Japan). Fluorescence analysis was measured using FluoroMate FS-2 from Scinco (Seoul, Korea).

2.2 Synthesis of ethyl 4-bromobenzoate b

4-bromobenzoic acid **a** (2.25 mmol) was added to ethanol with sulfuric acid and heated to 70-80°C for 5 hours. The progress of the reaction was confirmed by TLC. Thereafter, ethanol was obscure under

concentrated pressure, 100 ml of water was added to the residue, the reaction mixture was neutralized with sodium carbonate, and take out with ethyl acetate. The organic layer was removed with anhydrous sodium sulfate, and the solvent was evaporated under concentrated pressure to attain a solid product **b** (yield 83%). These were used as such in the next step without purification.

2.3 Synthesis of 4-bromobenzohydrazide c

Ethyl-4-bromobenzoate **b** (1.0 mmol) produced in the previous step was dissolved in ethanol, hydrazine hydrate (1.5 mmol) was added, and the mixture was refluxed for 5 hours. After completion of the reaction, ethanol was removed under reduced pressure, and the resulting solid was put in methanol and heated to dissolve it, and insoluble matter was filtered and stored in a fume hood for recrystallization. After recrystallization, a solid product **c** was obtained (yield 75%)

2.4 Synthesis of 4-amino-5-(4-bromophenyl)-4H-1,2,4-triazole-3-thiol e

4-bromobenzhydrazide **c** (1.0 mmol) was added to ethanol together with potassium hydroxide (1.5 mmol) and carbon disulfide (1.2 mmol), followed by stirring at 0 °C for 5 minutes. When the mixture was dissolved, diethyl ether was added thereto and filtered to obtain an intermediate salt **d**. Then, hydrazine hydrate (2.0 mmol) and distilled water were added and reacted overnight at 120 °C. After the reaction was completed, the reaction mixture was poured into distilled water (50 ml) and acidified with 5N HCl solution. Then, the resulting solid was filtered, washed with distilled water, stored in a fume hood for recrystallization, and dissolved in methanol. After recrystallization, a solid triazole intermediate product **e** was obtained (yield 90%). It was used as it is in the next step without purification.

2.5 Synthesis of (E)-5-(4-bromophenyl)-4-((pyren-1-ylmethylene)amino)-4H-1, 2, 4-triazole-3-thiol, TP

4-amino-5-(4-bromophenyl)-4H-1,2,4-triazole-3-thiol **e** (0.337 mmol) and 1-pyrenecarboxy-aldehyde (0.337 mmol) were added to methanol together with hydrochloric acid (2 drops) and reacted at 70° C for 3 hours. After completion of the reaction, the solid product was filtered and washed with ethanol, methanol and distilled water. After that, a dry and pure solid product **TP** was obtained (yield 90%).

(E)-5-(4-bromophenyl)-4-((pyren-1-ylmethylene)amino)-4H-1,2, 4-triazole-3-thiol (TP)

Yellow Solid; yield: 90%; ^{1}H NMR (500 MHz, DMSO-d6) δ 14.42 (s, 1H, S**H**), 10.91 (s, 1H. Imine C**H**), 8.74 (s, 1H. Ar), 8.69 – 8.66 (m, 1H, Ar), 8.47 – 8.40 (m, 4H, Ar), 8.38 (d, *J* = 8.9 Hz, 1H, Ar), 8.30 (d, *J* = 8.9 Hz, 1H, Ar), 8.18 (t, *J* = 7.6 Hz, 1H, Ar), 8.04 – 7.97 (m, 1H, Ar), 7.95 (d, *J* = 8.6 Hz, 2H, Ar), 7.81 (d, *J* = 8.6 Hz, 2H, Ar), 7.76 (d, *J* = 8.6 Hz, 1H, Ar). ^{13}C NMR (126 MHz, DMSO) δ 164.60, 162.46, 147.95, 133.82, 131.78, 130.60, 130.55, 130.29, 129.90, 129.73, 129.69, 127.28, 126.83, 126.77, 126.51, 125.32, 125.16, 124.74, 124.34, 124.32, 123.82, 123.36, 122.06. IR (KBr) 3098.96, 2927.63, 1907.86, 1740.51, 1624.75, 1592.96, 1573.90, 1535.62, 1497.98, 1422.23, 1397.63, 1375.87, 1320.02, 1303.63, 1272.79, 1258.45, 1234.21, 1184.89, 1165.36, 1139.68, 1108.18, 1072.05, 1013.18, 974.63, 901.95, 843.80, 820.18, 790.81, 766.89, 756.76, 733.10, 682.73cm^{-1}; (ESI, m/z), 485.4 [M+2].

3. Analysis

3-1. Sample preparation

Probe **TP** was synthesized under relatively simple experimental conditions, but its solubility was limited at room temperature. It was not well soluble in methanol and ethanol, but relatively well soluble in DMSO, DMF, and THF. However, since DMSO has a high freezing point, it was limited to experiment in winter. Therefore, the probe **TP** was tested at a concentration of 1mM in a THF solvent. An analysis sample was prepared using THF and HEPES pH 7.4 buffer (THF: HEPES 8:2 v/v). And the prepared metal ions (Na^{+}, K^{+}, Cs^{+}, Cu^{+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Cd^{2+}, Ba^{2+}, Fe^{3+}, Y^{3+}) are all dissolved in distilled water. It was prepared at a concentration of 1 mM. In the case of copper ions, both monovalent cations and divalent cations were prepared, and in the case of monovalent cations, since they are insoluble in distilled water, a drop of HCl was added. Probe **TP** and metal cations were placed in the vial, mix well to react, and measured.

3-2. UV-Vis Absorption Spectroscopy

The probe TP and metal cation samples (Na^{+}, K^{+}, Cs^{+}, Cu^{+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Cd^{2+}, Ba^{2+}, Fe^{3+}, Y^{3+}) were prepared at room temperature. A 1 cm quartz cell was used, and the measurement range was measured from 200 nm to 700 nm. The maximum absorption wavelength of probe **TP** is 400 nm.

