ISSN (Print) : 0974-6846
ISSN (Online) : 0974-5645
Indian Journal of Science and Technology, *Vol 10(27), DOI: 10.17485/ijst/2017/v10i27/115542, July 2017*

Bis (Salysylaldehyde) Benzidine for the Highly Selective Cu^{2+}-Sensing by Fluorescence Quenching

Zeyad A. Saleh and Dhaidan Kh. Kafi*

Department of Physics, College of Science, AL-Mustansiriyah University, Baghdad, Iraq;
dhkh77@yahoo.com, zeyad_saleh1958@yahoo.com

Abstract

Objectives: Preparation of an aromatic compound with high Fluorescence spectral properties that can be used as a sensor for metals in the water medium. **Methods/Statistical Analysis:** A new Fluorescent Sensor Bis (salysylaldehyde) Benzidine was produced by the interaction of benzidin with (salysylaldehyde).The designing and synthesizers of compunds to eclectic and detection of biological and environmental significant ionic types have involved extensive attention. **Findings:** Bis (salysylaldehyde) Benzidine an active fluorescent sensor for (Cu^{2+}) in water solution was considered and produced. A color change was simply observing when mixing of Cu^{2+}, also fluorescence quenching was identified. The fluorescent quenching of Bis (salysylaldehyde) Benzidine-Cu^{2+}complicationpresented the limit of detection was 1.96. **Application/ Improvements:** Bis (salysylaldehyde) Benzidine can performance as a high Selective for Cu^{2+} and can be utilized to quantitatively detect low levels of Cu^{2+} in water solution. In arrangement the test indicates high selectivity and affectability toward Cu^{2+}ion over other metal ions.

Keywords: Bis (Salysylaldehyde) Benzidine, Chemosensor, Copper Ions (II), Fluorescence Quenching, Fluorescent Sensors.

1. Introduction

In later years, the improvement of organic sensors for metal ions in water solution has been of growing prominence due to their possible uses in several fields such as environmental sciences, medical sciences, analytical chemistry, cell biology, and biochemistry[1]. Amongst the several chemosensors, best ones engage specific interest fluorescence-based because of their high sensitivity, selectivity, simplicity, low expense, and changeability[2,3]. In Fluorescent sensors, the spectral of a molecule and color of solution changes[4]. The reactions acquired at the molecule level in arrangement opened the entryway for the subjective and quantitative assurance of the objective analyte. As of late, the plan and preparation of sensitive and selective Fluorescent sensors for the specific location of move metal ion have increased colossal consideration on account of their cooperation in an assortment of central organic and physiological procedures[5,6]. Copper is one of the critical follow components existing in the human body, plants, and creatures. Notwithstanding, high measures of this component can bring about genuine medical issues, including disturbance of nose and throat, queasiness, heaving, and looseness of the bowels and additionally harm to the liver and kidneys[7]. In the perspective of the natural and ecological significance an impressive consideration has been centered around recognition of Cu (II) ion[8]. The reviews created around there have been normally relied on upon extinguishing of the fluorescence power of the utilized detecting material[9,10]. This is a direct result of the paramagnetic way of Cu (II) ion. A progression of spectrofluorometric Cu (II) specific sensors have been researched with their selectivity, affectability, and furthermore obstruction of other conceivable

*Author for correspondence

substantial metal sorts[11]. In this paper fluorescence Schiff base, Bis (2-Hydroxy Benzylidene) Benzidine, was orchestrated and created as a conceivable Cu (II) - specific fluorescence sensor. A vital preferred standpoint of the proposed Cu (II) sensor is simple generation (just a single stride response) with fine detecting properties. It was watched that Bis (2-Hydroxy Benzylidene) Benzidine is fit for specific complexation with Cu (II) particle which causes extraordinary extinguishing in the emanation force. Selectivity investigation of the new Cu (II) sensor was examined and a significant selectivity was gotten by relative intensity change esteems.

