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ORIGINAL ARTICLE

Coumarin Based Highly Selective "off-on-off" Type Novel Fluorescent Sensor for Cu^{2+} and S^{2-} in Aqueous Solution

Şükriye Nihan Karuk Elmas[1] · Furkan Ozen[2] · Kenan Koran[2] · Ibrahim Yilmaz[1,3] · Ahmet Orhan Gorgulu[2] · Serkan Erdemir[4]

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Abstract Solvent free synthesis of 6,7-dihydroxy-3-(3-chlorophenyl) coumarin (**CFHC**) was designed and obtained by the interaction of 2-(2,4,5-trimethoxyphenyl)-1-(3-chlorophenyl)acrylonitrile with pyridinium hydrochloride in the presence of silica gel by using microwave irradiation. The characterization of **CFHC** was confirmed by FT-IR, ^{1}H, ^{13}C, ^{13}C–APT and 2D HETCOR spectroscopy methods. The optical behavior of **CFHC** towards metal ions was investigated by UV-visible and fluorescence spectroscopy. **CFHC** showed "on–off" type fluorescence response towards Cu^{2+} with high selectivity in aqueous solution (CH_3CN/H_2O, 9/1, *v*/v). Once binding with Cu^{2+}, **CFHC**-Cu^{2+} complex also displayed high selectivity for sulfide, resulting in "off–on" type sensing of sulfide anion.

Keywords Coumarin · Fluorescent · Sensor · Copper · Sulfide

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✉ Ibrahim Yilmaz
iyilmaz@kmu.edu.tr

[1] Kamil Ozdag Science Faculty, Karamanoglu Mehmetbey University, 70100 Karaman, Turkey

[2] Science Faculty, Firat University, 23119 Elazıg, Turkey

[3] Kamil Ozdag Science Faculty, Karamanoglu Mehmetbey University, 70100 Karaman, Turkey

[4] Science Faculty, Selcuk University, 42075 Konya, Turkey

Introduction

In recent years, the preparation of fluorescent sensors for the recognition of heavy metal ions with high sensitivity and selectivity has received considerable attention because they play important role in environment and living systems [1–11]. Detection of the metal ions in aqueous is also essential. Copper is a very important trace element for the life of organisms. However, copper ions in abnormal levels can lead to diseases including Alzheimer's, Parkinson's, Menkes, Wilson's disease due to its oxidative and toxic effect [12–15]. So, there are many methods using several instruments for detection of copper ions including AAS [16], electrochemical [17, 18], colorimetric method [19, 20], etc. These techniques need expensive instrumentation and time consuming procedures that are important for sample pretreatment. Recently, the fluorescent methods have been paid great attention for the detection of the copper (II) ions. The detection of fluorescence offer several advantages including their simplicity, high-speed spatial analysis, high detection limit. Cu^{2+} usually leads to fluorescence quenching of the bound fluorophore due to its notorious paramagnetic nature, and this issue is generally regarded as a defect in fluorescent Cu^{2+} sensing [21–23]. However, the resultant fluorescence silent Cu^{2+}-fluorophore complex has potential applicability as a promising anion selective fluorescence turn-on sensor via anion induced Cu^{2+} displacement approach [24].

Sulfide is widely present in our daily life such as in pesticides, bleach, automobile exhaust, industrial waste gas, and corruption of organic matter [25]. Continuous and high concentration exposure of sulfide would lead to various physiological and biochemical problems. It can irritate the mucous membranes and even cause unconsciousness and respiratory paralysis [26, 27]. Once sulfide anion is protonated, it becomes even more toxic. Therefore, sulfide detection has also received considerable attention and a variety of detection strategies have

