Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 149 (2015) 208–215

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

A novel flavone-based fluorescent probe for relay recognition of HSO_3^- and Al^{3+}

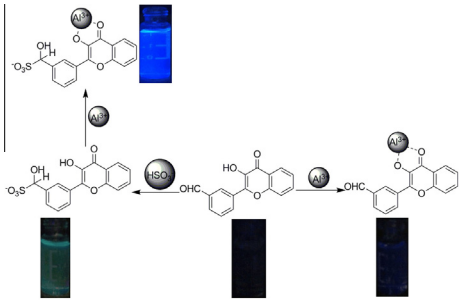
Shuai Xu, Ruiren Tang *, Zhen Wang, Yin Zhou, Rui Yan

School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

HIGHLIGHTS

- A novel flavone-based fluorescent sensor (3HFF) for HSO_3^- was developed.
- The in situ generated 3HFF + HSO_3^- system demonstrated nice relay recognition capability for Al^{3+}.
- A blue-shifted emission band is observed after the addition of Al^{3+} to 3HFF + HSO_3^- system.
- A novel relay recognition probe has realized sensing of HSO_3^- and Al^{3+} with sequence specificity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 November 2014
Received in revised form 20 April 2015
Accepted 22 April 2015
Available online 29 April 2015

Keywords:
Fluorescent probe
3-Hydroxyflavone
3-Hydroxy-3′-formylflavone
Relay recognition
Bisulfite anion
Aluminum ion

ABSTRACT

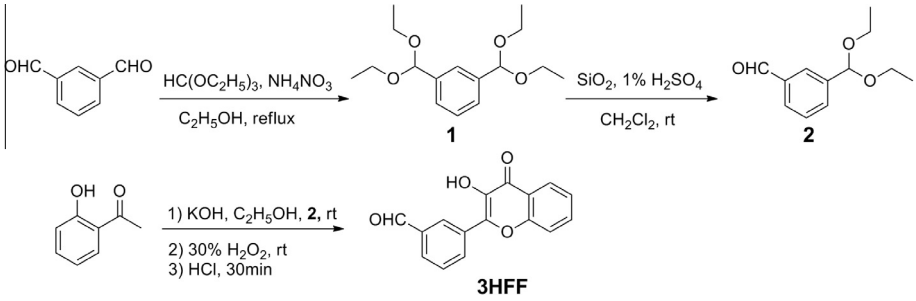
In this work, a new flavone-based fluorescent probe 3-hydroxy-3′-formylflavone (3HFF) was designed to achieve highly selective relay recognition of HSO_3^- and Al^{3+} in DMSO–H_2O (2:8, v/v) solution. 3HFF displayed a highly selective response to HSO_3^- with a green fluorescence appearing at 524 nm. Moreover, the in situ generated 3HFF + HSO_3^- system demonstrated eminent relay recognition capability for Al^{3+} with a blue fluorescence appearing at 453 nm by the formation of a 1:1 complex between 3HFF and Al^{3+} in DMSO–H_2O (2:8, v/v) solution. However, only slight change was observed in emission intensity with addition of Al^{3+} to 3HFF, and indicated HSO_3^- was essential for the sensing of Al^{3+}. This work achieves the detection of HSO_3^- and Al^{3+} by only one probe and provides another example for this rare combination (anion/metal).

Introduction

Most of life forms have a great requirement for anions and metals, as they play critical roles in various physical activities [1,2]. Among the biologically important anions, hydrogen sulfite is extensively used as antimicrobial agent, enzyme inhibitor and antioxidant for foods and beverages to preserve their freshness and shelf life [3–7]. However, it has been discovered that a certain concentration of hydrogen sulfite is harmful to skin, respiratory tract, and gastrointestine [8,9]. On the other hand, metal ions, as essential elements present in human body, play critical roles in many biological processes. Aluminum is the third most abundant metal in the earth's crust, and is found to distribute to all tissues in the body as well as natural waters everywhere [10]. However, aluminum may deposit in various organs and be harmful to humans [11]. Owing to the diversity of their functions mentioned above, the sensing of HSO_3^- and Al^{3+} is crucial in controlling their concentration levels in the environmental monitoring and their direct impact on human health [12]. Fluorescent probes are broadly used as powerful tools to spy on ionic species owing to their low cost, high selectivity, versatility and easy monitoring

* Corresponding author. Tel.: +86 731 88836961.
E-mail address: trr@csu.edu.cn (R. Tang).

http://dx.doi.org/10.1016/j.saa.2015.04.072
1386-1425/



Scheme 1. Synthesis of 3HFF.

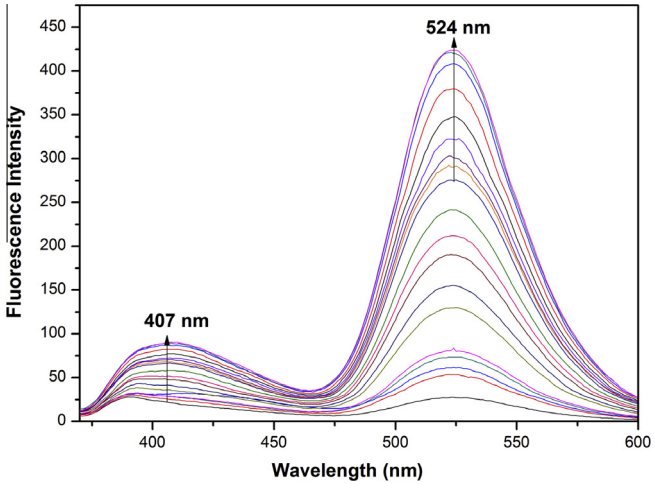


Fig. 1. Fluorescence emission spectra of 3HFF (10 μM) with the addition of HSO_3^- (0–40 equiv) in DMSO–H_2O (2:8, v/v, pH = 5) solution (λ_{ex} = 345 nm).