3-3. Fluorescence Spectroscopy

The approximate selectivity of TP towards metal ions was confirmed by the ultraviolet-visible absorption spectrum. Similarly, fluorescence intensity was also measured to confirm selectivity. The sample was measured using the same sample as in the absorption spectrum. The measurement starting wavelength of the fluorescence spectrum was 401 nm, and it was measured up to 700 nm. Also, 20 μM of Cu^{2+} and other metal cations were added to 10 μM of the probe **TP**, and the solvent was the same, and then the fluorescence intensity was measured to determine which ions preferentially react to the probe between Cu^{2+} and other metal ions. Also, Cu^{2+} was added to 10 μM of probe **TP** from 1 μM to 20 μM, and the fluorescence intensity was measured, and the fluorescence intensity was measured again from 0.1 μM to 2.0 μM, and the lower detection limit was calculated. Then, using the same concentration (25 μM) of probe and copper(II) chloride solution, it makes a sample with a ratio of 1:9 ([Probe]:[Cu^{2+}]) to 9:1 and measure the fluorescence intensity to analyze the binding ratio. Also, samples of pH 3 to pH 12 (HEPES buffer solution) were prepared and the fluorescence intensity was measured to determine the fluorescence intensity of each pH for Cu^{2+} ion with probe **TP**.

3-4. ^{1}H NMR Titration

To confirm the exact bonding position, a probe **TP** and copper(II) chloride solutions were prepared using the NMR solvent THF-d_8. A sample containing probe **TP** was prepared, and the amount of Cu^{2+} in the

presence of probe TP was gradually increased, and six more samples were prepared to measure the ^1H NMR titration.

4. Result

4-1. Selectivity

The colorimetric sensing ability of TP was investigated in THF: HEPES (8:2 v/v) upon the addition of a variety of metal ions. The probe TP with Cu^{2+} has a change in luminescence that can be distinguished from other ions with the naked eye through a UV lamp (365 nm). It confirmed that probe **TP** reacts selectively and preferentially to Cu^{2+} by using the ultraviolet-visible absorption spectrum and fluorescence emission spectrum. In the absorption spectrum, Hg^{2+} and Cu^{2+} in the presence of probe **TP** showed a slightly different shapes. In the case of Hg^{2+}, the absorption spectrum was generally shifted to the bathochromic shift. In the case of Cu^{2+}, the absorbance at 400 nm was significantly hypochromic shift (Fig. 1a.). On the other hand, the fluorescence intensity variation of probe **TP** towards various metal ions were evaluated systematically in THF: HEPES (8:2 v/v) . The rest of the metal cations except for Cu^{2+} emitted an intensity similar to that of the probe **TP** (Fig. 1b). Therefore, when Cu^{2+} and other metal cations, respectively, towards probe **TP** were put together and measured and compared, it was found that the most of the copper ion preferentially reacts with probe **TP.** That is, the fluorescence emission intensity outcomes of the probe **TP** in the presence of each metal ions(blue pillars) and probe **TP** + Cu^{2+} ion in the presence of the other metal ions(orange pillars) as shown in Fig. 2. It means that Cu^{2+} preferentially combines with probe **TP**. In addition, considering that the fluorescence intensity increased by 5 times more than any other metal ions, it is thought that copper ion reacts preferentially. Evidently, the results demonstrated that probe **TP** exhibited high sensitivity and selectivity for Cu^{2+} in THF: HEPES (8:2 v/v) .

4-2. Limited of Detection

The detection limit (LOD) is the minimum amount or minimum concentration that can detect an analyte contained in a sample. The calculation formula for the detection limit is

$$LOD = \frac{3.3\sigma}{K}$$

Where σ means the standard deviation of the response or signal, and K is the slope of the calibration curve.

Therefore, to calculate the detection limit for Cu^{2+} of probe **TP**, Cu^{2+} was added to 1-20 μM in probe **TP** (10 μM) and fluorescence intensity was measured. However, only samples up to 1~2 μM showed an increase in fluorescence, and 3 μM samples showed similar fluorescence intensity (Fig. 3). Therefore, it has adjusted the concentration range and then it measured again to 0.1-1.9 μM (Fig. 4). The fitting curve of fluorescence intensity of the probe **TP** with Cu^{2+}(0.1-1.9 μM) at 453.1 nm is shown as Fig. 5. The calculated detection limit is 0.234 nM.

Table 1. Comparison syntax between present method and already reported a method for detection of Cu^{2+}.

S. No.	Analysis method	Materials used	LOD	Reference
1	Fluorescence	Pyrene-based	0.87 nM	[12]
2	Colorimetric	Hexamethylbenzene-based	1.57 μM	[15]
3	Fluorescence	Peptide-based	54 nM	[16]
4	Colorimetric	Benzophenone-based	6.82 μM	[17]
5	Fluorescence	Triazole-based	12 nM	[18]
6	Colorimetric	Rhodamine 6G-based	1.0 μM	[19]
7	Colorimetric	1,5-Diphenylthiocarbazone-based	6.08, 6.21 μM	[20]
8	Colorimetric/ Fluorescence	quinoline-based	2.03 μM	[21]
9	Fluorescence	Triazole-pyrene-based	0.234 nM	**Our work**

When comparing the detection limit of the recently synthesized compound and the experimental method with the compound synthesized in this experiment, it can be seen that the detection limit belongs to the very lower side (**Table 1**.).

4-3. pH

Probe **TP** was tested at pH 7.4 (HEPES buffer solution). However, at different pHs, to determine which fluorescence intensity is exhibited by reacting to Cu^{2+} and to find an appropriate pH for detection, samples from pH 3 to pH 12 were prepared and fluorescence intensity was measured (Fig. 6). As a result, it shows low fluorescence intensity at acidic pH, moderate fluorescence at weakly basic pH than neutral, and better fluorescence intensity at weakly basic pH than neutral.

4-4. Binding

To confirm the binding method of probe **TP** and Cu^{2+}, Job's plot experiment, ^{1}H NMR titration experiment, and mass analysis were performed[22]. Job's plot experiment is performed to find out the binding ratio of the two substances. Therefore, when the complex of probe **TP** and Cu^{2+} was formed, fluorescence spectra were measured with nine samples with different molar fractions to confirm the ratio of probe **TP** and Cu^{2+}(Fig. 7). A conversion point occurred in the sample with the mole fraction of probe **TP** 7. It can be seen from this result that the mole fraction of probe **TP** is 7 and Cu^{2+} is 3, and it can be seen that probe **TP** : Cu^{2+} has a binding ratio of 2:1.

Next, a ^{1}H NMR titration experiment was performed to determine which functional group of probe **TP** reacts and binds with Cu^{2+} (Fig. 8).