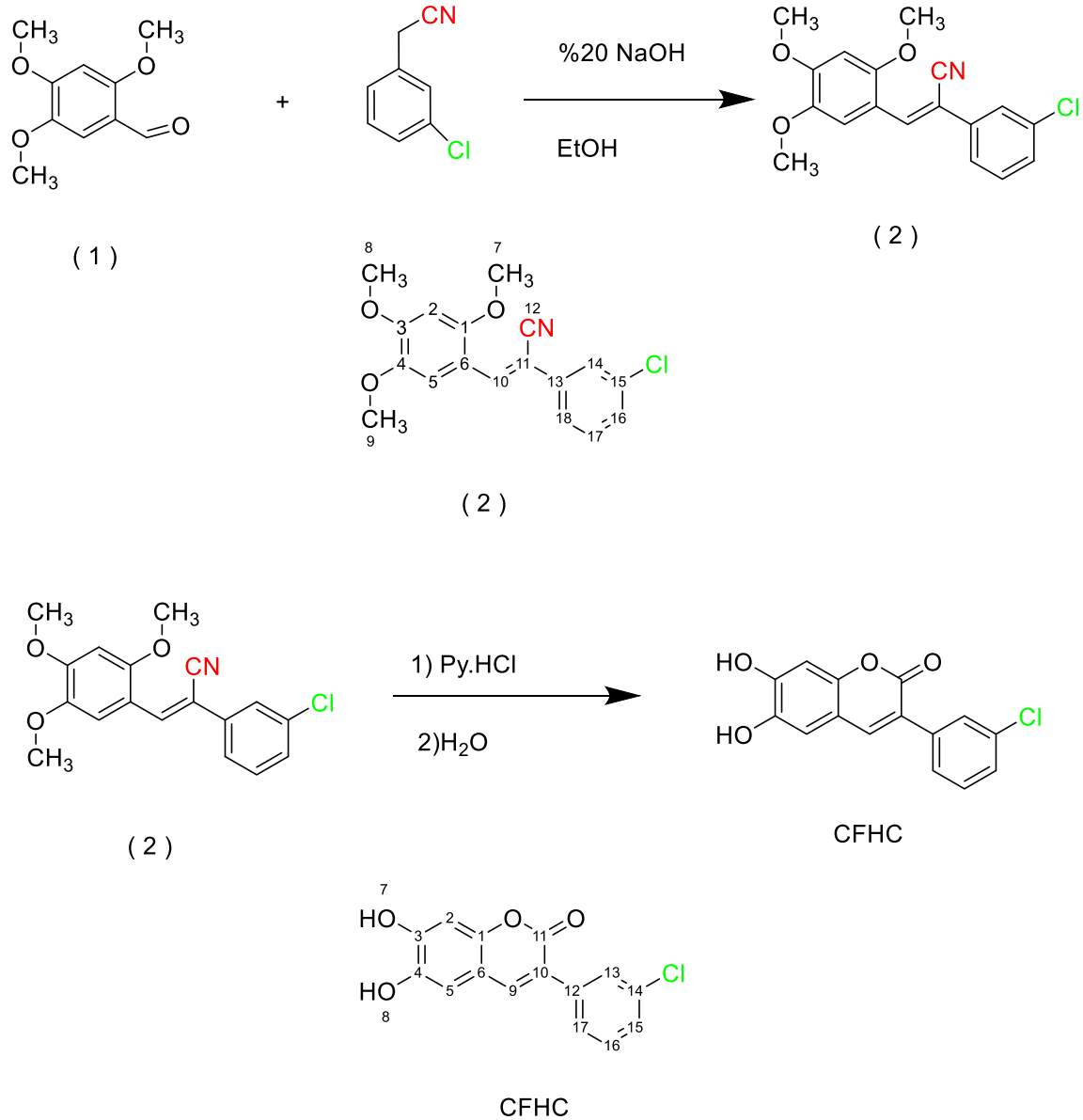
been developed for sulfide anions, such as spectroscopy, electrochemical methods, titration, ion chromatography, and chemiluminescence methods [28–33]. However, fluorescent recognition of sulfide in water solution still remains challenging because of the strong hydration nature of anions. To tackle this hurdle, employing sulfide selective probes based on Cu^{2+} displacement approach has been proved to be an effective method.

The coumarin ring is well known fluophore/chromophore in sensor studies due to its high photo-stability, large Stokes shift and intense fluorescence behavior in the blue-green region with high quantum yield [34–38]. Herein, we report the synthesis and spectroscopic investigation of 6,7-dihydroxy-3-(3-chlorophenyl)coumarin **(CFHC)** as a selective fluorescent probe for Cu^{2+} and S^{2-} ions. The binding behaviors of **CFHC** for cations were investigated by UV-vis and fluorescence spectroscopy. **CFHC** showed an effectively selective 'turn-off' fluorescence quenching for Cu^{2+} ion over metal ions to form new complex CFHC-Cu^{2+}. This complex indicated high sensitivity and selectivity for sulfide over other possible competitive anions, resulting in fluorescence enhancement in CH_3CN/H_2O (*v*/v, 9/1) at 455 nm.

Experimental

General

All the solvents and chemical reagents were provided from Merck and Sigma–Aldrich. Pyridinium hydrochloride was dried in the oven before use. FT-IR and NMR spectra were



Scheme 1 The synthesis of 6,7-dihydroxy-3-(3-chlorophenyl)coumarin (CFHC)

recorded on a Perkin Elmer spectrum one FT-IR and a Bruker DPX-400 spectrometer, respectively. For the NMR studies, the DMSO-d_6 was used as deuterated solvent. Positive ion and linear mode MALDI TOF-MS spectra were recorded MALDI matrix (in 1,8,9-anthracenetriol (20 mg/mL Tetrahydrofuran)) using nitrogen laser accumulating 50 laser shots. Elemental analysis was measured by a CHNS-932 (LECO) apparatus. Fluorescence spectra were determined on a Perkin Elmer LS 55 fluorescence spectrometer. Absorption spectra were determined on a *Perkin Elmer Lambda 25 UV-Vis* spectrophotometer using quartz cells of 1.0 cm path length.

Synthesis

2-(2,4,5-trimethoxyphenyl)-1-(3-chlorophenyl)acrylonitrile **(2)** was synthesized according to method in the literature [39].