[13]. Some of selective recognition probes based on the hydrogen bonding, electrostatic interactions or coordination with suitable metal ions have been exploited to detect anions [14–17]. Among these examples, the reaction-based probes, which adopt special chemical reactions triggered by target analytes, provide us multiple methods for investigating extensive analytes [18,19]. Aldehyde is known to react with hydrogen sulfite by forming an aldehyde–hydrogen sulfite adduct which can bring about changes in the electron acceptor strength [20]. Based on this process, many selective recognition probes bearing an aldehyde group have been designed to detect HSO_3^- [21–23]. However, the function of these probes is unitary and has not been further studied. The adduct subunit generated from the detection of HSO_3^- was deconjugated from the electron rich moiety. If another binding site for metal ion is existed in the electron rich moiety, optical properties for specific metal may be different between the probe and the adduct generated from the detection of HSO_3^-.

In order to detect these two biologically and environmentally important ions relying on only one probe, we designed a new compound, 3-hydroxy-3′-formylflavone (3HFF), which demonstrated highly selective and successive recognition of HSO_3^- and Al^{3+} in DMSO–H_2O (2:8, v/v) solution. To the best of our knowledge, this is the first report about aldehyde-based fluorescent probe to sense both HSO_3^- and Al^{3+}, although many Al^{3+} sensors have been reported [24–28]. Meanwhile, another compound, 3-hydroxyflavone (3HF), as an Al^{3+} probe based on the former research [29] was prepared as a reference substance to discuss the process of sequential recognition.

Experimental section

General information

The chemicals used were of analytical reagent grade and used without further purification, if not stated. Deionized water was used throughout the experiments. All reactions were carried out on the magnetic stirrers and their reaction processes were monitored on thin layer chromatography (TLC). Absorption and fluorescence spectra were taken on a Shimadzu UV-2450

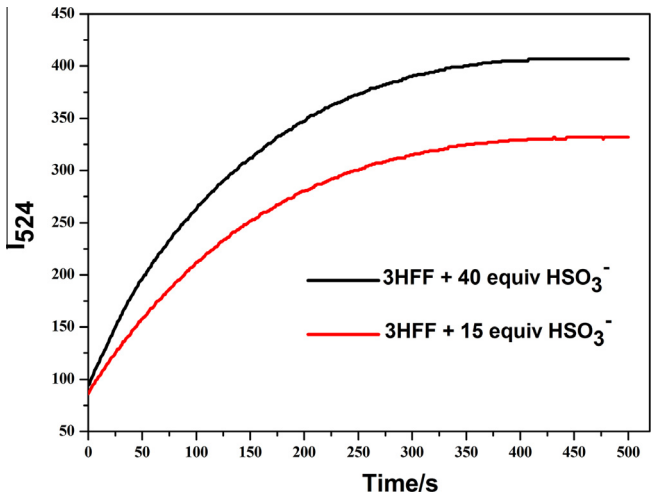


Fig. 2. Fluorometric traces for the reaction of 3HFF (10 μM) with 40 equiv and 15 equiv HSO_3^- in DMSO–H_2O (2:8, v/v, pH = 5).

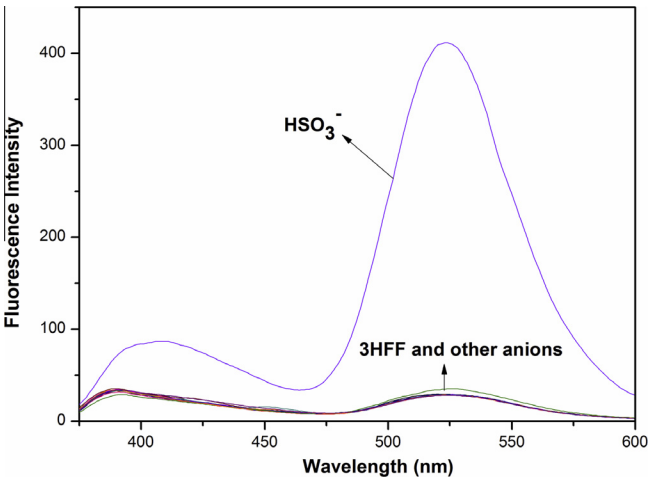


Fig. 3. Emission spectra of 3HFF (10 μM) in the absence and presence of 40 equiv anions in DMSO–H_2O (2:8, v/v, pH = 5) solution with an excitation of 345 nm.

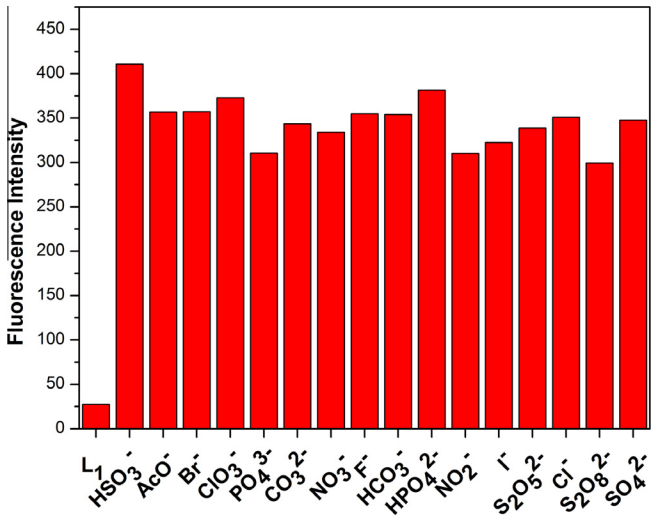


Fig. 4. Competitive selectivity of 3HFF (10 μM) (labeled as L_1) toward HSO_3^- (400 μM) in the presence of various anions (0.2 mM).

spectrophotometer and a Hitachi F-7000 fluorescence spectrometer, respectively. IR spectra were measured on KBr pellets on a Nicolet NEXUS 670 FT-IR spectrophotometer. Melting points were recorded on an X-4 digital melting-point apparatus. ^{1}H NMR and ^{13}C NMR measurements were performed on a Bruker-400 MHz nuclear magnetic resonance spectrometer with DMSO as solvent and TMS as internal reference. All pH measurements were made with a pH-10C digital pH meter.

