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A Flavone Fluorescent Probe for Cysteine Detection

SALEH N. AL-BUSAFI*, SALMA M. AL-KINDI, FAKHR ELDIN O. SULIMAN and ALIYA A. AL-KALBANI

Department of Chemistry, College of Science, Sultan Qaboos University, B.O. Box: 36, Al-Khodh-123, Sultanate of Oman

*Corresponding author: Fax: +968 24141469; Tel: +968 24142305; E-mail: saleh1@squ.edu.om

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A new blue-emitting fluorescent probe **1** based on flavone structure was prepared for the selective detection of cysteine. The probe was prepared through three synthetic steps from commercially available starting materials. Selective detection of cysteine by probe **1** in the presence of other non-thiol amino acids was established by UV-visible and fluorescent experiments. A remarkable fluorescence emission was observed at 469 nm when cysteine was mixed with probe **1**. The Michael addition reaction of cysteine to probe-**1** was confirmed by ^{1}H NMR technique.

Keywords: Cysteine, Fluorescent, Flavone, Michael addition reaction.

INTRODUCTION

Alongside its vital structural task in proteins and enzymes by making disulfide bridges, cysteine plays key role in numerous biological processes such as participating in cellular growth, promoting antioxidant defense system and enhancing the immune system [1-3]. In addition, diet supplemented with cysteine was found to induce senescence and decelerate cell growth in melanoma [4]. The deficiency of cysteine has been linked to many diseases, for instance, slow child growth, loss of hair colouring, liver damage and weakness [5]. On the other hand, high level of cysteine can cause many health problems such as Parkinson′s disease, neurotoxicity and cardiovascular difficulties [6-8]. Accordingly, there is a growing interest in scientific community to explore innovative methods for selective detection and determination of trace amounts of cysteine in biological samples. Several classic analytical techniques were used to detect cysteine such as HPLC, GC-MS, UV-visible spectroscopy and electrochemical assay [9-12]. During the last decade, a new analytical technique based on fluorescent probes has been developed and tested for cysteine detection and quantification in physiological solutions. The strength of this detection method is based on many attractive merits such as simplicity, versatility, selectivity, low detection limit and inexpensive [13-23].

Numerous fluorescent molecular probes for cysteine have been designed using different anchoring mechanisms such as Michael reaction, ligand displacement by thiol in metal complex, cyclization reaction with aldehyde, cleavage of sulfonamide, formation of thiazolidine, and formation of iminium ion [24-29]. Due to their high reactivity and sensitivity towards thiol group, Michael acceptors become an appealing anchoring method for thiols in many of the recent designed fluorescent molecular probes [30]. Such high reactivity is stimulated by the robust nucleophilicity of thiol group and the electron-poor Michael acceptor component. The pronounced fluorescence sensitivity of these probes is attributed to the inhibition of intramolecular charge transfer mechanism (ICT) that occurs in the chromophore fragment after breaking the double bond [31]. Different α,β-unsaturated Michael acceptors have been used in fluorescent probes such as ester, ketone, nitrile [32-34]. Nitroolefin moiety is known for its selective reaction with thiol through Michael addition reaction by breaking the C=C double bond [35]. As a result, the fluorescence is quenched in its conjugate form, but not in its thiol adduct.

Moreover, various molecular frameworks were used as fluorescent entity such as cyanine, coumarin, acrylate, pyrene, fluorescein and napthalimide [36-41]. Although most flavonoid compounds exhibit fluorescence when excited with visible or UV-light due to the presence of rigid, flat rings with delocalized π-electrons, reports that describe using them as fluorescent molecular probes are scarce [42]. Literature investigation shows that synthetic diethylamino substituted flavonol has been

utilized as a turn-on fluorescent probe to analyze cysteine [43]. Recently, flavonol (3-hydroxyflavone) was investigated for various metal ions detection in aqueous samples [43,44]. In this work, a novel fluorescent molecular probe **1** based on flavone skeleton was synthesized in three synthetic steps starting from 4-formylbenzyol chloride (**2**). The probe is equipped with nitro-olefin moiety as a Michael acceptor to selectively detect cysteine and with electron-withdrawing chlorine atom at position 6 (Fig. 1).