Synthesis of 6,7-Dihydroxy-3-(3-Chlorophenyl)Coumarin (CFHC)

A mixture of 2-(2,4,5-trimethoxyphenyl)-1-(3-chlorophenyl) acrylonitrile **(2)** (1 g, 3.03 mmol), 15 g silica gel and pyridinium hydrochloride (5 g) was stirred under solvent free conditions. The reaction mixture was continued at 320 watt for 25 min under microwave irradiation. After the reaction reached completion, it was quenched with acidified with 1 M HCl (150 mL) and then the mixture filtered. The residue was dissolved in acetone (4 × 25 mL) and it was separated by filtration through silica gel. Acetone was evaporated on a rotary evaporator under reduced pressure. The solid washed with water many times and dried under vacuo. The obtained solid was resolved in ethyl acetate (10 mL) and precipitated with n-hexane (200 mL). The crude solid was purified to column chromatography using chloroform:hexane and then analyzed. A Fawn colored solid (**CFHC)** obtained (0.79 g, 90%), Anal. Calc. for $C_{15}H_9FO_4$ (MW: 288.68): C, 62.41; H, 3.14; Found C, 62.40, H; 3.13%. FT-IR (KBr, cm^{-1}): 3368, 3170 $\nu_{O\text{-}H}$, 3060 $\nu_{C\text{-}H(Ar)}$, 1662 $\nu_{C=O}$, 1622, 1600, 1579 $\nu_{C=C}$. ^{1}H NMR (400 MHz, DMSO-d_6):δ6.79 (1H, s, H^5), 7.07 (1H, s, H^2), 7.49 (1H, d, J = 8.4 Hz, H^{15}), 7.51 (1H, t, J = 8.0 Hz, H^{16}), 7.73 (1H, s, H^9), 7.76 (1H, d, J = 6.8 Hz, H(^{17}), 8.16 (1H, s, H^{13}), 9.55 (1H, s, H^7), 10.36 (1H, s, H^8). ^{13}C–NMR (400 MHz, DMSO-d_6):δ102.69 C^2, 111.89 C^6, 112.94 C^5, 121.27 C^{10}, 128.61 C^{13} and C^{17}, 130.49 C^{15} and C^{16}, 132.98 C^{12}, 134.64 C^{14}, 141.93 C^9, 132.22 C^{15}, 143.61 C^1, 148.66 C^4, 151.22 C^3, 160.65 C^{11}. MALDI-MS: m/z calc.288.68; found: 288.372 $[M]^+$ and 310.474 $[M + Na]^+$.

UV-Vis/Fluorescence Experiments

The stock solutions of the **CFHC** (10 mM) in CH_3CN-H_2O (9/1, *v*/v) and guest cations/anions (10 mM) in H_2O were prepared. The volume of **CFHC** receptor solution used in the UV-vis and fluorescence measurements was 3.0 mL. Absorption and fluorescence spectra were obtained by adding various amounts of cation solution to the **CFHC** solutions. For **CFHC**, the excitation wavelength was determined as 360 nm.