0.2 mol L^{-1} Na_2HPO_4 citric acid buffers were prepared in deionized water. Stock solutions of the anions (1×10^{-3} mol L^{-1}) and metal ions (2×10^{-3} mol L^{-1}) were prepared from their sodium salts and chloride salts in deionized water, respectively. All the measurements were performed at room temperature. For fluorescence measurements, both the excitation and emission slit widths were 5.0 nm, and the PMT voltage was 700 V.

Synthesis

*Synthesis of 1,3-bis(diethoxymethyl)benzene (**1**), 3-(diethoxymethyl)benzaldehyde (**2**) and 3-hydroxyflavone (3HF)*

In the process of synthesis of 3-hydroxy-3′-formylflavone, 1,3-bis(diethoxymethyl)benzene (**1**) and 3-(diethoxymethyl)benzaldehyde (**2**) were also used. The 3HF [30], compound **1** and compound **2** [31] were synthesized according to reported procedures.

Synthesis of 3-hydroxy-3′-formylflavone (3HFF)

3HFF was synthesized by one pot method. KOH (5.6 g, 10 mmol) was added to a ethanolic solution (10 mL) of 2′-hydroxyacetophenone (0.15 g, 1.1 mmol). The obtained solution was cooled to room temperature. Compound **2** (0.18 g, 1 mmol) was added and the reaction mixture was stirred for 12 h. Then, the solvent was evaporated under reduced pressure. Deionized water (2 mL) and methanol (6 mL) were added to the reaction mixture. The reaction mixture was placed in an ice-water bath and 1 mL of 30% H_2O_2 solution was slowly added, and then stirred at room temperature for another 5 h. After this period, concentrated HCl (37%) was added until pH = 2 and then the reaction mixture was stirred for another 30 min. Then the precipitate was collected by filtration, washed with cold ethanol, and dried in vacuum. The crude product was purified by chromatography on silica gel (dichloromethane/petroleum ether = 1:6, v/v) to afford 3HFF as a colorless powder in 30.1% yield (0.08 g); m.p. 224–226 °C. IR (cm^{-1}, KBr): 3178.97, 2956.39, 2870.66, 1691.84, 1633.11, 1623.85, 1597.19, 1573.5, 1483.83, 1471.62, 1275.97, 799.59 and 753.35. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.13 (s, 1H), 9.95 (s, 1H), 8.76 (t, J = 1.2 Hz, 1H), 8.54 (dt, J = 6.4 Hz, 1.2 Hz, 1H), 8.15 (dd, J = 6.4 Hz, 1.2 Hz, 1H), 8.05 (m, 1H), 7.81–7.87 (m, 3H), 7.49–7.52 (m, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 193.4, 173.6, 155.1, 144.4, 140.1, 136.9, 134.4, 133.5, 132.8, 131.2, 130.0, 128.8, 125.3, 125.2, 121.8, 118.9. Anal. Calcd for $C_{16}H_{10}O_4$ (266.06): C, 72.16; H, 3.78%. Found: C, 71.63; H, 3.52%.

Results and discussion

General information

A standard procedure was used to prepared the intermediate **2**, 3-(diethoxymethyl)benzaldehyde, which was reacted with 1-(2-hydroxyphenyl)ethanone in ethanol solution by one pot method at room temperature to afford 3HFF in modest yield (Scheme 1).

3HFF was characterized by IR, ^{1}H NMR, ^{13}C NMR, and Elemental analysis (Figs. S1–S3). The photo-physical properties of 3HFF with several anions in DMSO–H_2O (2:8, v/v) solution were investigated by UV–vis and fluorescence measurements. After that, the spectral characteristics of the 3HFF + HSO_3^- system with various metal ions were also further studied.

Sensing properties of 3HFF toward HSO_3^-

The fluorescence spectra of 3HFF containing different concentration of HSO_3^- solution were recorded at 370–600 nm upon excitation at 345 nm in DMSO–H_2O (2:8, v/v, pH = 5) (Fig. 1). As we can see, 3HFF alone exhibits weak dual emission maximum at 407 nm and 524 nm. The reason is that 3HFF transforms from a normal isomer (N) in the ground state to the tautomer (T*) through the excited-state intramolecular proton transfer (ESIPT) process upon photoexcitation [32,33]. In this process, blue (407 nm) and green (524 nm) fluorescence occur from N* and T*, respectively. There was a low fluorescence quantum yield (Φ = 0.0009) using coumarin 1 (Φ = 0.50 in ethanol) as standard [34]. Upon addition of increased amounts of HSO_3^-, the initial fluorescence intensities at 407 nm and 524 nm were gradually increased with a relatively higher fluorescence quantum yield (Φ = 0.0065) and accompanied by a visual fluorescence color change from colorless to green. Fig. S4 is the calibration graph for HSO_3^- and the graph is linear for the hydrogen sulfite concentration between 4 and 60 μM, R = 0.99014. According to IUPAC, the detection limit is calculated as 1.97 μM based on the 3α/slope where α is the standard deviation of the blank solution.

Response time is a very important point in sensing for most reaction-based probes. We then proceeded to investigate the time required for the reaction of 3HFF and HSO_3^- at 25 °C. As shown in Fig. 2, when 40 equiv and 15 equiv HSO_3^- were added to 3HFF solutions, the fluorescence intensities at 524 nm increased with reaction time and then levels off at reaction time greater than about 8 min. It showed that 3HFF could use to detect HSO_3^- with a rapid analytical method.

Selectivity is a very important parameter to evaluate the performance of a new fluorescent probe. Emission spectra of 3HFF exposed to 40 equiv of various anions such as SO_4^{2-}, CO_3^{2-}, HCO_3^-, PO_4^{3-}, HPO_4^{2-}, AcO^-, Cl^-, Br^-, I^-, F^-, ClO_3^-, $S_2O_8^{2-}$, $S_2O_3^{2-}$, HSO_3^- were investigated at the same test condition in order to validate the specific affinity of 3HFF towards hydrogen sulfite (Fig. 3). There was a clear fluorescence enhancement (14-fold) at 524 nm with addition of HSO_3^- to 3HFF, but little fluorescence intensity changes were observed with other anions, indicating the probe could be utilized to selectively detect HSO_3^- without interference from other anions.