2. Experimental

2.1 Materials and Techniques

All chemicals utilized as a part of this paper were acquired from business providers from fluka chemicals and Sigma Chemical Company. The techniques used in this research for experimental calculations can be mentioned as follows: (i) Shimadzu company 8400S FTIR spectrometer for Fourier transform-infrared spectra (FT-IR) calculations in the region of 4000–400 cm-1. (ii) Perkin Elmer Lambda 35 UV–Vis spectrometer for absorbance spectrum of the Bis (salysylaldehyde) Benzidine calculated in the range 200–800 NM. (iii) The nmr ready pro 60 MHz spectrometer was used to Proton magnetic resonance spectrum. The chloroform-d solvent was used in the measurements of the 1H NMR. (iv) A Shimadzu RF-5301PC spectrofluorophotometer utilized in fluorescence computations. The title compound desolved in THF solvent with concentration 2×10^{-5} M. Chloride salts were used in the preparation of standard solutions for metal ions and the stock solution of (2.0×10^{-5}) was prepared in THF. Chlorate metal salts of cations (Al^{2+}, Cu^{2+}, Co^{2+} Ni^{2+}, Pb^{2+}, Fe^{3+}, Zn^{2+} and Ag^{2+}) were utilized in the experiments.

2.2 Synthesis

The Schiff base synthesized from the mixing (two moles) 2-hydroxy benzylidene, with benzidine (one mole) in 25ml benzene. Then add a few drops of acetic acid. This resulting mixture is inserted into the water reflux system for several hours. After obtaining quantities of precipitation we cool the ingredients for a period of time and then we filter it Figure 1.

Yield: 75%.Colour: Yellow. Melting Point: 210-212°C. Molecular formula $C_{26}H_{20}N_2O_2$. FT-IR (KBr, ν, cm^{-1}): 1616 (C=N), 1568 (C=C), 3554 (OH), 3057 (C-H). UV–Vis (THF): λ_{max} / nm (log ε) 400. 1H NMR (300 MHz, Chloroform-d6, δ, ppm):7.2, 7.34-7.76 and 8.68 ppm are the proton signals due to the Chloroform solvent, protons ofaromatic and (-CH=N-)azomethine proton one-to-one, the proton signal of phenolic (-OH) proton disappear.

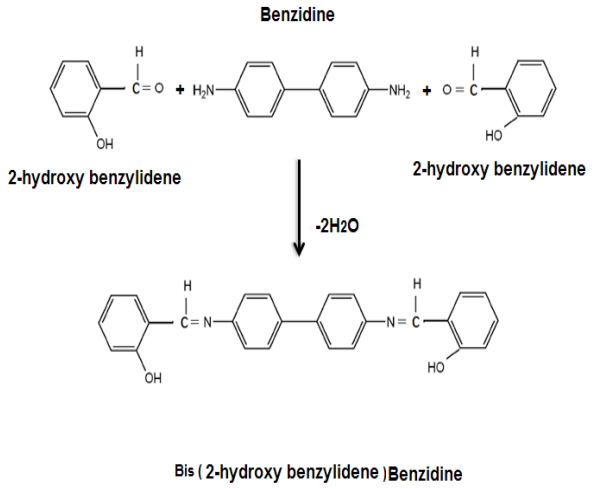

Figure 1. Synthesis ofN, N' bis (salysylaldehyde) benzidine.

3. Results and Discussion

3.1 Fluorescence Characteristics

The Figure 2 shows the fluorescence spectrum of the Bis (salysylaldehyde) benzidine compound. The tetrahydrofuran solvent was used to dissolve the compound. The concentration of the compound used of 2×10^{-5} M at room temperature. The acidic water solution of the compound was [6]. Through the Figure shows a single emission peak at 553 nm when the wavelength is excited at 400 nm. The spectral properties, especially fluorescence were high. The spectral properties, especially fluorescence were high. This result is due to the structure of the compound used in this research. The compound is the result of an aromatic compound with the salysylaldehyde1 which provides different ringed structures which expands the density of states and allowing electronic HOMO/LUMO excitation at lower energies[12].