When a small amount of copper(II) chloride solution was added to the probe **TP**, it was difficult to see the change of each peak, but as the amount of copper(II) chloride solution increased, the thiol peak near 13ppm moved to upfield. And it was shown that the imine hydrogen peak near 11.5ppm moved to the downfield as well. By the shift of each peak obtained through ^{1}H NMR titration, it can be seen that the sulfur of the thiol group attached to the triazole ring and the nitrogen of the imine group interact with copper.

The modified Benesi-Hildebrand (B-H) equation was used to find the association constant (Ka) between the probes **TP** and Cu^{2+}.

$$\frac{1}{F - F_0} = \frac{1}{(F_{MAX} - F_0)} + \frac{1}{K_a(F_{MAX} - F_0)}\frac{1}{[Cu^{2+}]^n}$$

Where, F_{max}, $F_{0,}$ and F are the fluorescence intensities of probe **TP** as maximum in the presence of Cu^{2+}, in absence of $Cu^{2+,}$ and presence of Cu^{2+} at particular concentration i.e. [Cu^{2+}], respectively. A 'n = 1' is the number of Cu^{2+} bound per probe **TP**. The association constant (Ka) was calculated by drawing a Benesi-Hildebrand graph for the fluorescence intensity measured by putting the concentration of Cu^{2+} in the probe **TP** while increasing (Fig. 9). The larger the binding constant, the stronger the bonding strength between the probe and the ion, and less dissociation. The calculated binding constant is $3.33x10^{5}$ M^{-1}.

Through Job's plot experiment, it was found that probe **TP** and Cu^{2+} reacted 2:1, and through the ^{1}H NMR titration experiment, it was found that sulfur of thiol group of probe **TP** and nitrogen of imine group are bound to Cu^{2+}. Based on the results obtained so far, the binding structure of probe **TP** and Cu^{2+} can be considered as follows (Fig. 10).

5. Conclusion

Probe **TP** can be easily synthesized under relatively simple reaction conditions. And the synthesized probe **TP** was confirmed using IR, NMR, and Mass Spectroscopy. When investigating the photophysical

properties, there was a limit to the solvent selection due to the nature of the pyrene derivative, but there were no major problems in experimenting. In the selectivity, the obtained results imply that the chemosensing mechanism is mainly the binding of Cu(II) by probe **TP** and formation of a probe **TP**-Cu(II) complex. The detection limit of Cu^{2+} is 0.234 nM, and the probe **TP** and Cu^{2+} were found to react at a ratio of 2:1 TP-Cu(II) complex. Through ^{1}H NMR, it was confirmed that the sulfur of the thiol group of probe **TP** and the nitrogen of the imine group and Cu^{2+} were binded. Probe **TP** can used as a chemosensor for Cu^{2+} due to its good sensitivity and sufficient selectivity for Cu^{2+}, and further application experiments such as cytotoxicity experiments are possible.

Declarations

Credit Author Statements

Nam Gyu Choi has synthesized and characterized the compounds and prepared the manuscript; Balasaheb D. Vanjare and Prasad G. Mahajan have contributed to analysis; Rajendran Nagarajan has performed analysis with constructive discussion; Hyang Im Ryoo has contributed for photophysical measurements of compounds; Ki Hwan Lee has provided the idea and supervised the project.

Ethical approval Not applicable.

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Data Availability

The data used to support the findings of this study are included within the article.

Declaration of Competing Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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Figures

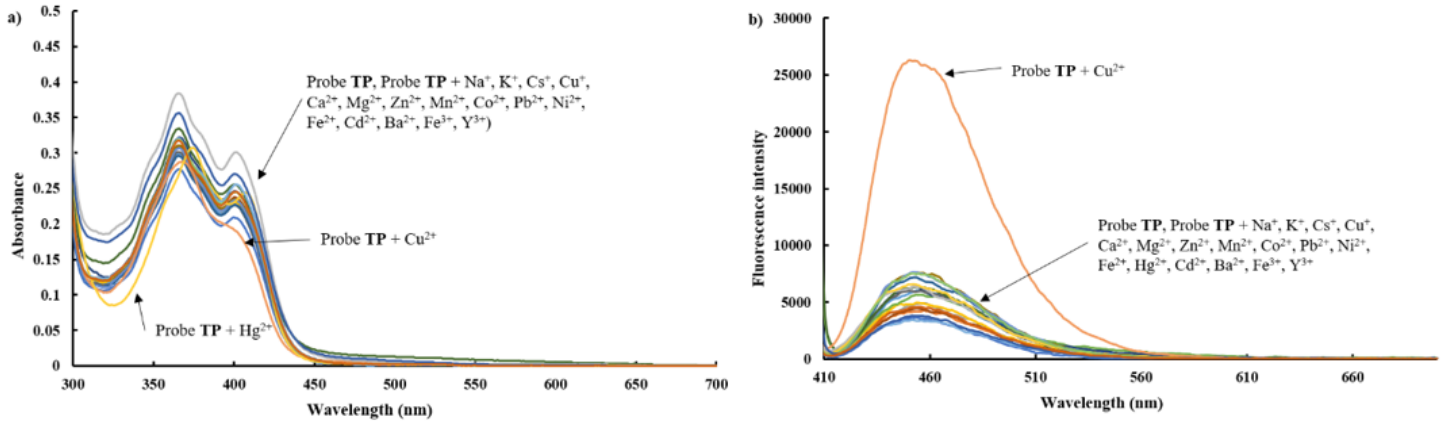

Figure 1

a) Absorption spectra of TP (10 μM) in the existence of various metal ions (Na+, K+, Cs+, Cu+, Ca2+, Mg2+, Zn2+, Mn2+, Co2+, Pb2+, Ni2+, Cu2+, Fe2+, Hg2+, Cd2+, Ba2+, Fe3+, Y3+) (20 μM) in THF:HEPES (pH 7.4) 8:2 (v/v). b) Fluorescence spectra of TP (10 μM) in the existence of various metal ions (20 μM) in THF:HEPES (pH 7.4) 8:2 (v/v).