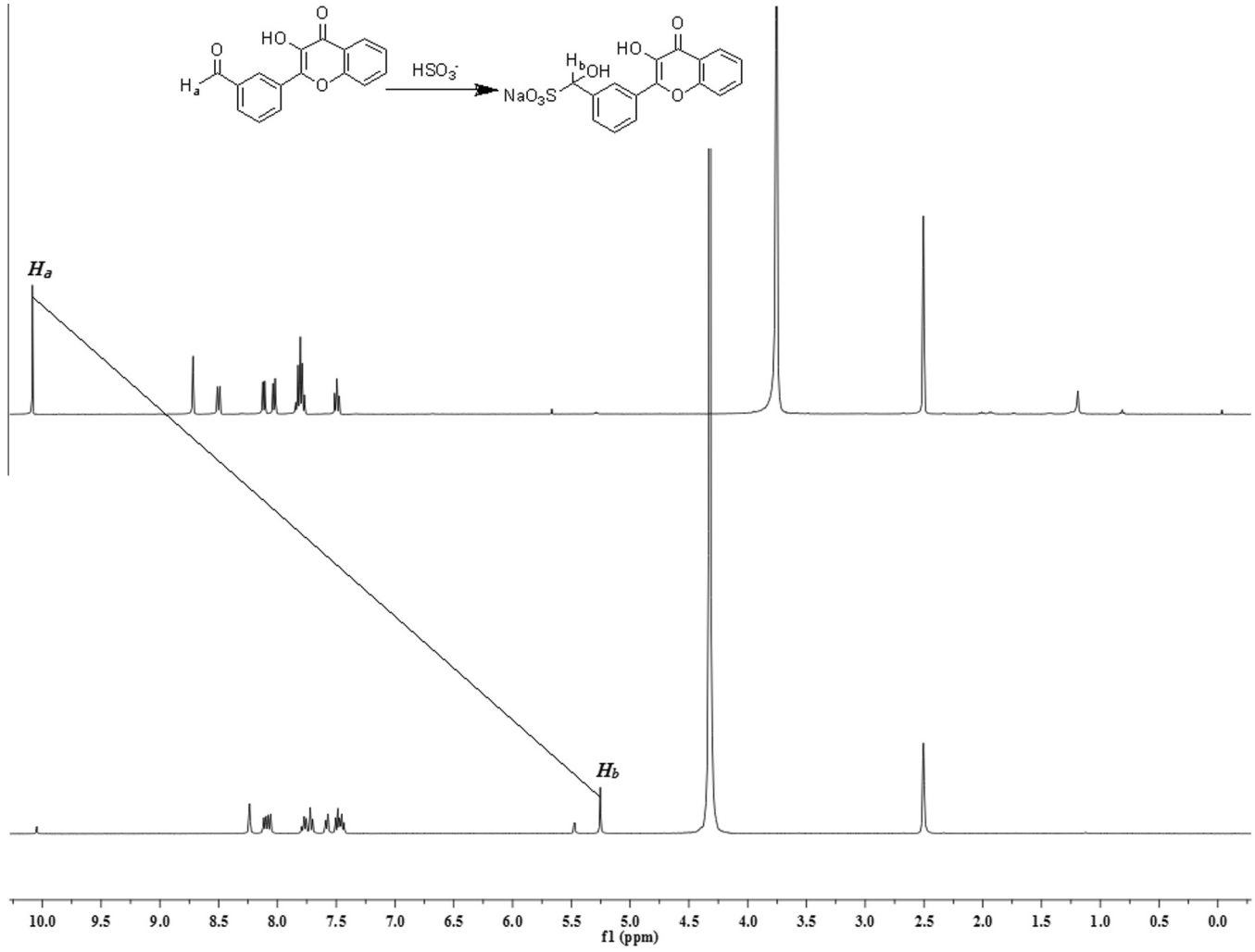


Fig. 5. ^{1}H NMR spectra of 3HFF without (top) and with (40 equiv) HSO_3^- (base) in 2/3DMSO – d_6 + 1/3D_2O.

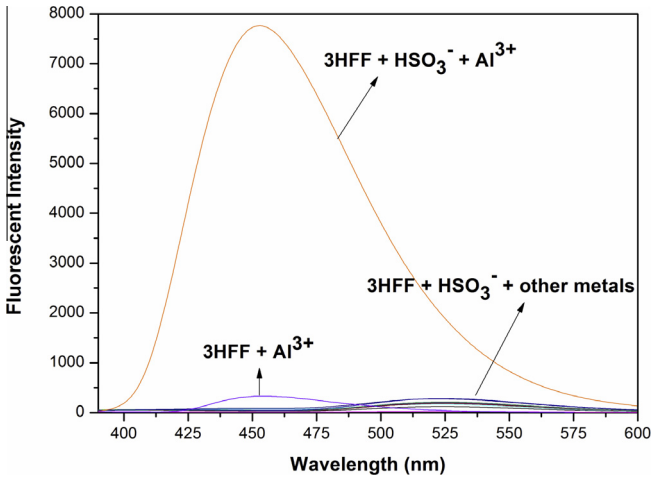


Fig. 6. Fluorescence emission spectra of 3HFF (10 μM) with Al^{3+} (500 μM) and 3HFF + HSO_3^- (10 μM + 400 μM) with various metal ions (500 μM) in DMSO–H_2O (2:8, v/v) solution (λ_{ex} = 345 nm).