PH is one of the factors affecting the intensity of Aggregation Induced Enhanced Emission (AIEE) of the

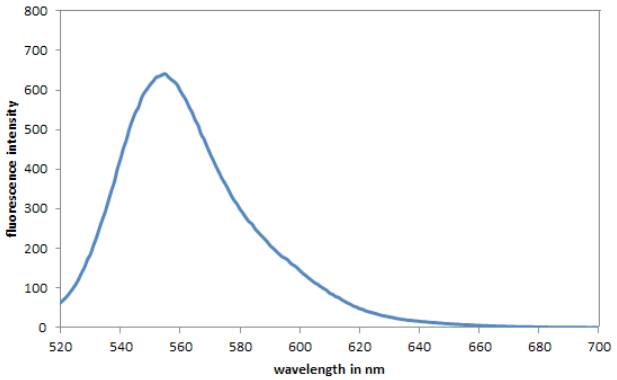

Figure 2. Fluorescence intensity of Bis(salysylaldehyde) benzidine.

arrangement[13]. In this study, the effect of pH on the spectral properties as shown in Figure 3. HCL and NaOH were used to study the effect of acidity on a fluorescence spectrum. Through the Figure it is clear that when the pH is reduced from 2 to 5 the fluorescence spectrum gradually increases. In pH 5 we combine the increase and stability of the fluorescence spectrum to the 7 point. After point 7, the intensity begins to decrease rapidly and continues to decrease to point 10. The PH range is noted suitable for the steadiness of title compound because of this acidic pH (5-7) the critical micelle concentration (CMC). Finally the intensity of fluorescence decreases rapidly until point 10. The highest and best value of intensity recorded at pH 6 is acidity which has been adopted in experimental measurements. This indicates that quantum efficiency is high at this point.

The optimal emission and excitation wavelengths of Bis(salysylaldehyde) benzidine in different solvents are determined and shown in Table 1.The emission intensity of Bis (salysylaldehyde) benzidine in different solvents are also shown in Figure 4. Through these results these results salysylaldehyde has the best intensity in THF solvent, Table 1 shows the calculation of the Stoke shift values in several different solvents as in literature[14]. A fluorescence sensor is influenced by several factors, one of which is Stoke shift. The high value of the stoke switch in the material leads to the reduction of undesirable signals which makes the material better in the fluorescence sensor. Bis (salysylaldehyde) Benzidine in THF solution shows the highest of Stoke shift(153 nm) compared to the other the solvents, but the other used solvents it has ΔλST values between (102-105) nm. This indicates that the usage of

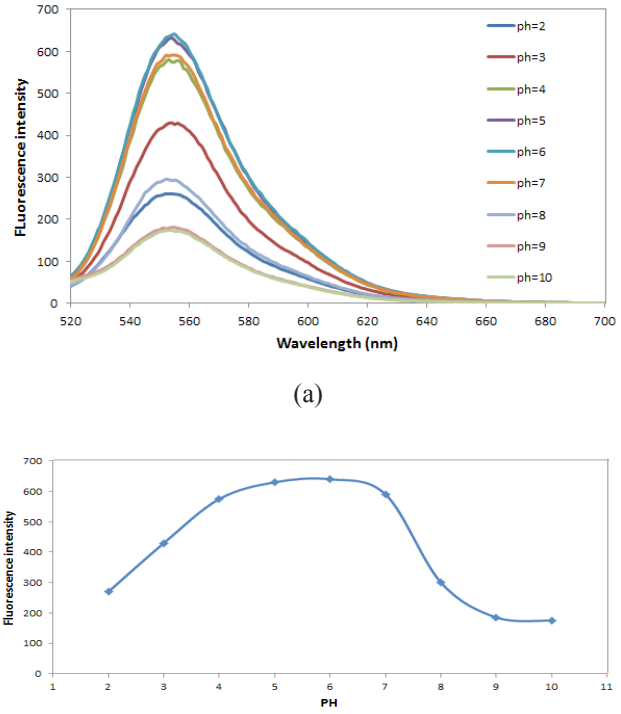

Figure 3. Fluorescence intensity of Bis(salysylaldehyde) benzidine at different pH.