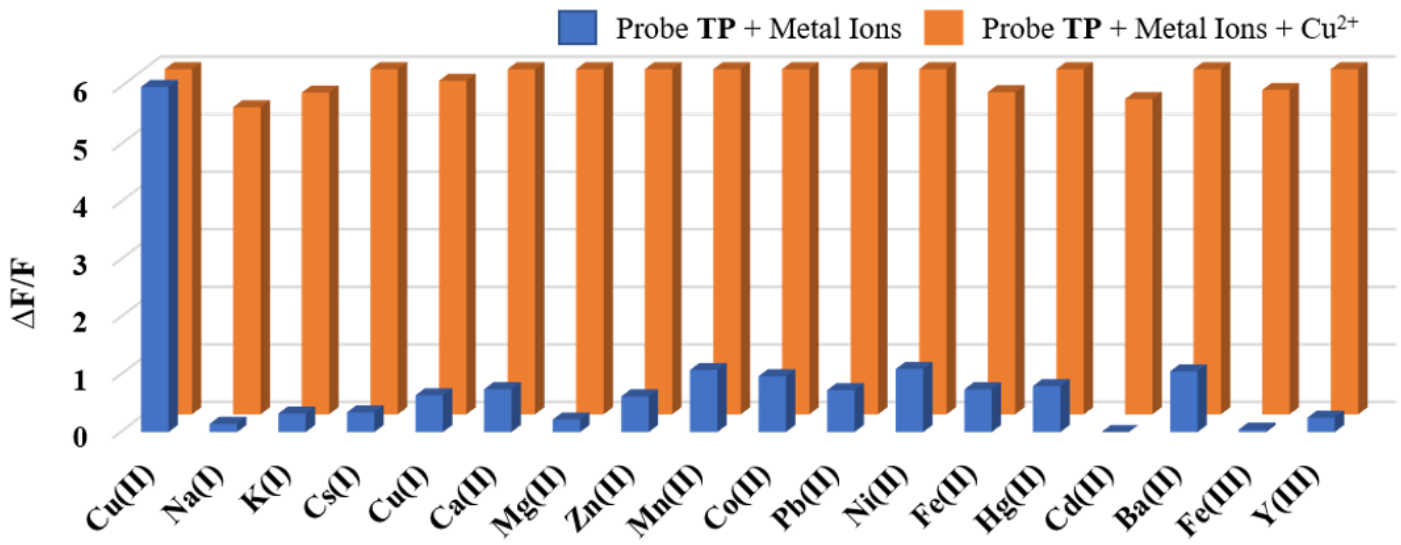

Figure 2

Competitive binding studies between Probe TP (10 μM) with various metal ions (Na+, K+, Cs+, Cu+, Ca2+, Mg2+, Zn2+, Mn2+, Co2+, Pb2+, Ni2+, Cu2+, Fe2+, Hg2+, Cd2+, Ba2+, Fe3+, Y3+) (20 μM)

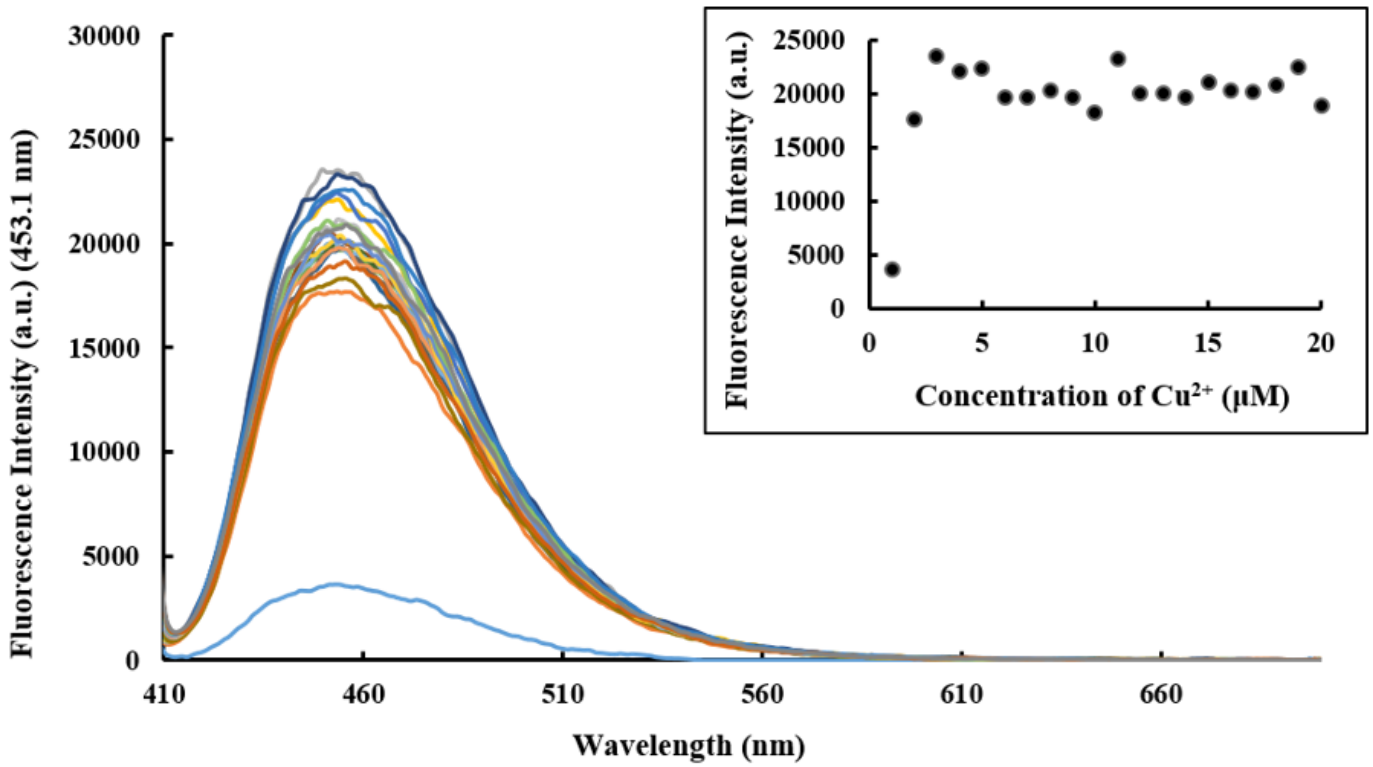

Figure 3

Fluorescence emission spectrum of each sample containing Cu2+ up to 1 μM-20 μM in 10 μM Probe TP.