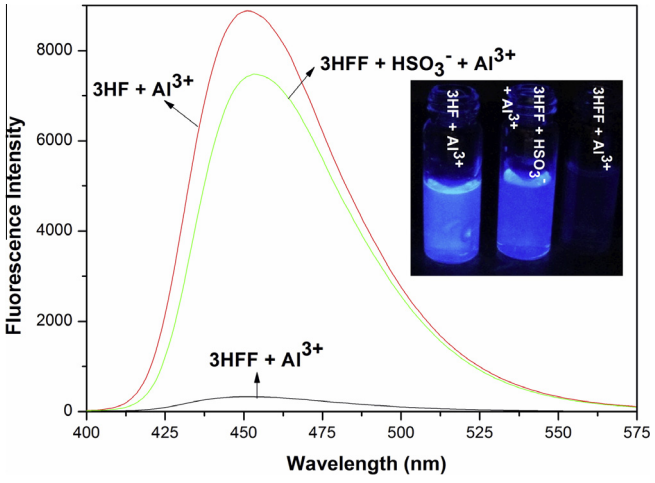


Fig. 7. Fluorescence emission spectra of 3HFF (10 μM), 3HFF + HSO_3^- (10 μM + 400 μM) and 3HF (10 μM) in the presence of Al^{3+} (500 μM) in DMSO–H_2O (2:8, v/v) solution (λ_{ex} = 345 nm).

Furthermore, competition experiments were conducted in order to examine practical applicability of this sensor. As shown in Fig. 4, the presence of other anions resulted in almost no disturbance with the determination of hydrogen sulfite in DMSO–H_2O (2:8, v/v) solution which indicated that 3HFF was feasible for practical.

To exam the effect of pH on the fluorescence properties, the fluorimetric titration in the absence and presence of hydrogen sulfite

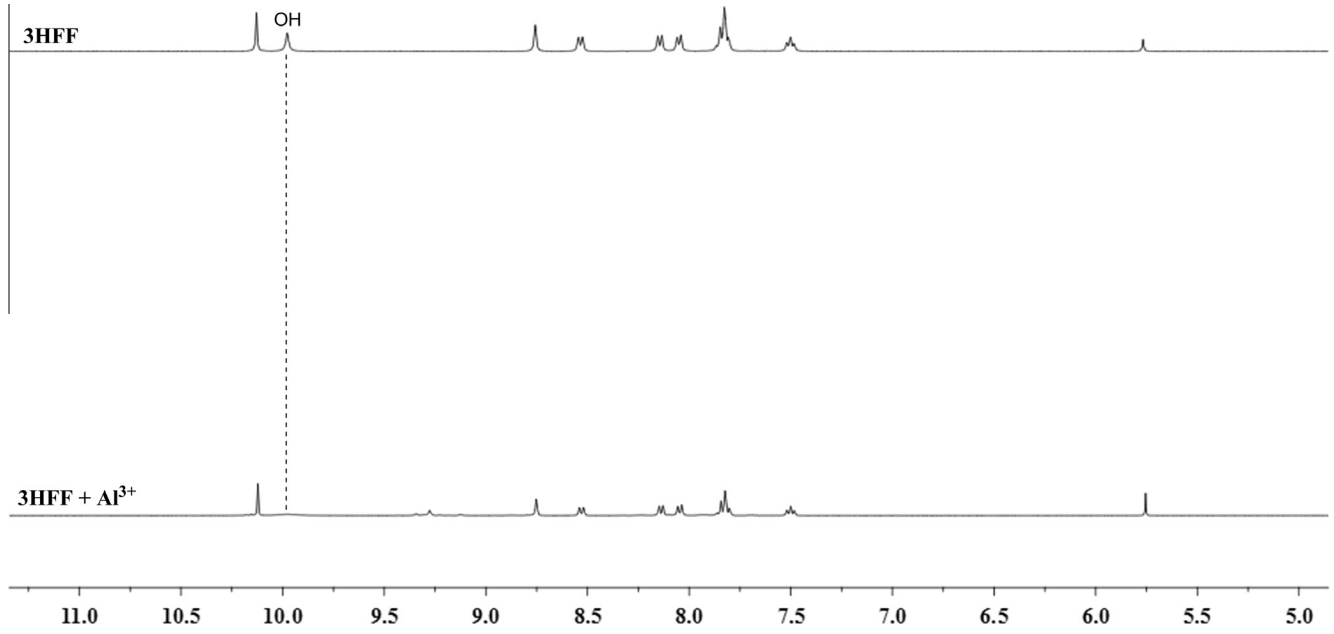


Fig. 8. The interaction mechanism between 3HFF and Al^{3+}.

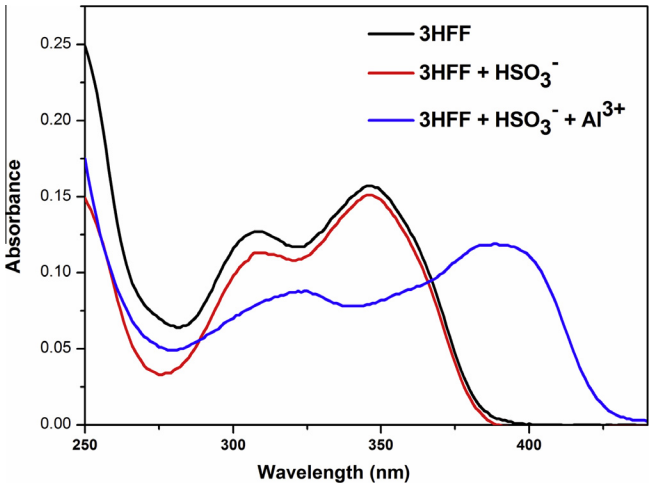


Fig. 9. The absorption responses of 3HFF (10 μM) with relay recognition of HSO_3^- (400 μM) and Al^{3+} (500 μM) in DMSO–H_2O (2:8, v/v) solution.