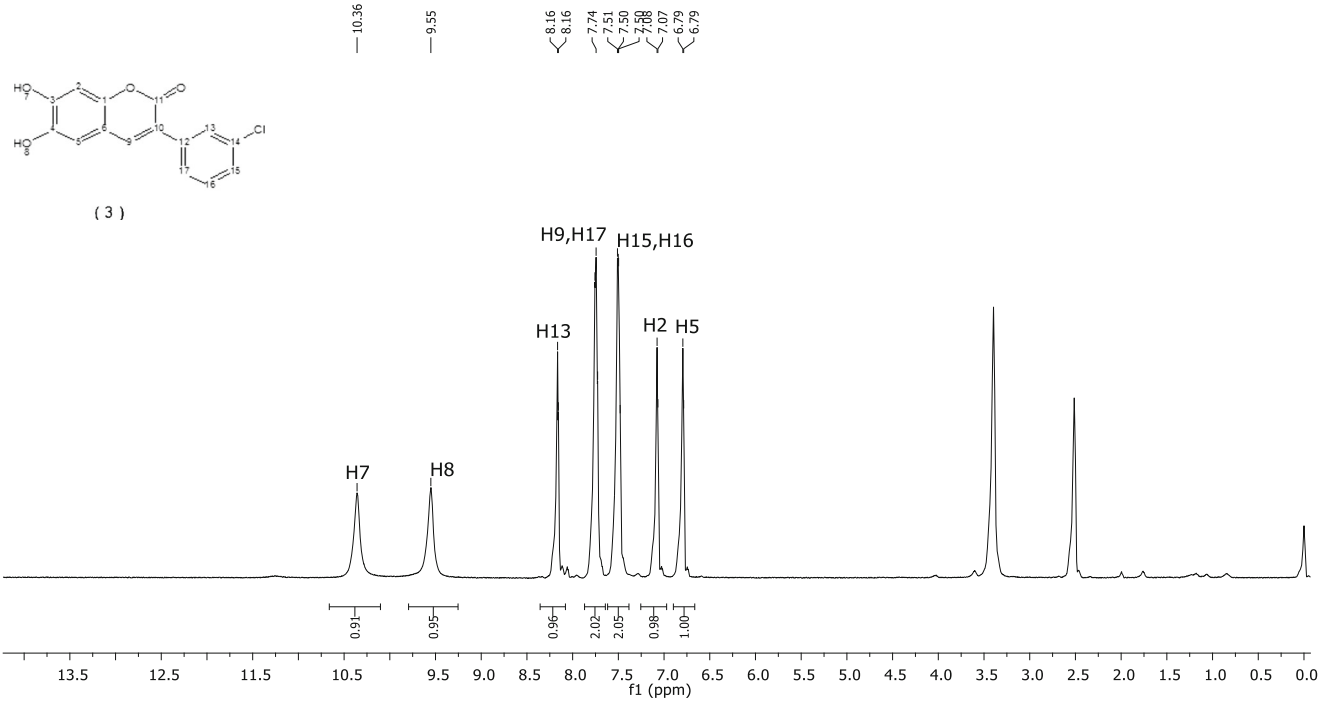


Fig. 1 ^{1}H NMR spectrum of **CFHC**

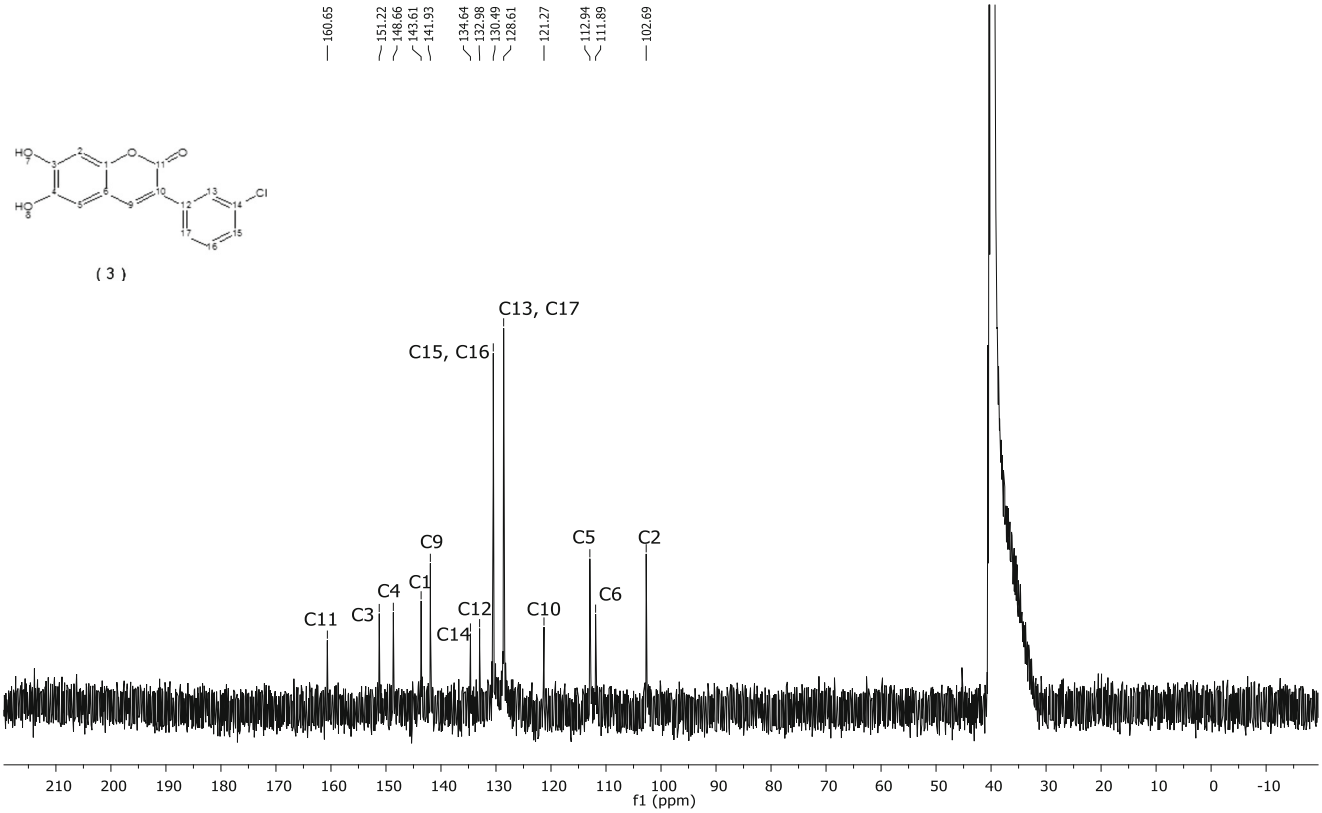


Fig. 2 ^{13}C NMR spectrum of **CFHC**

Results and Discussion

Synthesis

6,7-dihydroxy-3-(3-chlorophenyl)coumarin **(CFHC)** was obtained at excellent yield that from the reaction of **2** with pyridinium hydrochloride in the presence of silica gel as support material by using microwave irradiation under solvent free conditions. The crude solid was purified to column chromatography. General synthesis procedure of compounds is displayed in Scheme 1. The characterization of all compounds have been made by a combination of FTIR, elemental analysis, ^{1}H, ^{13}C, ^{13}C–APT, 2D HETCOR NMR and MALDI-TOF-MS techniques (Supplementary data, Figs. S1–S11). The nitrile peaks (−C ≡ N) in the structure of compound **2** were not observed at infrared spectra of compound **CFHC**. The methoxy groups in the compound **2** were converted to hydroxyl groups. The presence of OH stretching