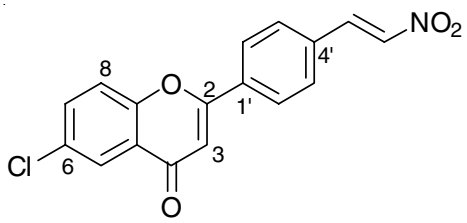


Fig. 1. Structure of **1**

EXPERIMENTAL

All the chemicals and solvents used in this study were obtained from Sigma-Aldrich Chemical Company and used without further purification. Melting point of prepared compounds was determined using Gallenkamp-MPA350 melting point apparatus. The purity of the compounds was checked by TLC and analyses were carried out on 0.25 mm thick pre-coated silica plates (Merck Fertigplatten Kieselgel 60F_{254}). Column chromatography was performed using Merck silica gel 60 (40-63 µm). IR spectra were obtained by a Cary 630 FTIR spectrometer (Agilent Technologies, USA). ^{1}H NMR and ^{13}C NMR spectra were recorded using 700 MHz Bruker Avance spectrometer (Bruker Corp., USA). Chemical shift (δ) are expressed in parts per million (ppm) relative to TMS as internal standard and the values of coupling constant (*J*) was measured in Hz unit. Mass spectra were obtained by using a Quattro Ultima Pt tandem quadruple mass spectrometer (Waters Corp. MA, USA). A Shimadzu, (model multispec-1501) UV-Vis spectrophotometer was used to measure UV spectra and reported as λ_{max} in nm. Fluorescence spectra were recorded on a Perkin Elmer LS55 Luminescence spectrometer.

Synthesis of 2-acetyl-4-chlorophenyl 4-formylbenzoate (3): A solution of 4-formylbenzoyl chloride (**2**) (5.6 g, 33.6 mmol) and 5-chloro-2-hydroxyacetopenone (5.68 g, 33.6 mmol) in pyridine (40 mL) was heated for 5 h at 80 ºC. After cooling to room temperature, the reaction mixture was poured into a 250 mL beaker containing 60 g of ice. The product was extracted with (4 × 30 mL) dichloromethane. The collected organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with 8:2 (hexane:ethyl acetate) to produce compound **3** as white solid (5.9 g, 57.5 %); m.p.: 119.3-119.5 ºC; IR (neat) λ_{max} in cm^{-1}: 3050 (C-H arom.),1738 (C=O, ester), 1693 (C=O), 1537 (C=C), 1202 (C-O); ^{1}H NMR (700 MHz, $DCCl_3$) δ in ppm: 10.10 (s, 1H,), 8.34 (d, 2H, *J* = 8.3 Hz), 8.03 (d, 2H, *J* = 8.3 Hz), 7.83 (d, 1H, *J* = 2.6 Hz), 7.56 (dd, 1H, J_1 = 2.6 and J_2 = 8.5 Hz), 7.21 (d,1H, *J* = 8.5 Hz), 2.51 (s, 3H); ^{13}C NMR (127.9 MHz, $DCCl_3$), δ in ppm 195.99 (C=O), 191.46 (HC=O), 164.09 (C=O, ester), 147.43 (C), 139.76 (C), 133.86 (C), 133.36 (CH), 132.05 (C), 131.89 (C), 130.91 (2 × CH), 130.33 (CH), 129.73 (2 × CH), 125. 34 (CH), 29.3 (CH_3); 109.2. MS (ESI) *m/z* calcd. for $C_{16}H_{11}O_4Cl$ 303; found 303.