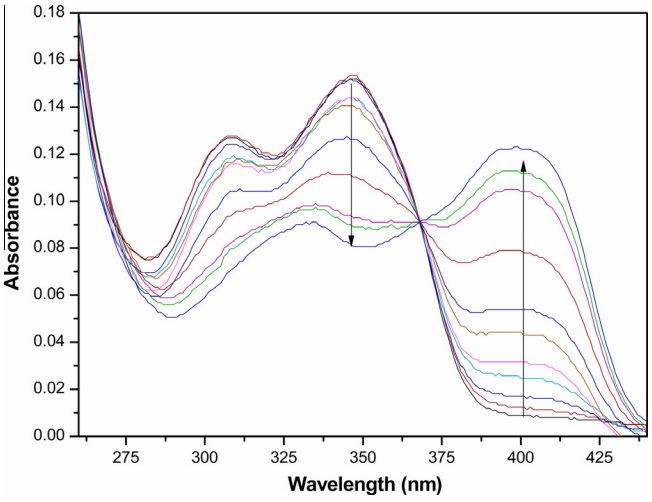


Fig. 10. UV–vis spectral changes of 3HFF + HSO_3^- system (10 μM + 400 μM) as a function of Al^{3+} in DMSO–H_2O (2:8, v/v) solution.

was investigated in different pH solutions. As shown in Fig. S5, the fluorescence signals of 3HFF at 524 nm were quite weak and the changes were minor in the pH range from 2 to 10. Meanwhile, the fluorescence intensity of the 3HFF + HSO_3^- system increased sharply from pH 2.0 to 4.0 and decreased at pH values above 7.0, but maintained relatively invariable from 4.0 to 7.0. Considering practical application, a pH 7.0 solution was selected for the analytical system in subsequent experiments.

The increase of fluorescence at 407 nm and 524 nm is also explained. The fluorescence quenching due to a possible charge transfer from the flavonol HOMO to the aldehyde carbonyl LUMO in 3HFF is depressed in the 3HFF + HSO_3^- system, where the sp^2 hybrid carbonyl is transformed to an sp^3 hybrid carbon owing to the addition reaction of aldehyde.

To further analyze the reaction pathway, ^1H NMR titrations were carried out in 2/3DMSO-d_6 + 1/3D_2O. ^1H NMR spectra of 3HFF before and after treatment with 40 equiv of HSO_3^- are shown in Fig. 5. The proton signal of δ 10.08 could be assigned to the aldehyde proton and the signal was shifted to 5.25 after the addition of HSO_3^-. The proton signals of the phenol group at 7.47–8.72 were shifted to 7.24–8.24. These results are attributed to the nucleophilic addition of the probe's formyl group to the bisulfate ion.

Now, 3HFF and the 3HFF + HSO_3^- system would be expected to serve as a probe for the sensing of some metal ions because several binding sites exist for coordination. With this in mind, a series of metal ions including Na^+, Ca^{2+}, Cu^{2+}, Mg^{2+}, Al^{3+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ag^+, Fe^{3+}, Pb^{2+}, K^+ and Ni^{2+} were added to the 3HFF and 3HFF + $HSO3^-$ system, respectively. To our surprise, the addition of Al^{3+} to 3HFF + HSO_3^- system leaded to a dramatic enhancement of fluorescence intensity at about 453 nm and other metal ions induced almost no fluorescence increase. However, only a slight change was observed with the addition of Al^{3+} to 3HFF solution (Fig. 6).

In order to explain the difference in emission spectrum caused by Al^{3+}, 3-hydroxyflavone (3HF) was synthesized and the fluorescence spectrum response to Al^{3+} was examined in DMSO–H_2O (2:8, v/v) solution. The results show that 3HF has a similar

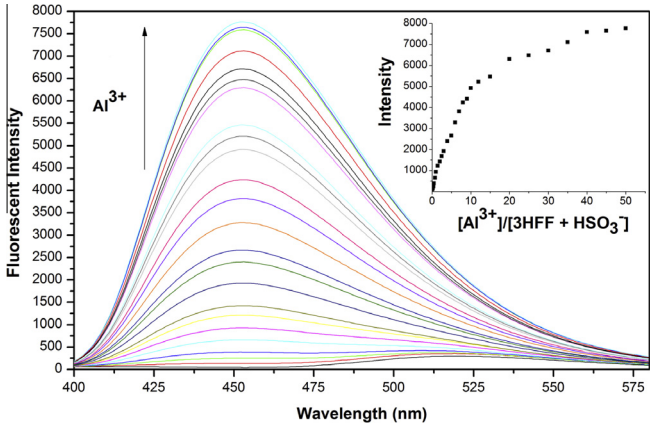


Fig. 11. Fluorescence titration spectra of 3HFF + HSO_3^- (10 μM + 400 μM) upon the addition of 0–50 equiv of Al^{3+} in DMSO–H_2O (2:8, v/v) solution (λ_{ex} = 345 nm) Inset: the relationship between the concentration of Al^{3+} and emission intensity at 453 nm.

response with 3HFF + HSO_3^- system towards Al^{3+} (Fig. 7). The fluorescence intensity of 3HF appearing at about 453 nm can be attributed to the formation of the complex with Al^{3+} [29], which blocks the ESIPT process and results in quenching of the T emission.

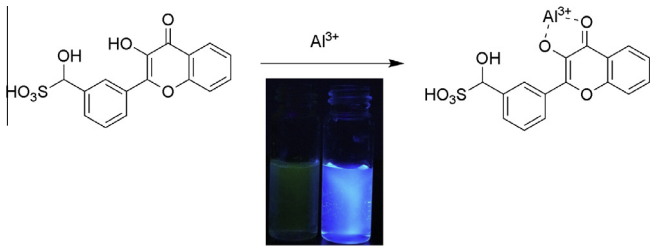
However, the aldehyde group which functions as an electron acceptor in 3HFF may cause electron transfer from the Al^{3+} complex and lead to the slight change in fluorescence intensity. The interaction mechanism between 3HFF and Al^{3+} was also studied by performing ^{1}H NMR titration (Fig. 8). When HSO_3^- was added to 3HFF, the aldehyde group was deconjugated from the flavonol moiety and a significant enhancement in fluorescence emission intensity at about 453 nm was observed after the further addition of Al^{3+} to 3HFF + HSO_3^- system. The absorption responses of 3HFF with relay recognition of HSO_3^- and Al^{3+} were also carried out (Fig. 9). All these data indicate that 3HFF can be served as a specific probe to detect HSO_3^- and Al^{3+} with sequence specificity in the same media.