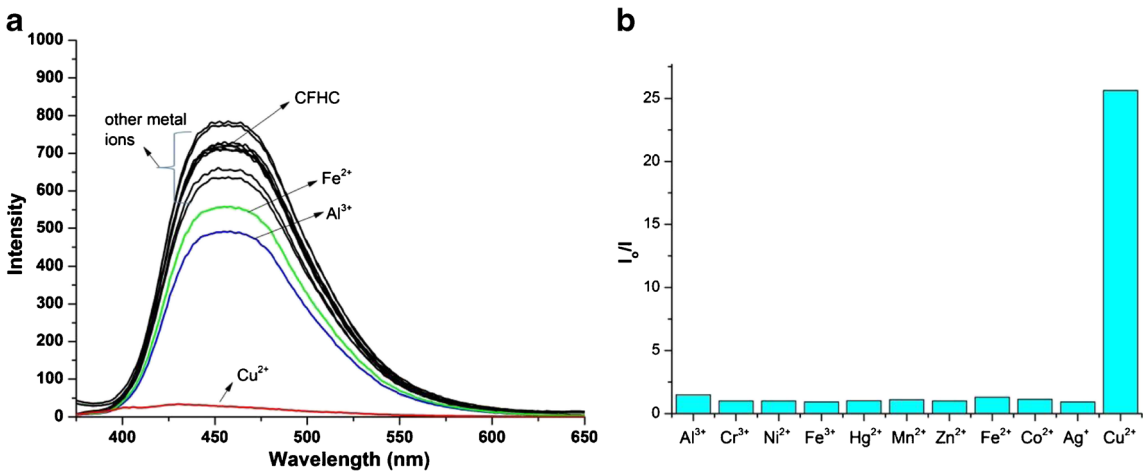


Fig. 3 **a** Fluorescence spectra recorded by addition of various metal ions (5.0 eq.) to **CFHC** (0.5 μM) **b** Changes in the fluorescence intensity ratio (I_o/I) of **CHFC** in the presence of various metal ions at 455 nm in CH_3CN/H_2O (90:10, *v*/v)

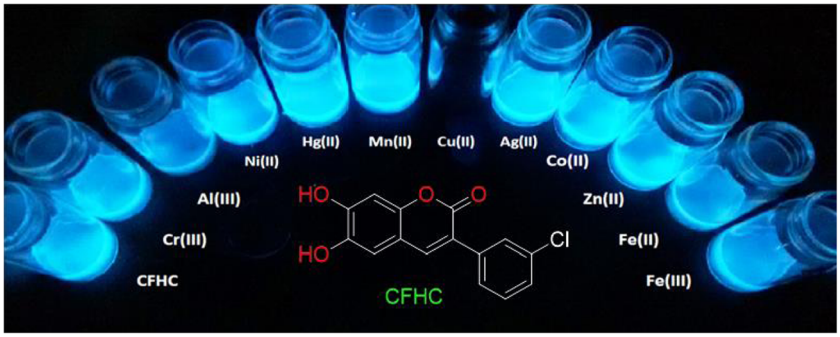


Fig. 4 A selective visual fluorescence change upon addition of a selective visual fluorescence change upon addition of Cu^{2+} ion to **CFHC** solution over other various metal ions various metal ions(5.0 eq.) to **CFHC** solution

vibration in the FT-IR spectra of compound **CFHC** proves that methoxy groups in the compound **2** and converted to hydroxyl groups. The OH stretching vibration for **CFHC** was observed at 3368 and 3170 cm^{-1}. The -C = O stretching vibrations in the lactone ring, which are observed at 1662 cm^{-1}, is characteristic for coumarin compound. (Figure S1 and S5). The methoxy protons were not observed at ^{1}H NMR spectrum of coumarin compound (**CFHC).** ^{1}H NMR and ^{13}C NMR spectra of CFHC were depicted in Figs. 1 and 2. The –OH protons in the structure of **CFHC** (7 and 8 number protons in the Scheme 1) were observed at 9.55 and 10.36 ppm. In addition, the ratio of the protons integral height in the ^{1}H–NMR spectra supports the proposed structures. As seen in Fig. 2, the lactone -C = O carbon peak (C^{11}) for **CFHC** was observed at 160.65 ppm. In addition, the places of primary, secondary and tertiary carbon atoms were supported with ^{13}C–APT NMR technique. Furthermore, the directly-bonded proton-carbon atoms were determined with the 2D Heteronuclear Chemical-Shift Correlation (HETCOR) technique (Supplementary data).

Spectral Studies of CFHC

The sensing ability of **CFHC** was investigated with the help of UV–vis and fluorescence experiments in presence of various metal ions (Al^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Ag^{+}, Cu^{2+}) in CH_3CN-H_2O (*v*/v, 9/1). The fluorescence properties of **CFHC** were investigated in the presence of 5.0-fold excess of different metal ions. The fluorescence spectra were observed at 455 nm (excitation: 360 nm) for **CFHC** (Fig. 3a). As can be seen in Fig. 3a, **CFHC** gave rise to a marked Cu^{2+} fluorescence quenching as compared with other metal ions. The prominent fluorescence was completely quenched by Cu^{2+} ion, indicating strong complex formation with this cation. This selectivity is due to the fact that although transition metals do not differ too much in size, they can establish coordinative interactions at very different energies which can be used for discriminative purposes, especially for fluorescent sensing [40]. This phenomenon is consistent with copper that occurs highest on the Irving–Williams series. However, the addition of other metal ions did not lead to significant