Table 1. Fluorescence spectra related data of Bis (salysylaldehyde) benzidine

Solvent	λmax ($_{Ex}$)	λmax ($_{Em}$)	I ($_{Em}$)	$\Delta\lambda_{ST}$
THF	400	553	640	153
$CDCL_3$	428	532	575	104
Toluene	429	534	610	105
Acetone	427	529	270	102

Bis(salysylaldehyde) benzidine in as the sensor is useful in THF solution.

3.2 Fluorescence Response of Bis (salysylaldehyde) Benzidine to Cu^{2+}

Figure 5 demonstrates an examination of the extinguishing of fluorescence between Cu^{+2} and a few other metal ions. The tests were performed in 1×10^{-4} M Pb^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Ag^{+2} isolate arrangements each of which contain 2×10^{-5} M Bis (salysylaldehyde) benzidine in 1:1 (v:v) THF/deionized water blend The outcomes demonstrate that title compound has very brilliance extinguishing without Cu^{+2} particle. However, there is no wonderful phantom change on introduction to alter-

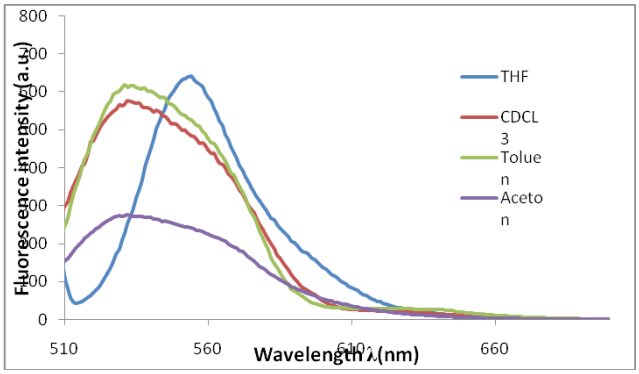

Figure 4. Emission spectra of Bis(2-hydroxy benzylidene) benzidinein in different solvents.

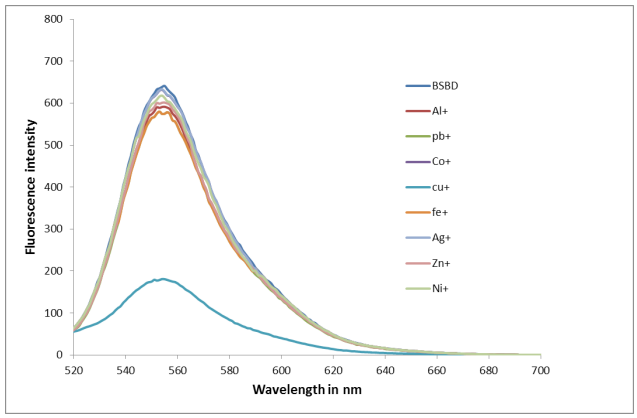

Figure 5. Fluorescence of Bis(salysylaldehyde) benzidine) with various metal ions.

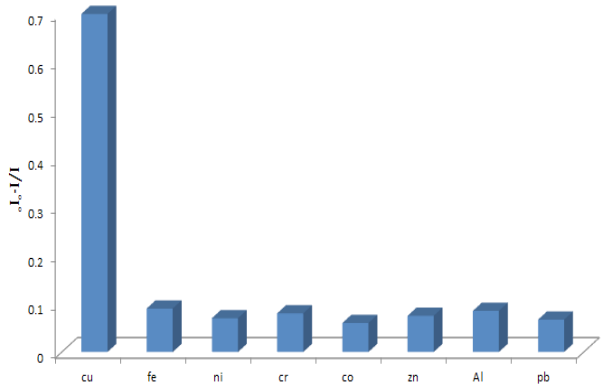

Figure 6. Response of Bis(salysylaldehyde) benzidine with different metal.