Synthesis of 6-chloro-4′-formylflavone (4): Compound **3** (5.9 g, 19.5 mmol) was dissolved in pyridine (21 mL) at 50 ºC. Then, finely powdered KOH (1.8 g, 32.1 mmol) was added to the mixture. The reaction mixture was stirred for 1.5 h at 50 ºC. A brown solid appeared. After cooling, aqueous acetic acid solution (10 %) was added to the reaction mixture and the resultant yellow solid was filtered under vacuum using Buchner funnel. The product was dried under vacuum. The resulted intermediate was dissolved in a mixture of acetic acid (24 mL) and H_2SO_4 (0.73 mL) and heated under reflux for 2 h. The cold reaction mixture was poured into ice-water and the resulted solid was collected by Buchner filtration and washed by water. The product was purified by recrystallization using hot ethanol to produce brown solid (5.1 g, 80.1 %); m.p.: 117.5-119.4 ºC; IR (neat) λ_{max} in cm^{-1}: 3096 (C-H arom.), 1701 (C=O), 1637 (C=O), and 1603,1560 (C=C), 1214 (C-O), 800 (C-Cl); ^{1}H NMR (700 MHz, $DCCl_3$) δ in ppm: 10.12 (s, 1H,), 8.19 (d, 1H, *J* = 2.7 Hz), 8.09 (d, 2H, *J* =8.5 Hz), 8.05 (d, 2H, *J* =8.5 Hz), 7.68 (dd, 1H, J_1 = 2.7 and J_2 = 8.8 Hz), 7.57 (d,1H, *J* = 8.8 Hz), 6.91 (s, 1H); ^{13}C NMR (127.9 MHz, $DCCl_3$), δ in ppm: 191.59 (HC=O), 177.41 (C=O), 162.63 (C), 154.73 (C), 138.45 (C), 136.87 (C), 134.59 (CH), 131.82 (C), 130.54 (2 × CH), 127.13 (2 × CH), 125.16 (CH), 125.01 (C), 120.06 (CH), 109.23 (CH); MS (ESI) *m/z* calcd. for $C_{16}H_9O_3Cl$ 284; found 284.

Synthesis of 6-chloro-4′-(2-nitrovinyl)flavone (1): A mixture of compound **4** (1.9 g, 6.69 mmol), ammonium acetate (1.17 g, 15.2 mmol), nitromethane (12.78 mL, 14.53 g, 0.24 mol) and acetic acid (18 mL) was heated under reflux at 150 ºC for 6 h. The reaction progress was checked by TLC using 7:3 hexane:ethyl acetate. The mixture was poured into beaker contain cold water and the resultant solid was obtained by Buchner filtration. The crude product was purified by column chromatography on silica gel with 7:3 (hexane: ethyl acetate) to yield orange powders (0.73 g, 66.4 %); m.p.: 210.9-211.5 ºC; IR (Neat) λ_{max} in cm^{-1}: 3081(C-H arom.), 2926 (C-H), 1636 (C=O), 1519 (C=C arom.), 1438, 1339 (NO_2), 821 (C-Cl); ^{1}H NMR (700 MHz, $DCCl_3$) δ in ppm: 8.19 (d, 1H, *J* = 2.6 Hz), 8.04 (d, 1H, *J* = 13.7 Hz), 8.01 (d, 2H, *J* = 8.4 Hz), 7.72 (d, 2H, *J* = 8.4 Hz), 7.67 (dd, m, J_1 = 2.6 and J_2 = 8.6 Hz), 7.66 (d, 1H, *J* = 13.7 Hz), 7.55 (d, 1H, 8.6 Hz), 6.88 (s, 1H); ^{13}C NMR (127.9 MHz, $DCCl_3$), δ in ppm 176.94 (C=O), 162.4 (C), 154.5 (C), 138.6 (C-H), 137.5 (CH), 134.5 (CH), 133.2 (C), 132.9 (C), 132.5 (C), 131.4 (C), 129.60 (2 × CH), 127.58 (2 × CH), 125.27 (CH), 119.84 (CH), 109.18 (CH). MALDI- TOF *m/z* calcd. for $C_{17}H_{10}NO_4Cl$ 328; found 328.