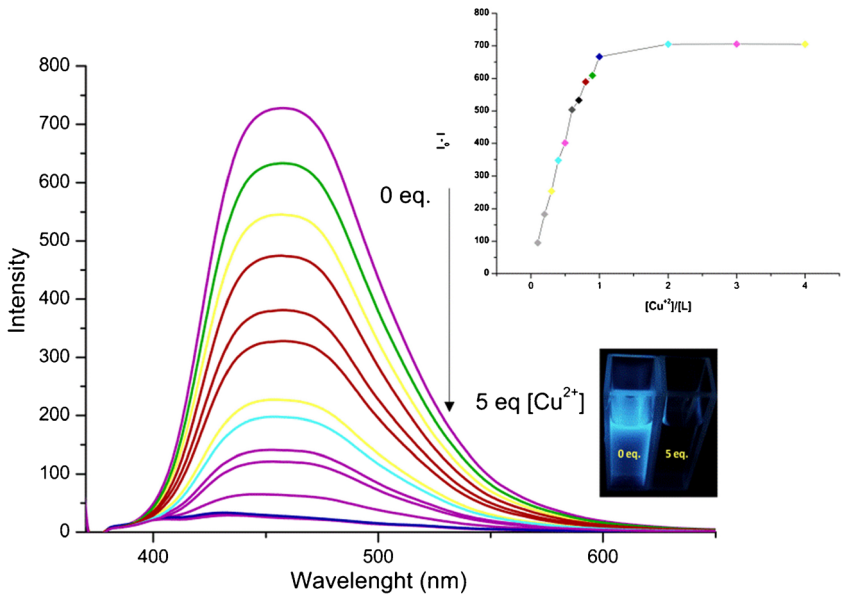


Fig. 5 Fluorescence response of **CFHC** (0.5 μM) with the addition of various amounts of Cu^{2+} (0–5.0 equiv.) in CH_3CN/H_2O (90:10, *v*/v)

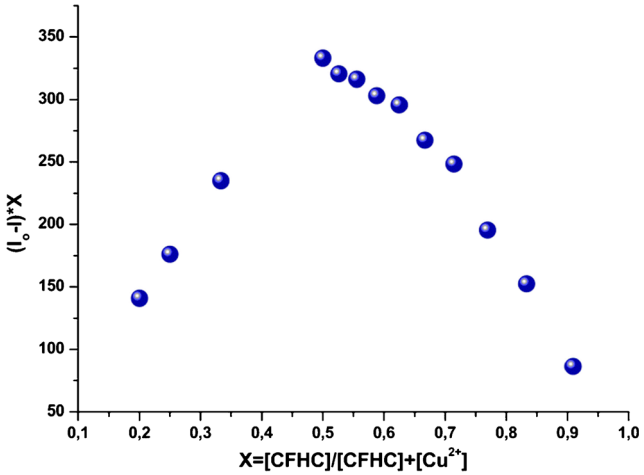


Fig. 6 Job's plot for CFHC and Cu^{2+} complexation in CH_3CN/H_2O (9/1, *v*/v) solution

fluorescence changes, only Fe^{2+} and Al^{3+} caused partially decreases of fluorescence emission, indicating that **CFHC** allowed selective fluorescence quenching against Cu^{2+} (Fig. 3b). The quenching efficiency of **CFHC** as expressed by the ratio (Io/I) of fluorescence intensity in the absence (I_o) and presence (I) of metal ions at 455 nm was 25.6 for Cu^{2+}, and the ratios for other metal ions varied in a relatively limited range from 0.93 to 1.48 (Fig. 3b). Moreover, we observed a selective visual fluorescence change upon addition of various metal ions to **CFHC** solution (Fig. 4).

The fluorescence titrations were also realized by adding the increasing amounts of Cu^{2+} to a solution of **CFHC** (0.5 μM), and remarkable fluorescence decrease was detected (Fig. 5). Figure 5 shows the changes in fluorescence spectra of **CFHC** upon titration with Cu^{2+} (0.0–5.0 equiv). The fluorescence intensity of **CFHC** decreased gradually when the amount of Cu^{2+} was increased stepwise. When 5.0 equiv. of Cu^{2+} was added to solution of **CFHC** (0.5 μM), the signal at 455 nm was almost completely quenched (Fig. 5). Job's method for the determination of the binding stoichiometry of **CFHC** and Cu^{2+} were utilized and shown in Fig. 6. The emission intensity at 455 nm is plotted against the molar fraction of Cu^{2+} ion and a maximum value of the graph is about 0.5, indicating that 1:1 stoichiometry. Using the fluorescence titration data, the binding constant of **CFHC** with Cu^{2+} in CH_3CN-H_2O was found to be $0.8 \times 10^6\ M^{-1}$ according to Benesi–Hildebrand plot [41] (Fig. S12). Fluorometric titration data were also used to obtain the detection limit of **CFHC** for Cu^{2+}. The fluorescence intensity at 455 nm was plotted as a function of the Cu^{2+} concentration. The detection limit of **CFHC** toward Cu^{2+} cation found to be 33.2 nM (based on S/*N* = 3) (Fig. S13). Moreover, the quantum yield (Φ) measurements for CFHC and CFHC-Cu^{2+} complex were carried out at different concentrations in CH_3CN/H_2O (*v*/v, 9/1). CFHC (Φ = 0.212) indicated about 8 times higher Φ value than that of CFHC-Cu^{2+} complex (Φ = 0.027) (Fig. S14). On the other hand, we performed UV–vis experiments to evaluate the binding affinity of **CFHC** towards metal ions. Absorbance spectra of complex [**CFHC** + metal ion] recorded after the addition of each metal ion (5.0 equiv.) is shown in Fig. 7a. On addition of other species no significant modulation in the UV–vis absorption spectra was observed thus, showing the specificity of the chemosensor for selective binding interaction with Cu^{2+} ion. Figure 7b shows the UV–vis absorption spectra of the mixture of a solution of **CFHC** and the solutions of Cu^{2+} with different concentrations. The UV-vis absorption spectra of **CFHC** is dominated by absorption bands at 265, 310 and 365 nm in the absence of cations which could be attributed to π–π* and n–π* transitions. Upon the addition of Cu^{2+}, while the absorption peak at 310 and 365 nm were decreased correspondingly, new absorption band was observed at about 420 nm which means **CFHC** and Cu^{2+} form 1:1 complex (Fig. 7b). The color of **CFHC** solution change from colorless to yellow after the addition of Cu^{2+} while other cations did not induce any color changes.