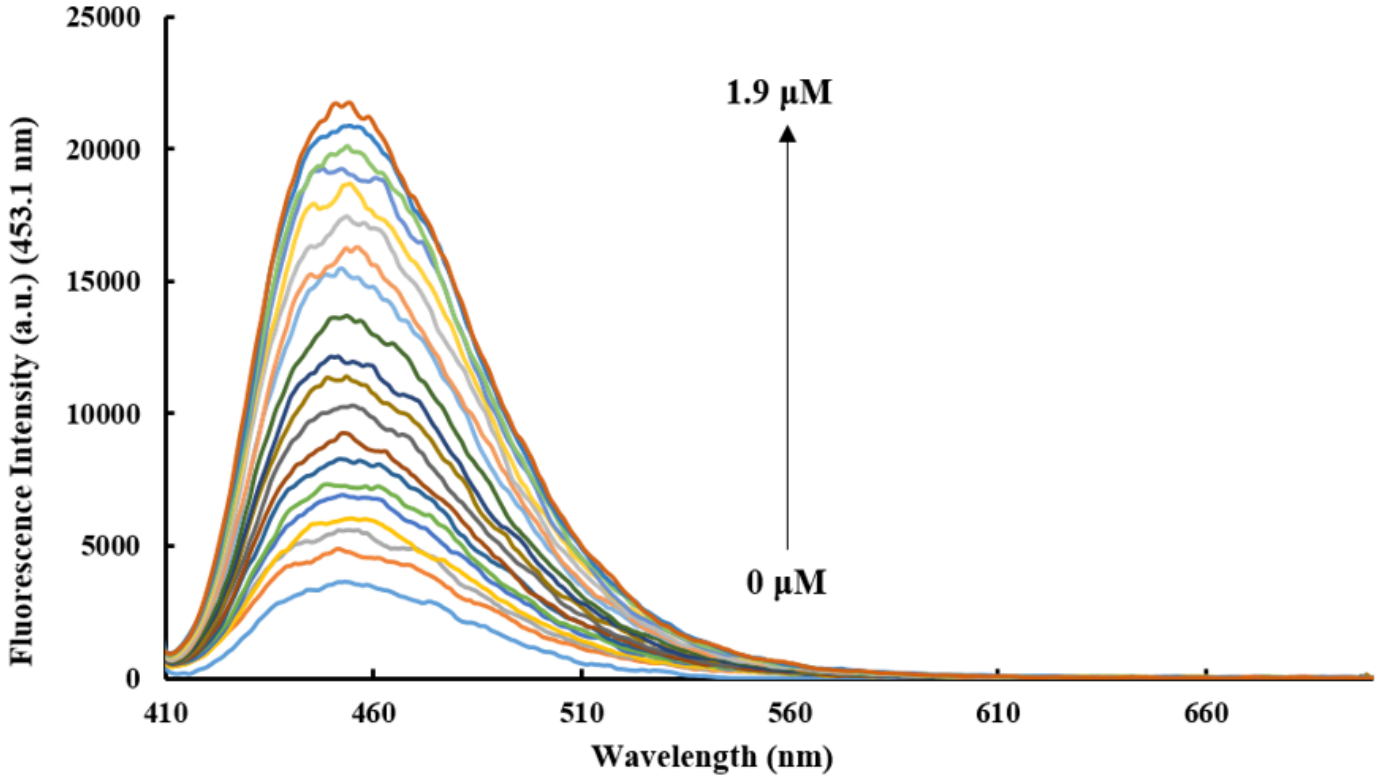

Figure 4

Fluorescence emission spectrum of each sample containing 0.1-1.9 μM Cu2+ in 10 μM probe TP.

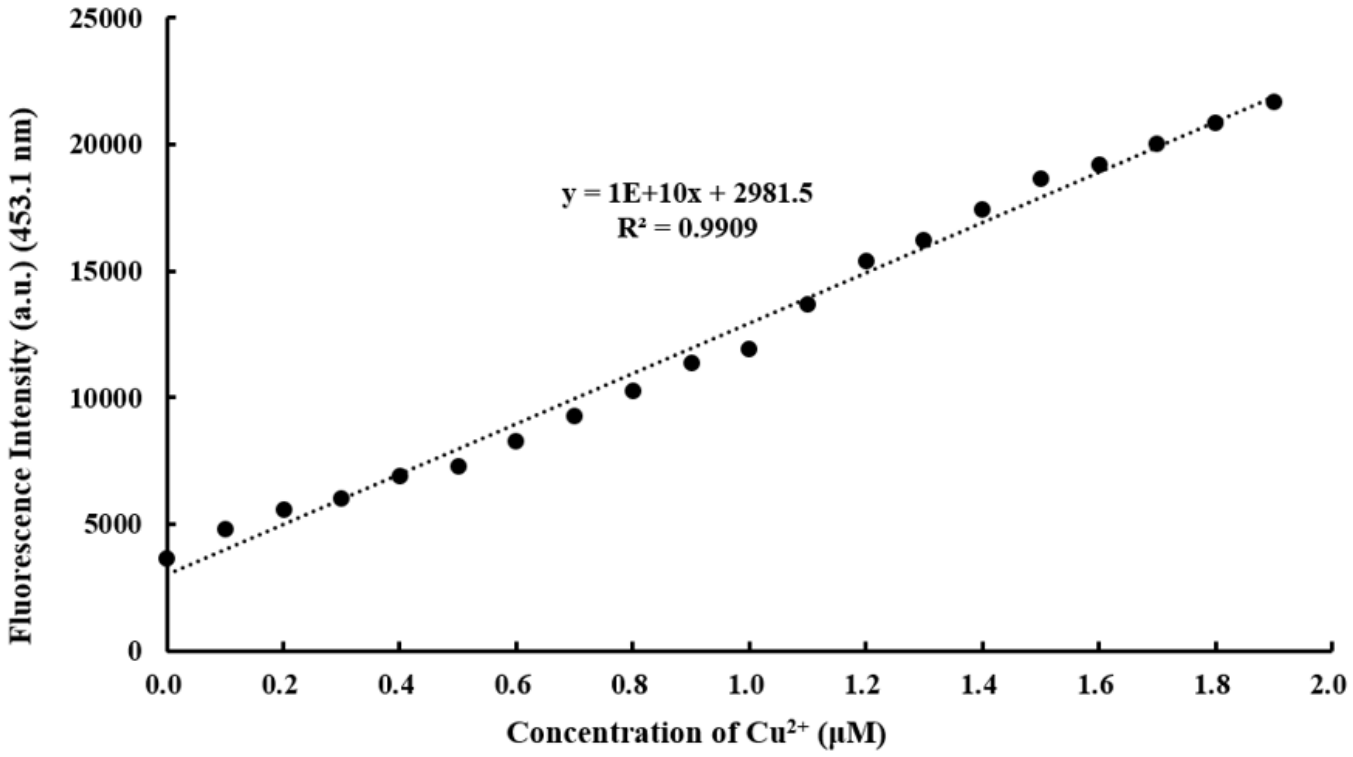

Figure 5

Fitting curve of fluorescence intensity of the chemosensor TP with Cu2+(0.1-1.9 μM) at 453.1 nm