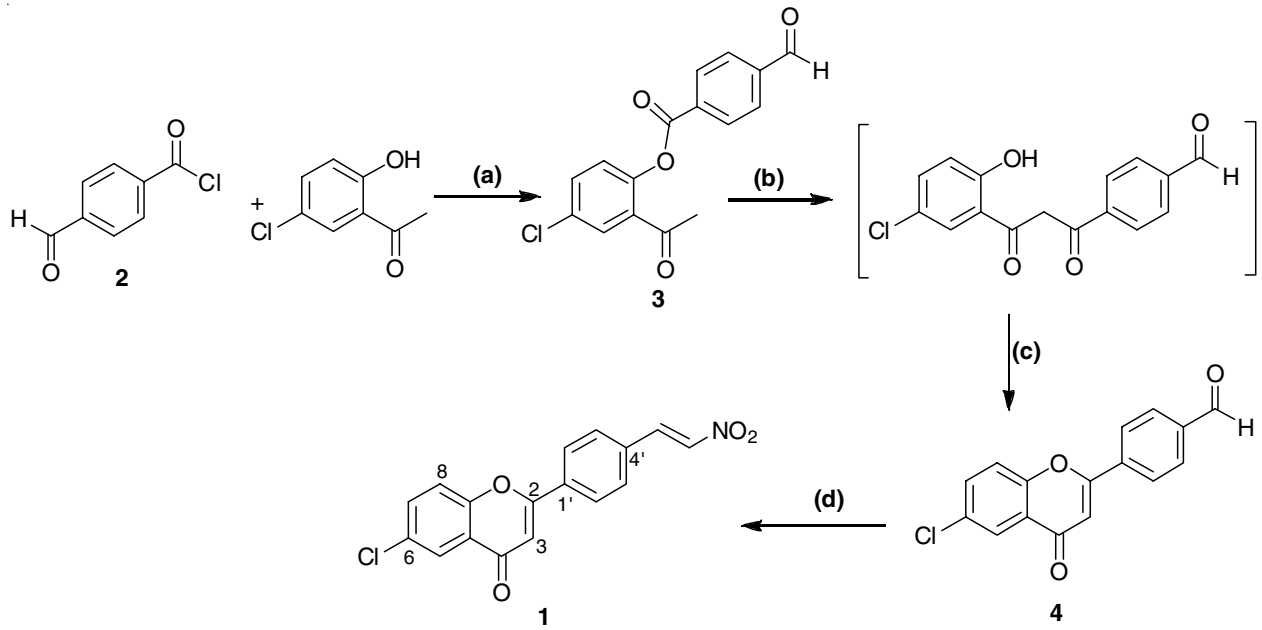
Synthesis of probe 1-cysteine adduct 5: Cysteine (0.24 g, 2.0 mmol) was added to 50 mL round bottom flask containing compound **1** (0.3 g, 0.92 mmol) and acetonitrile (10 mL). Few drops of 0.1 M NaOH was added to the reaction mixture until cysteine dissolved. The reaction mixture was heated under reflux for 2 h. The reaction progress was checked by TLC. After 2 h, the reaction was cooled to room temperature, dried, filtered and concentrated under reduced pressure. The oily product was purified by using column chromatography on silica gel with 9:1 (DCM:MeOH) to give brown powder (0.08 g, 20%).

UV-visible and fluorescence analyses: Stock solutions (8 mM) of amino acids including Cys, Phe, Ser, Arg, His, Ala, Asp, Asn, Met, Pro, in HEPES buffer (10 mM, pH7.5) were prepared. Stock solution of probe **1** (5 mM) was also prepared in acetonitrile. For UV-visible spectra measurements, 10 µL of probe stock solution was mixed with 30 µL of each amino acid, diluting the mixture to 5 mL with HEPES/ACN (3:2, v/v). For fluorescence spectrum measurement, (1mM) working stock solution of probe was prepared by placing 1 mL of the probe stock solution into 5 mL volumetric flask. All the fluorescence measurements were done using 301 nm excitation wavelength with the excitation and emission slit widths of 10 nm. Fluorescence spectra were measured 15 min after the addition of analyte.