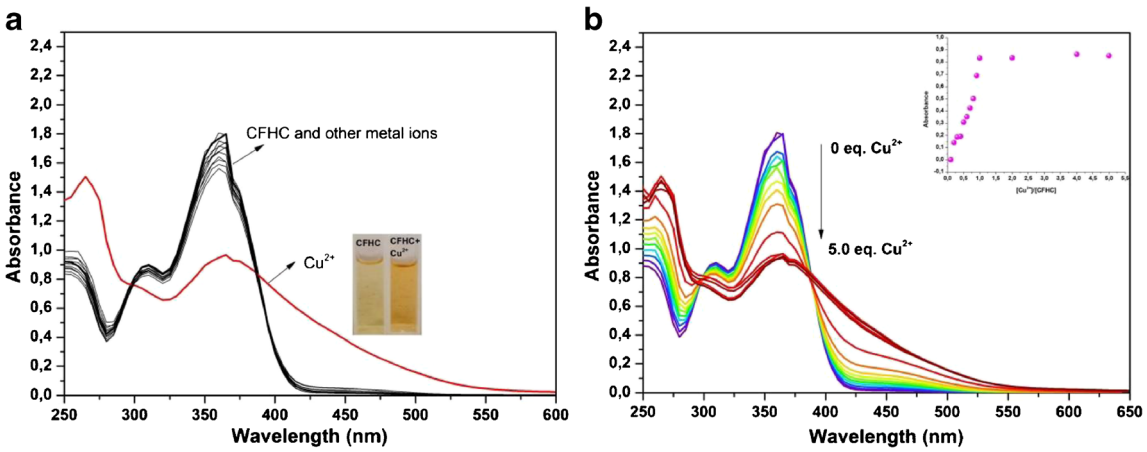


Fig. 7 **a** UV–vis absorption spectra obtained by addition of various metal ions (5.0 equiv.) **b** UV–vis titration spectra recorded by addition of Cu^{2+} (0–5 eq) to) to CFHC in CH_3CN/H_2O (9/1, *v*/v)

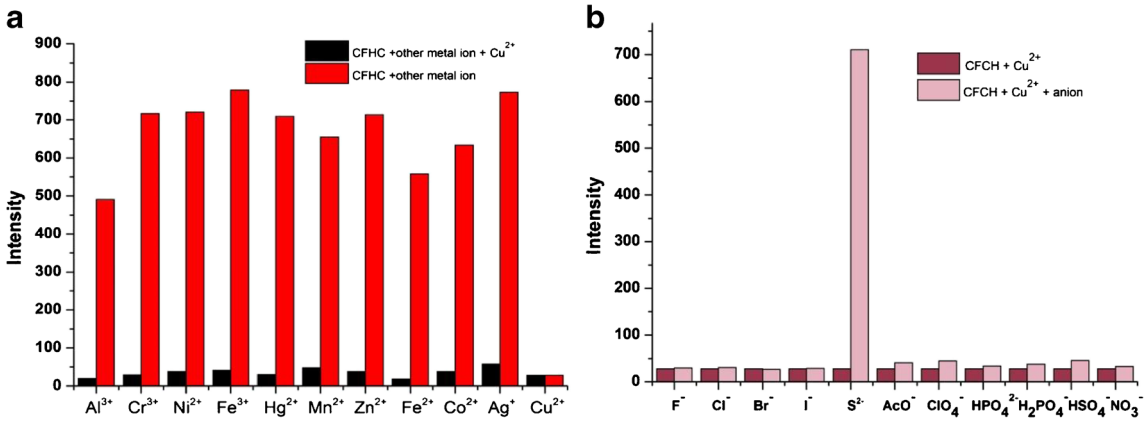


Fig. 8 Fluorescence responses of CFHC (0.5 μM) to Cu^{2+} in the presence or absence of other competition metal ions **a** and anions **b** in CH_3CN/H_2O (*v*/v, 9/1)