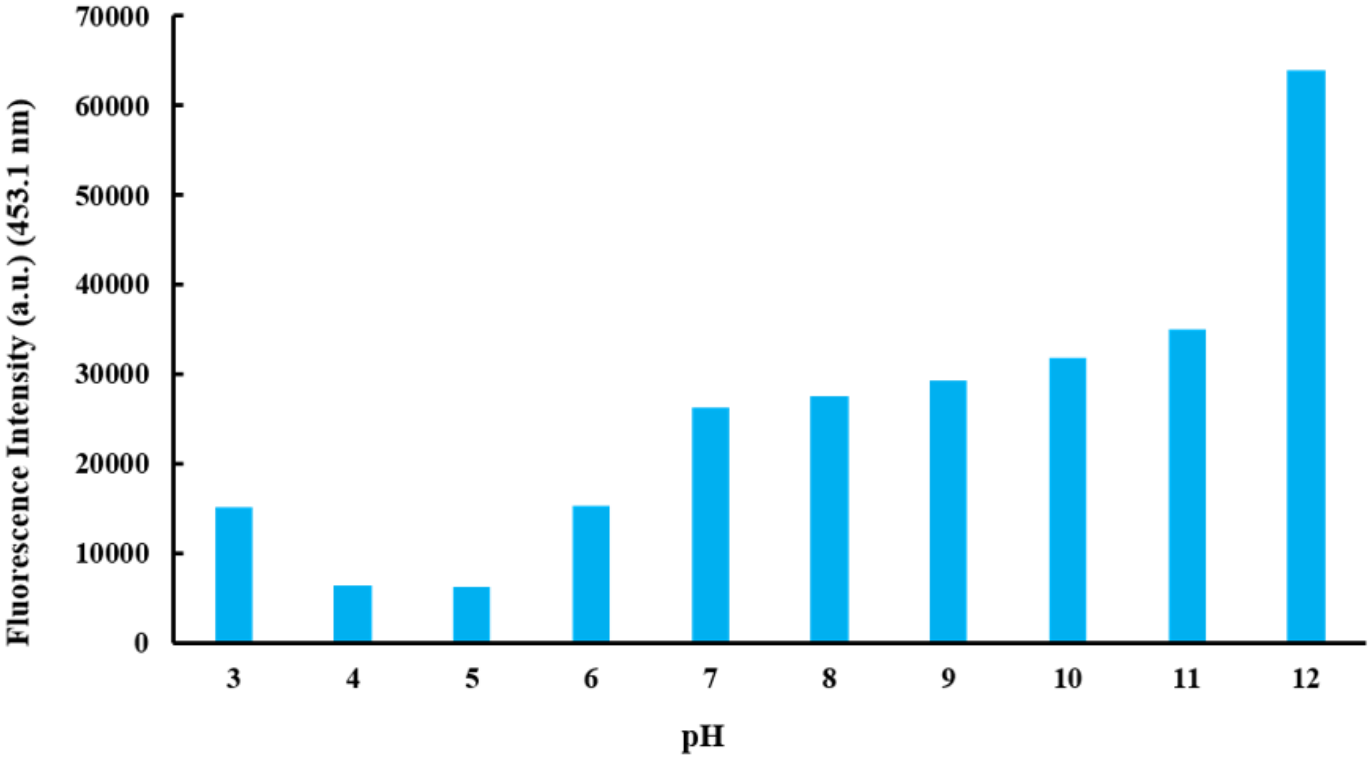

Figure 6

Fluorescence intensity of Cu2+ (20 μM) of probe TP (10 μM) measured using THF and each pH buffer (8:2 v/v) as a solvent.