Sensing properties of 3HFF + HSO_3^- system toward Al^{3+}

Spectroscopic investigations of 3HFF + HSO_3^- system and 3HF with Al^{3+} were carried out in DMSO–H_2O (2:8, v/v) solution.

The UV–vis titration of 3HFF + HSO_3^- system in the presence of different concentration of Al^{3+} was recorded (Fig. 10). Upon introduction of Al^{3+} to the solution, the absorbance bands at about 345 nm gradually decrease and shift to 400 nm. Meanwhile, one isosbestic point at 368 nm is observed which prove the existence of only two absorbing species in equilibrium.

In order to study the fluorescence-sensing behavior of 3HFF + HSO_3^- system with Al^{3+}, a quantitative investigation was carried out by fluorescence titration in DMSO–H_2O (2:8, v/v) solution (Fig. 11). Upon addition of Al^{3+}, the fluorescence intensity of 3HFF + HSO_3^- system at about 453 nm is increased 177-fold with a high fluorescence quantum yield (Φ = 0.34407). The linear response range cover a concentration range of Al^{3+} ions from 5 to 100 μM, R = 0.991 (Fig. S6). According to IUPAC, the detection limit of 3HFF + HSO_3^- system for Al^{3+} is calculated as 0.521 μM and the relative standard deviation is 8.11 for 3HFF + HSO_3^- system (10 μM + 400 μM). The possible binding mode of 3HFF + HSO_3^- system and Al^{3+} is also presented in Scheme 2.



Scheme 2. Proposed binding model of 3HFF + HSO_3^- system with Al^{3+}.

Time course for the change in the fluorescence intensities of 3HFF + HSO_3^- system in the presence of 50 equiv and 15 equiv of Al^{3+} was also studied in the neutral aqueous conditions (Fig. 12). Before the tests, 40 equiv of HSO_3^- was added to 3HFF and the mixture was shook for 10 min. As we can see, the fluorescence intensity reaches the maximum value within 8 min. It reveals that 3HFF + HSO_3^- system detect Al^{3+} rapidly and can be used to monitor Al^{3+} in real time.

To further check the practical applicability of this sensor, the competition experiments were also measured by addition of 50 equiv of Al^{3+} to 3HFF + HSO_3^- system in the presence of 250 equiv of other cations. As shown in Fig. 13, the fluorescence enhancement caused by Al^{3+} is not disturbed by Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ag^+, Cr^{3+} and Pb^{2+} except Cu^{2+}, Mn^{2+} which

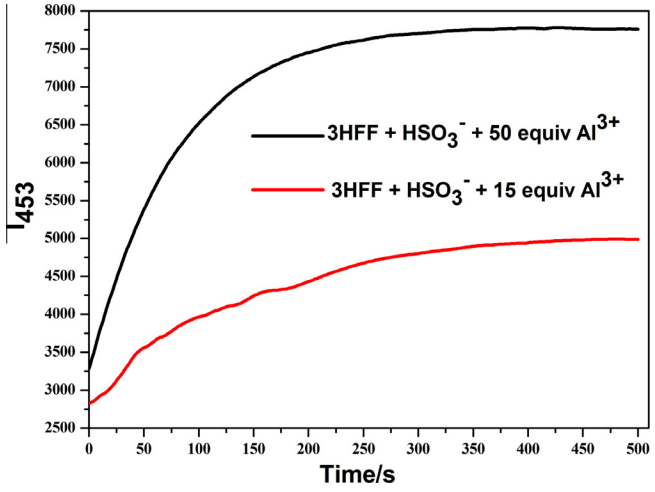


Fig. 12. Fluorometric traces for the reaction of 3HFF + HSO_3^- system with 50 equiv and 15 equiv Al^{3+} in DMSO–H_2O (2:8, v/v, pH = 7).

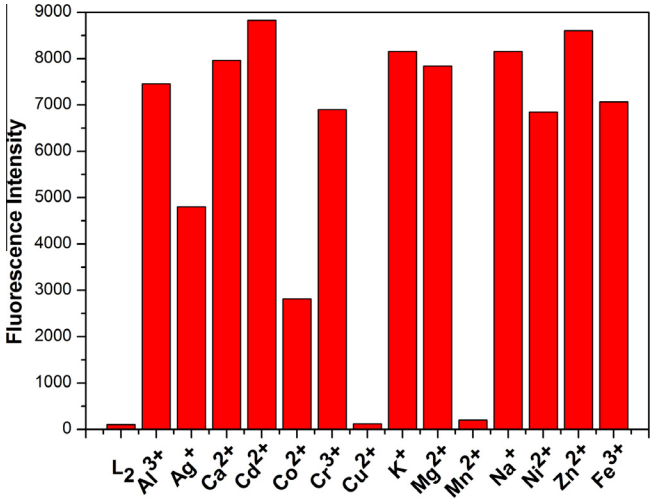


Fig. 13. Competitive selectivity of 3HFF + HSO_3^- system (10 μM + 400 μM) (labeled as L_2) toward Al^{3+} (500 μM) in the presence of various anions (0.25 mM).