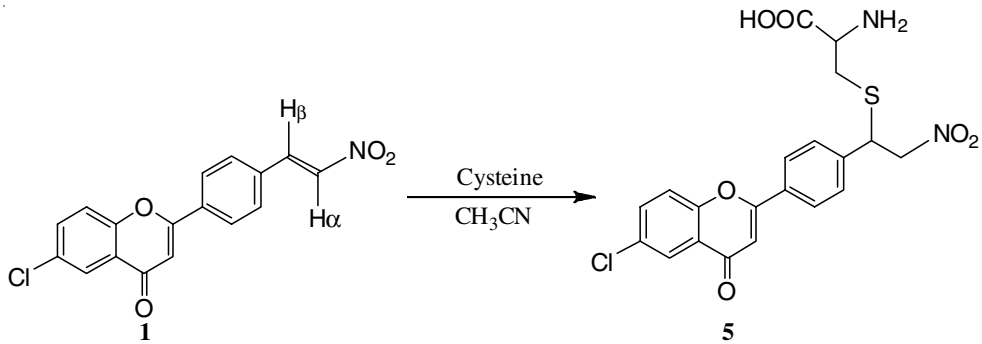
RESULTS AND DISCUSSION

Synthesis of probe 1: The synthesis of probe **1** commenced from 4-formylbenzoyl chloride (**2**) which was prepared successfully from the reaction of 4-formylbenzoic acid with thionyl chloride and used without further purification. When acid chloride **2** reacted with 5-chloro-2-hydroxyacetophenone for 5 h at 80 ºC in pyridine, ester intermediate **3** was produced at moderate yield (57.5 %) after purification by column chromatography. Conversion of ester **3** into flavone structure **4** was achieved by employing Baker-Venkataraman rearrangement reaction using KOH and pyridine at 50 ºC in the first part of the reaction to give a yellow solid intermediate. Then, intramolecular cyclization of the intermediate in acetic acid/sulfuric acid mixture generated flavone aldehyde **4** in 80.1 % after recrystallization from hot ethanol. Finally, probe **1** was synthesized by reacting flavone aldehyde **4** with nitromethane in an Aldol condensation reaction using ammonium acetate as a base in acetic acid. The reaction took 5 h to reach completion according to thin layer chromatography (TLC) monitoring and the product was purified by column chromatography to give probe **1** as an orange solid at good yield (66.4 %). The overall synthetic pathway of probe **1** is sketched in **Scheme-I**.

Reaction of probe 1 with cysteine: In order to confirm the specific reactivity of the newly prepared probe **1** towards cysteine, the probe was reacted with cysteine in acetonitrile for 2 h at refluxing temperature. The product was purified by column chromatography using dichloromethane:methanol (9:1) as eluting solvent to give probe **1**-Cys adduct as brown solid. The nucleophilic thiol group in cysteine is expected to link with β-carbon of probe **1** in a distinctive Michael addition reaction (**Scheme-II**).



Scheme-I: Synthesis of probe **1**, (a) pyridine, 80 °C, 5 h, yield 57.5 %, (b) pyridine, KOH, 50 °C, 15 min, (c) AcOH, H_2SO_4, reflux, 1 h, yield 80.1 % from **3**, (d) nitromethane, ammonium acetate, AcOH, reflux, 5 h, yield 66.4 %



Scheme-II: Reaction of probe **1** with cysteine to form adduct **5**

The ^{1}H NMR plays crucial role to disclose the mode of reaction between probe **1** and cysteine. In ^{1}H NMR spectrum of probe 1, two doublets belonging to H_β and H_α are clearly seen at 8.04 and 7.66 ppm, respectively, with *J* value equal to 13.7 Hz which indicates *trans*-orientation (Fig. 2A). After reacting with cysteine, two doublets have disappeared with some changes in the chemical shifts of other hydrogens in adduct **5** (Fig. 2B). The disappearance of two doublets indicates the reaction between cysteine and probe **1**.

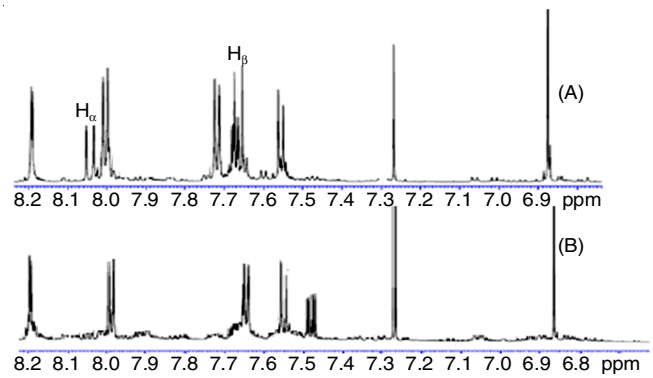


Fig. 2. ^{1}H NMR spectra of probe **1** (A) and probe-Cys adduct (B) [aromatic hydrogens shown only]