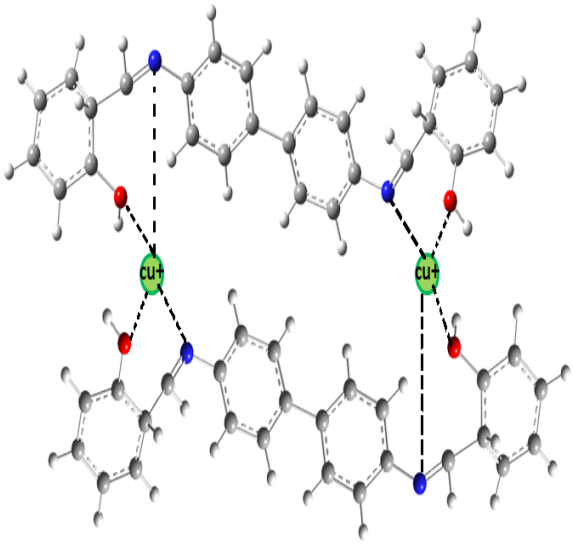

Figure 7. Structure of Cu^{+2} complex of title compound.

nate cations, which are the same thought the relative force changes with the tried particles are additionally appearing in Figure 6. The selectivity comes about demonstrating that Bis (salysylaldehyde) benzidine can be effortlessly unpredictable with Cu^{+2} particle is relied upon to resemble in the Figure 7. This Attribute to the title compound one of the imperative Schiff bases with two reasonable gatherings for framing coordination bonds with move metal cations: the hydroxyl group assembles and the azomethine nitrogen amass, it has great retention and discharge unearthly properties, which are changed when the legend Cu^{+2} complex is shaped. The great thermodynamic partiality of Cu^{2+}ion for ligands with N or O as chelating components and the sufficient energy of the coupling procedure (the lead of Irving– Williams) that can be realized on this response makes the Bis (salysylaldehyde) benzidine ligand fitting to be utilized as a fluorescene sensor for this metal. The selectivity for Cu^{2+} may be deciphered utilizing the geometrical distinction between the copper unpredictable and other metal edifices. As indicated by the run of Irving–Williams, among the significant paramagnetic metal particles, copper(II) has an especially high thermodynamic partiality for ordinary N, O-chelate ligands and quick metal-to-ligand restricting kinetics[15]. Although the other metal particles additionally can shape edifices, it is not as solid as that of

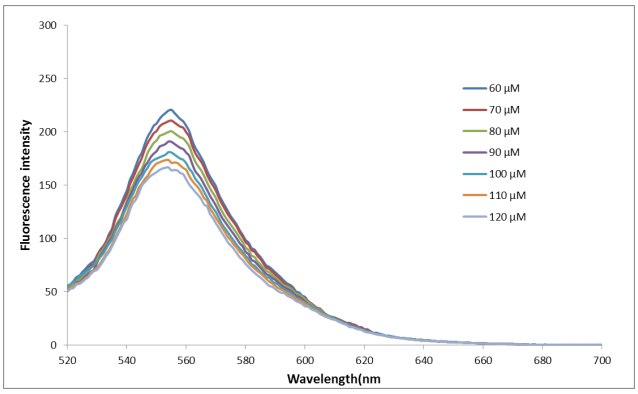

Figure 8. Fluorescence quenching spectra of Bis(salysylaldehyde) benzidine increasing concentration of Cu2+ion.

copper particles, prompting to the diminishing of fluorescence to just a specific degree[16].

The effect of increasing the concentration of copper metal added to the compound was studied as shown in Figure 8. The concentrations used were from 60 to 120 at room temperature. The fluorescence intensity of title compound reduces orderly without any spectral shift.

3.2.1 *Calibration Curve and Limit of Detection (LOD)*

Figure 9 shows the changes in fluorescence intensity (F_0/F) versus the Quantity of cu^{2+} ions. The fluorescence intensity quenching was studied by the relationship of the Stern–Volmer, which is shown by the following equation:

$$\frac{F_0}{F} = 1 + Ksv[Q]$$

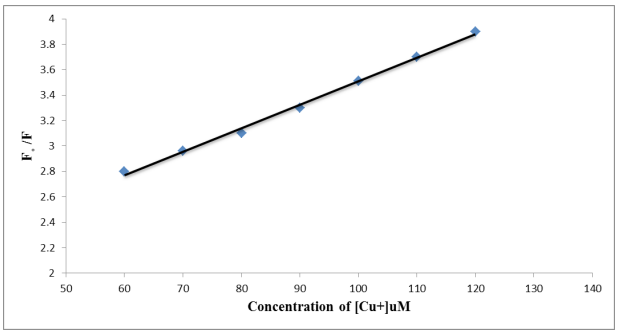

Figure 9. Fluorescence quenching with concentration (stern-volmer).