To utilize **CFHC** as a selective sensor for Cu^{2+}, the effect of competing metal ions has been examined by recording the fluorescence spectra of **CFHC** (0.5 μM) with Cu^{2+} (1.0 equiv.) in the presence of a competing metal ion (5.0 equiv). As seen in Fig.8a, Cu^{2+} ion detection by **CFHC** is not influenced by the presence of other competing metal ion. Therefore, Cu^{2+} can be easily detected in the presence of most competing metal ions through fluorescence 'turn off' behavior. Also, we tested various anions for their potential interfering effects in the fluorescence spectroscopy measurements. The competition experiments were realized by adding various anions, namely, F^-, Cl^-, Br^-, I^-, S^{2-}, AcO^-, ClO_4^-, HPO_4^{-2}, $H_2PO_4^-$, HSO_4^- and NO_3^- to CH_3CN-H_2O (*v*/v, 9/1) solution containing **CFHC**–Cu^{2+} complex. When a solution of S^{2-} anion (1.0 equiv) was added to a solution containing **CFHC** and Cu^{2+} ions (1.0 equiv), an increase in the intensity of the peak at 455 nm was observed due to the high affinity of sulfide to Cu^{2+} ion [42]. Under the same conditions, slightly changes occurred when 1.0 equiv. of the other anions was added, as shown in Fig. 8b.

The reversibility of a sensor is particularly attractive property for practical application. Therefore, we realized the reversibility experiments of **CFHC** by the alternate addition of Cu^{2+} and S^{2-} ions based on the obtained results in Fig. 8b. The interaction between S^{2-} and **CFHC**–Cu^{2+} system was reversible. This reversibility can be verified by the addition of Cu^{2+} to solution containing S^{2-} and **CFCH**–Cu^{2+} complex. The results indicated that the addition of Cu^{2+} could immediately restore the fluorescence intensities of **CFCH**–Cu^{2+}–S^{2-} system. When S^{2-} was added to the solution again, the fluorescence of solution was enhanced. This reversible process could be repeated several times with little fluorescent efficiency loss (Fig. 9a). As known, the response time for many fluorescent sensors is also very important. Thus, the effect of the reaction time on the binding process of Cu^{2+} ion to **CFHC** was investigated as shown in Fig. 9b. Following the addition of 1.0 equiv. Cu^{2+} ion to **CFHC** solution (0.5 μM), the fluorescence intensity of **CFHC** reached a stable value within 20 s and remaining constant from 20 s to 5 min Thus, a reaction time of 20 s may be used for this system.

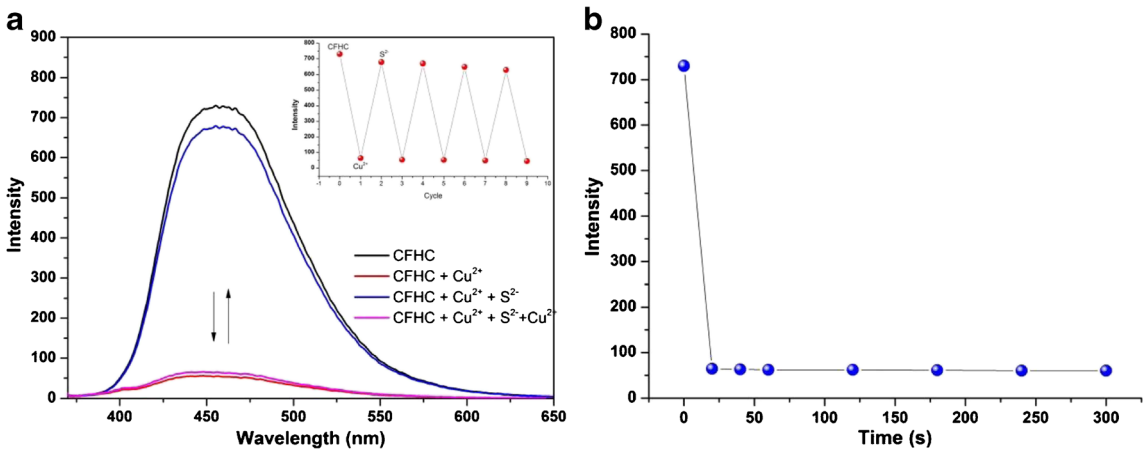


Fig. 9 **a** Fluorescence spectra showing reversibility of Cu^{2+}coordination to CFHC by sulfide (S^{2-}) **b** Fluorescence decreasing profile of addition Cu^{2+} to CFHC (0.5 μM) in in CH_3CN/H_2O (*v*/v, 9/1) from 0 to 5 min

Conclusion

In conclusion, we designed a novel coumarin based fluorescent probe (CFHC) which is employed as a naked-eye and "turn-off" sensor for Cu^{2+} in aqueous solution. Interaction of CFHC with Cu^{2+} induced completely quenching of fluorescence intensity through a 1:1 binding mode. The complexation process for Cu^{2+} gave rise to color changes from blue to colorless. The system showed a detection limit as low as 33.2 nM toward Cu^{2+} with high selectivity and sensitivity. The formed CFHC-Cu^{2+} complex in solution also indicated high sensitivity to sulfide anions via Cu^{2+} displacement approach. This "on–off–on" type fluorescence recognition system was a reversible process that could be repeated several times with little fluorescence intensities loss. These properties make CFHC suitable for the direct and rapid detection of Cu^{2+} and sulfide ions.

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