UV-visible absorption spectra: Series of UV-visible absorption studies were performed for the probe, the probe and cysteine and the probe with other non-thiol amino acids. In addition, a UV-visible study was performed for probe **1** with cysteine at different pH values. As shown in Fig. 3, free probe **1** displays a main absorption at 328 nm in pH 7.5 HEPES buffer (25 % acetonitrile), hence displaying a characteristic flavone dye absorption. However, when probe **1** was mixed with cysteine (5 equiv.), the maximum absorption descended to a blue-shifted peak at 301 nm. This decrease in maximum absorption wavelength supports the Michael addition reaction between thiol group of cysteine and β-carbon of nitro-olefin moiety in probe **1**. As a result of this addition, the double bond in nitro-olefin moiety disappears leading to less conjugated system in probe **1**, consequently, absorb at shorter wavelength.

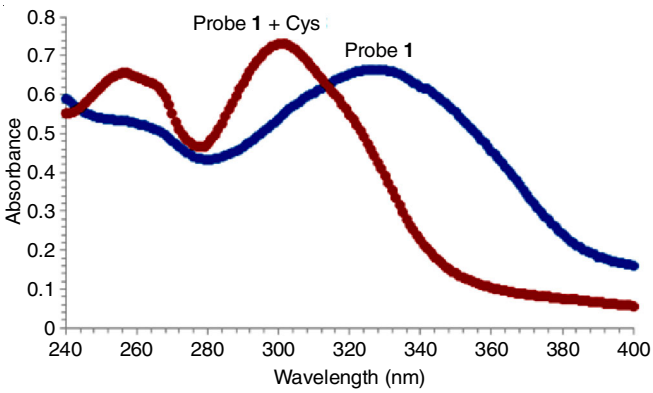


Fig. 3. UV-visible absorption of probe **1** (0.01 mmol/L) in CH_3CN/HEPES (10 mM, pH 7.5) alone and in the presence of 0.05 mmol/L Cys

To check further the effect of pH on the absorption of probe **1**-cysteine mixture, a pH dependent study was carried out using pH range from 3.0 to 9.0. As shown in Fig. 4, there

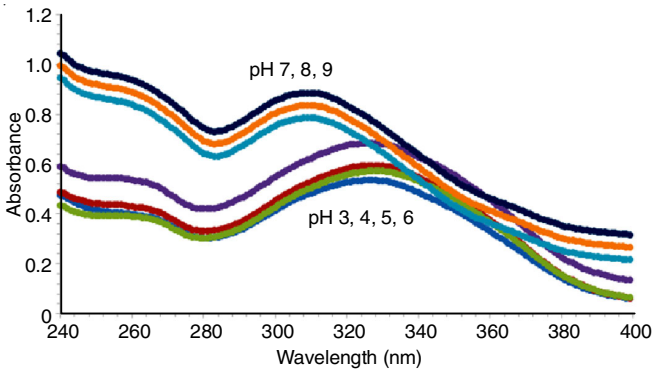


Fig. 4. Effect of pH on the UV-visible absorption of probe **1** (0.01 mmol/L) win the presence of Cys (0.08 mmol/L)

was no interaction between probe **1** and cysteine in solutions with pH range from 3 to 6, but when pH increases to 7 and above, the maximum wavelength decreased to 301 nm which indicate that the detection of cysteine by probe **1** is clearly established.

The selectivity of probe **1** towards cysteine was determined by carrying out UV-visible absorption study of the probe with cysteine and with other non-thiol amino acids (Phe, Ser, Arg, His, Ala, Asp, Asn, Met and Pro). Fig. 5 displays clearly that there is no recognition between probe **1** and non-thiol amino acids since they all show the same absorption of probe **1** (λ_{max} = 328 nm).