Where F the fluorescence intensities of the reagent in the existence of Cu and F_0 the fluorescence intensities of the reagent and without of Cu^{2+} ion. [Q] is Cu^{+2}concentration and K_{SV} is the Stern–Volmer quenching constant. In the system that follows the Stern-Volmer relationship, the relationship between the intensity of the presence of copper to the intensity without copper(F_0/F) and the concentration of copper is linear. This linear relationship does not continue to infinity. They change in high concentrations. The obtained experimental results for Cu^{2+}close-fitting, well to the following experimental equation: y = 0.0275x +1

The linear relationship in the range of 60 – 120 uM. The correlation coefficient is 0.9917. This results which obtained can be utilized as a new fluorescence sensor to detect the concentration of Cu^{+2} ion in any solution contingent on the relative intensity change. The limit of detection is studied by the next equation [17].

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

Where, K is the slope that is derived from the graph, σ is the standard deviation of the regression line. Now, the LOD was 1.96 µM. This means that the fluorescence quenching technique is highly sensitive and selective. This way is excellent of lower detection limit (LOD) with a broader linear variety of concentrations for Cu^{2+} over the other methods[18–21]. Table 2 shows a comparison between current method and other methods.

Table 2. Comparison Data of Cu^{2+} analysis

Detection method	LOD µM	References
10-(benzo[d]thiazol-2-yl)-2,3,6,7-tetrahydro-1H-pyrano[2,3-f] pyrido[3,2,1-ij]quinolin-11(5H)-imine(L)	2.39	21
Zinc porphyrin-dipyridylamino	1.5	19
2-hydroxybenzaldehyde benzoylhydrazone	5.6	18
L-cysteine-capped ZnS QDs	7.1	20
This Method	1.96	-

4. Conclusion

An aromatic compound with high spectral properties was synthesized N, N′ Bis (salysylaldehyde) Benzidine. The effect of different solvents on the fluorescence intensity of the resulting compound was studied. The effect of various solvents on fluorescence intensity was studied, the best solvent that can be used was Tetrahydrafuran. The effect of pH was very evident on the intensity of fluorescence. The best point was 5-7. This result of the PH value will increase quantum efficiency. Fluorescence intensities of N, N′ Bis (salysylaldehyde) Benzidine in several solvents were studied. Stoke's shift values in the several solvents showed that THF was the finest solvent to use N, N′ Bis (2-Hydroxy Benzylidene) Benzidine as fluorescent probes. The results obtained were excellent. A regression coefficient of 0.9917 was obtained as a result of the linear change. Experimental studies were carried out with selected transition metal ions those have the same concentration. It was discovered that Bis(salysylaldehyde) benzidine has quite greatest selectivity to Cu^{+2} ion. As a result, Bis(salysylaldehyde) benzidine Can be used as a good sensor for copper metal in the water medium.