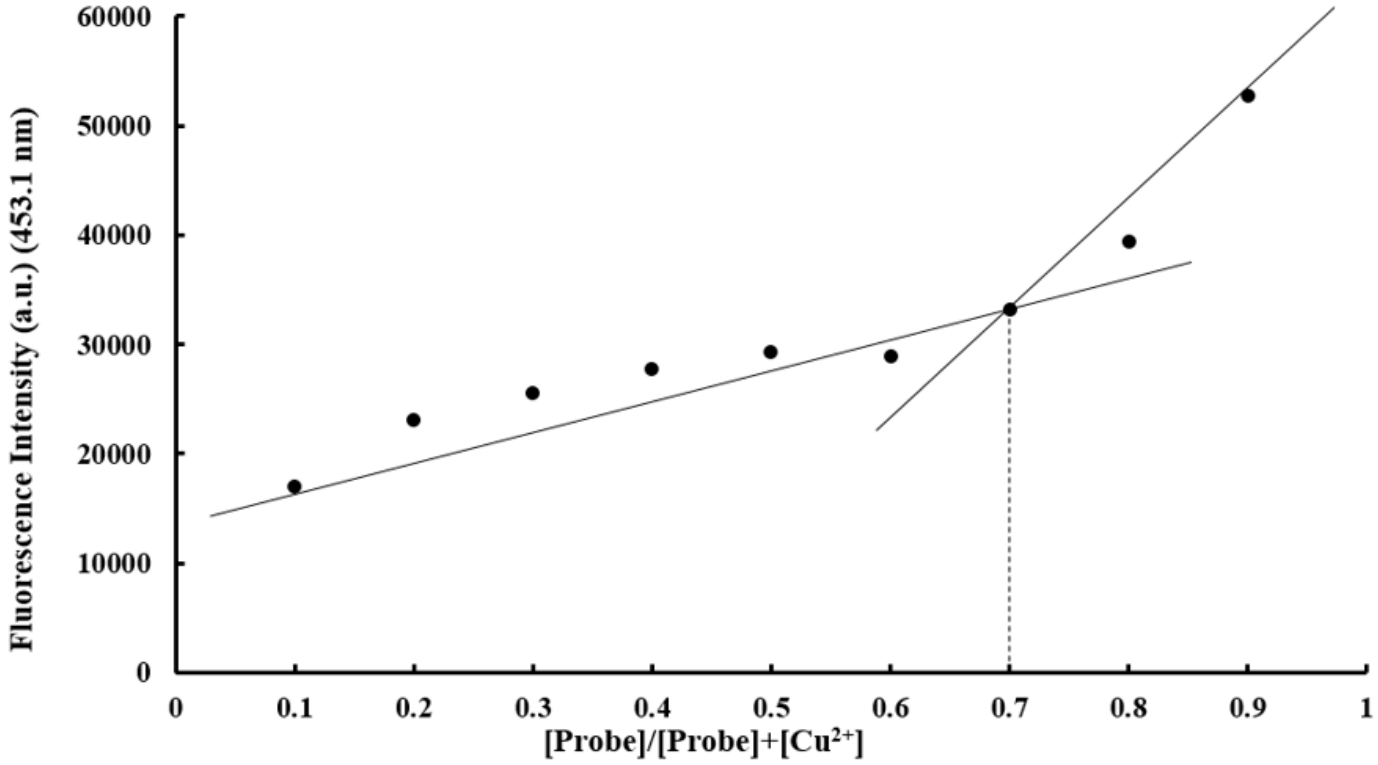

Figure 7

Job's plot for detecting the stoichiometry of probe:copper(II) complex according to the mole fraction of probe TP.

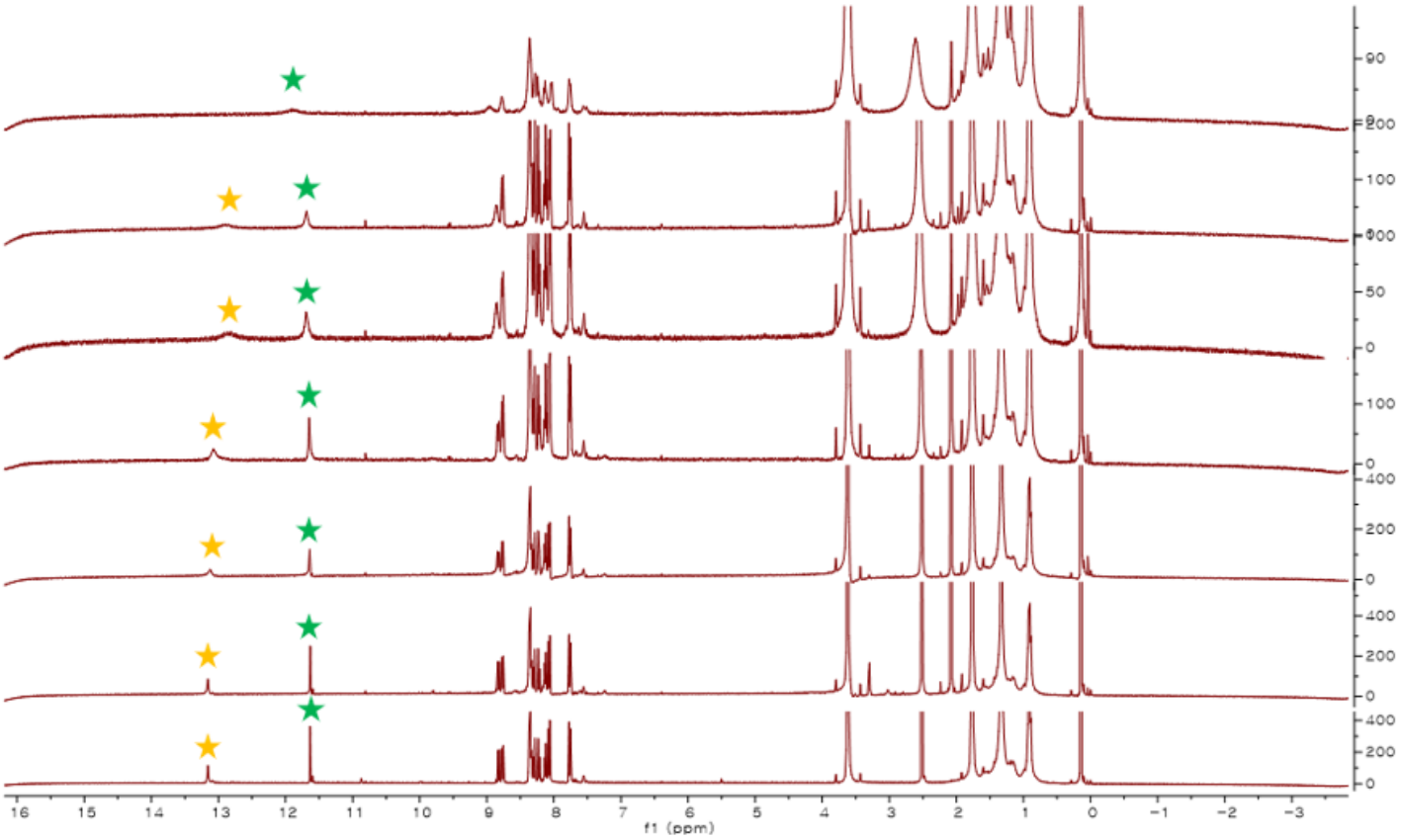

Figure 8

1H NMR titration spectrum for Cu2+ of probe TP.