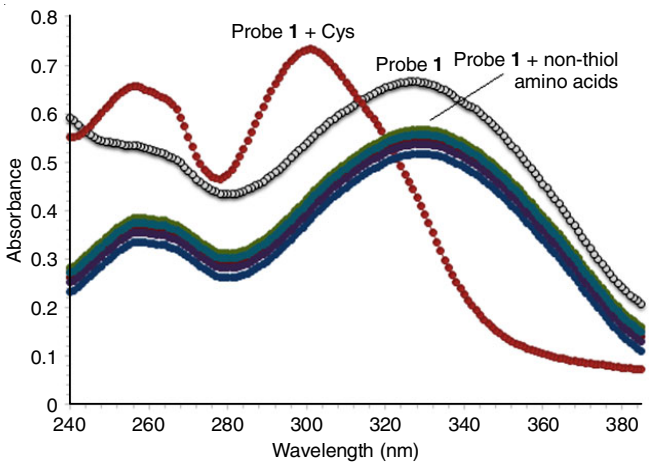


Fig. 5. UV-visible absorption of probe **1** (0.01 mmol/L) in CH_3CN/HEPES (10 mM, pH 7.5) alone and in the presence of 0.05 mmol/L Cys, Phe, Ser, Arg, His, Ala, Asp, Asn, Met and Pro. The spectra were attained after 60 min after analytes addition

Fluorescence study: After showing the capability of prepared flavone probe to selectively detect cysteine from other amino acids, a fluorescence spectroscopy study was also conducted to examine its sensitivity towards cysteine. In this regard, probe **1** in HEPES buffer/CH_3CN (3:1, v/v) at pH 7.5 shows no significant fluorescence with the excitation of 301 nm. Such weak fluorescence of probe **1** can be attributed to the presence of electron-acceptor nitro-olefin group that acts as a quencher for the photoinduced electron-transfer process. The same finding was reached when probe **1** mixed with non-thiol amino acids (Phe, Ser, Arg, His, Ala, Asp, Asn, Met and Pro). Contrary to that a strong fluorescence response of probe **1** to cysteine was observed

at 469 nm upon excitation by 301 nm at pH 7.5 (Fig. 6). In addition, introducing cysteine to the solution of probe **1** results in a strong blue emission colour in pH 7.5 HEPES buffer (25 % acetonitrile) (Fig. 6 inset).

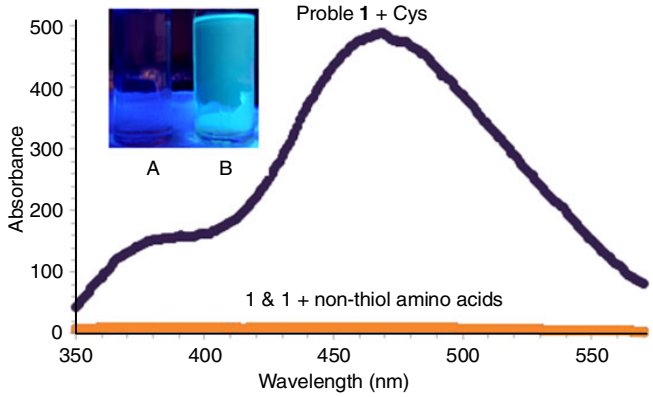


Fig. 6. Fluorescence spectra of probe **1** (0.01 mmol/L) in CH_3CN/HEPES (10 mM, pH 7.5) and after addition of 0.05 mmol/L Cys, Phe, Ser, Arg, His, Ala, Asp, Asn, Met and Pro. Inset photo of probe **1** in the absence of Cys (A) and presence of Cys (B)

Conclusion

A blue-emitting fluorescent probe based on flavone framework having a nitro-olefin electron-acceptor moiety that undergoes Michael addition with cysteine is successfully prepared. The probe was easily synthesized from 4-formylbenzoyl chloride and 5-chloro-2-hydroxyacetophenone *via* Baker-Venkataraman rearrangement reaction. The probe exhibited excellent selectivity and sensitivity towards cysteine over other non-thiol amino acids. The mode of reaction between the probe and cysteine was concluded by ^{1}H NMR analysis.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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