5. References

1. Espada E, Galindo M, Vargas M, Narayanaswamy R. Selective Chemosensor for Copper Ions Based on Fluorescence Quenching of a Schiff-Base Fluorophore. Applied Spectroscopy. 2010; 64 (7):727–32. Crossref
2. Prodi L, Bolletta F, Montalti M, Zaccheroni N. Luminescent chemosensors for transition metal Ions. Coordination Chemistry Reviews. 2000; 205(1):59–83. Crossref
3. Martinez R, Sanceno F. Fluorogenic and chromogenic chemosensors and reagents for anions. Chemicl Reviews. 2000; 103(11):4419–76. Crossref
4. Bhalla V, Arora H, Kumar M . Aggregates of a triphenylene based chemosensing ensemble for sensitive detection of cyanide ion in an aqueous medium. Dalton Trans. 2013; 42: 4450–5 Crossref
5. Valeur B, Leray I. Design principles of fluorescent molecular sensors for cation recognition. Coord Chemical Reviews. 2000; 205:3–40. Crossref
6. Callan JF, Silva AP, Magri DC. Luminescent sensors and switches in the early 21st century. Tetrahedron. 2005; 61:8551–88. Crossref
7. Aksuner N, Henden E, Yılmaz İ, Çukurovalı A. Selective optical sensing of copper (II) ions based on a novel cyclobutanesubstituted Schiff base ligand embedded in polymer films. Sens Actuators B. 2008; 134: 510–5. Crossref
8. Li GK, Xu ZX, Chen CF, Huang ZT. A highly efficient and selective turn-on fluorescent sensor for Cu2+ ion based on calix[4] arene bearing four iminoquinoline subunits on the upper rim. Chem Commun. 2008; 15:1774–6. Crossref
9. Kim HJ, Park SY, Yoon S, Kim JS. FRET-derived radiometric fluorescence sensor for Cu2+. Tetrahedron. 2008; 64:1230–94. Crossref
10. Mu HL, Gong R, Ma Q, Sun YM, Fu EQ. A novel colorimetric and fluorescent chemosensor: synthesis and selective detection for Cu+2 and Hg+2. Tetrahedron Letter. 2007; 48: 5525–9. Crossref
11. Martinez R, Zapata F, Caballero A, Espinosa A, Tarraga A, Molina P. 2-Aza-1, 3-butadiene derivatives featuring an anthracene or pyrene unit: highly selective colorimetric and fluorescent signaling of Cu+2 cation. Org Letter. 2006; 8(5):3235–8. Crossref
12. Yuste R. Fluorescence microscopy today. Nat Methods. 2005; 2(12):902–4. Crossref
13. Yıldırım M, Kaya I. Synthesis of a Novel Fluorescent Schiff Base as a Possible Cu(II) Ion Selective Sensor. Journal of Fluorescence. 2010; 20(3):771–7. Crossref
14. Oter O, Ertekin K, Kılınçarslan R, Ulusoy M, Çetinkaya B. Photo characterization of a novel fluorescent Schiff base and investigation of its utility as an optical Fe+3 sensor in PVC matrix. Dyes Pigments. 2007; 74:730–5. Crossref
15. Bellido E, RiaNo M, Vargas M, Narayanaswamy R. Selective Chemosensor for Copper Ions Based on Fluorescence Quenching of a Schiff-Base Fluorophore. Applied Spectroscopy. 2010; 64(7):727–32. Crossref
16. Liang Z, Liu Z, Jiang L, Gao Y. A new fluorescent chemosensor for copper(II) and molecular switch controlled by light. Tetrahedron Letter. 2007; 48(9):1629–32. Crossref
17. Mahajan PG, Bhopate DP, Kolekar GB, Patil SR. N-methyl is at in nanoparticles as a novel probe for selective detection of Cd 2+ ion in aqueous medium based on chelation enhanced fluorescence and application to environmental sample. Sensor and Actuators B-Chemical. 2015; 220:864–72. Crossref
18. Bellido E, RiaNo M, Vargas M, Narayanaswamy R. Selective Chemosensor For Copper Ions Based On Fluorescence Quenching Of A Schiff-Base Fluorophor. Applied Spectroscopyvolume. 2010; 64(7):727–32. Crossref
19. Weng Y, Teng Y, Yue F, Zhong Y, Ye B. A new selective fluorescent chemosensor for Cu(II) ion based on zinc porphyrin-dipyridylamino. Inorganic Chemistry Communications. 2007; 10 (4):443–46. Crossref
20. Koneswaran M, Narayanaswamy R. l-Cysteine-capped ZnS quantum dots based fluorescence sensor for Cu2+ ion. Sens. Actuators. 2009; B 104, 139.
21. Li LQ. A Colorimetric and Fluorescent Chemosensor for Cu2+ Detection in Aqueous Solution. Inorganic, Metal-Organic, and Nano-Metal Chemistry. 2016; 46(12):1854–6. Crossref