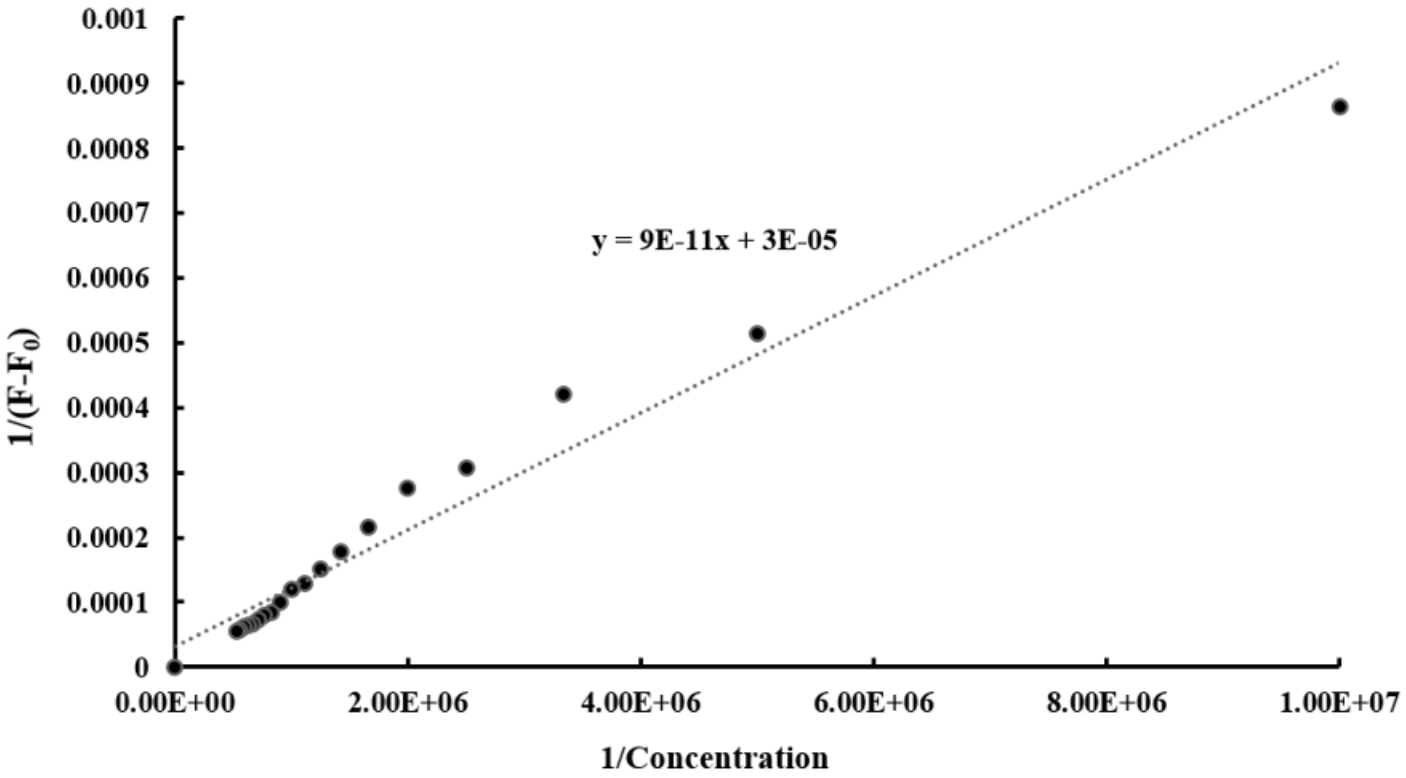

Figure 9

Benesi-Hildebrand graph created by calculating fluorescence intensity for Cu2+ at 453.1 nm of Probe TP concentration.

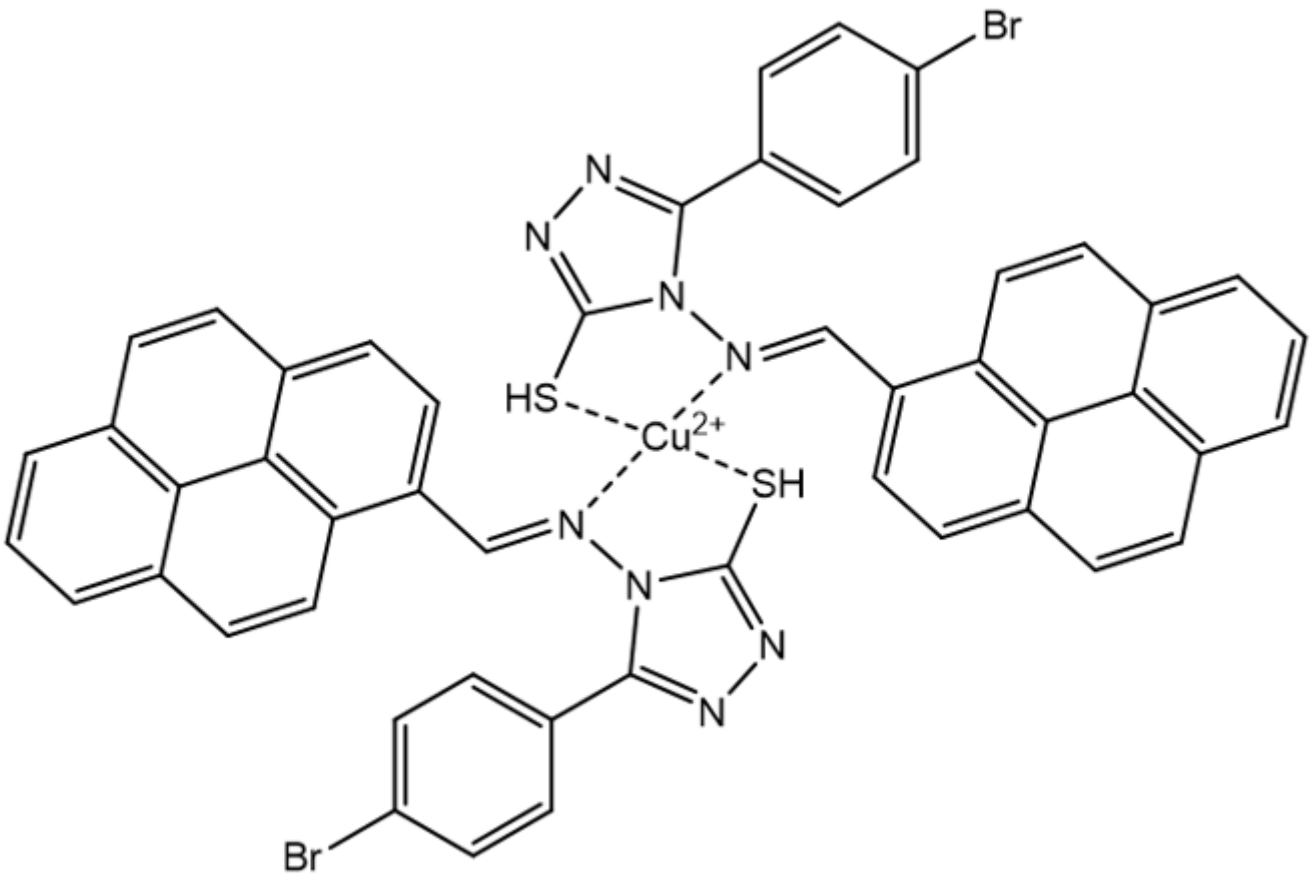

Figure 10

Proposed coupling structure of Probe TP-Cu2+.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Schema.png
- SupportingInformation.docx