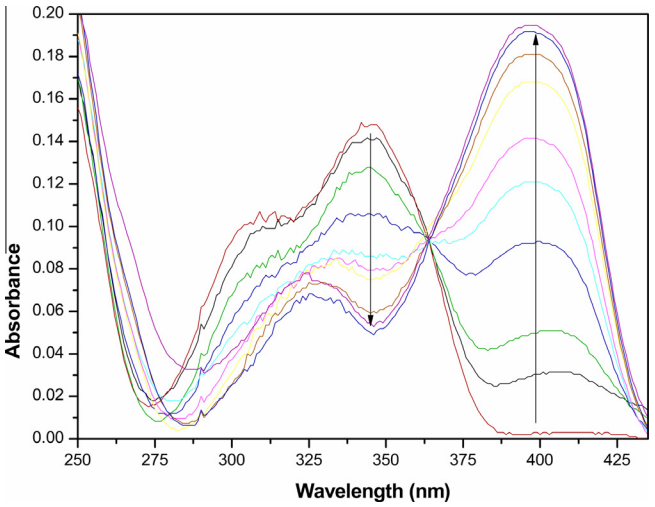


Fig. 14. UV–vis spectral changes of 3HF (10 μM) as a function of Al^{3+} in DMSO–H_2O (2:8, v/v) solution.

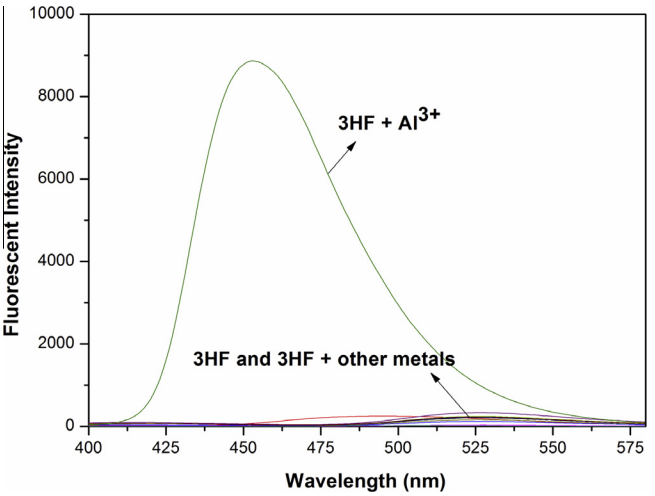


Fig. 16. Fluorescence emission spectra of 3HF (10 μM) in the presence of various metal ions (500 μM) in DMSO–H_2O (2:8, v/v) solution (λ_{ex} = 345 nm).

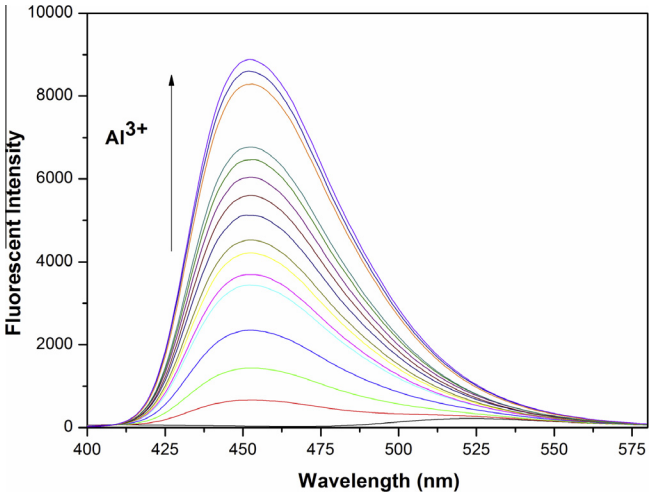


Fig. 15. Fluorescence titration spectra of 3HF (10 μM) upon the addition of 0–50 equiv of Al^{3+} in DMSO–H_2O (2:8, v/v) solution (λ_{ex} = 345 nm).

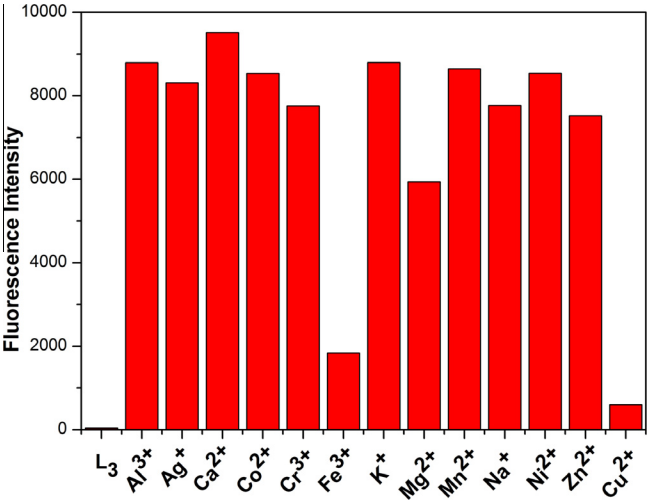


Fig. 17. Competitive selectivity of 3HF (10 μM) (labeled as L_3) toward Al^{3+} (400 μM) in the presence of various anions (0.2 mM).

somewhat inhibit the interaction between the 3HFF + HSO_3^- system and Al^{3+}.

Detection of HSO_3^- and Al^{3+} in water sample

As already indicated, it is necessary to monitor the level of HSO_3^- and Al^{3+} in water samples as they may contaminate water sources. 3HFF was employed to determine HSO_3^- and Al^{3+} concentrations in water samples from Xiang River and YueLu spring (Tables S1 and S2). The results show that HSO_3^- and Al^{3+} can be detected with good recovery in the water samples. It also means that the relay recognition concept from HSO_3^- to Al^{3+} is feasible in water samples.

Absorption and fluorescence studies of 3HF toward Al^{3+}

The UV–vis titration of 3HF was recorded upon the addition of different concentrations of Al^{3+} in DMSO–H_2O (2:8, v/v) solution (Fig. 14). With the increase of Al^{3+}, the absorption peak at 346 nm gradually decreases while a new peak appears at 413 nm, which is consistent with the work of pioneer contributors [29].

To study the fluorescence-sensing behavior of 3HF, a quantitative fluorescent titration of 3HF with Al^{3+} was also carried out (Fig. 15). Upon an enhancement in the concentration of Al^{3+}, the emission intensity is gradually increased at about 453 nm, which contributes to the formation of the complex between 3HF and Al^{3+}.

Moreover, the selectivity of 3HF for various metal ions was investigated in DMSO–H_2O (2:8, v/v) solution. As shown in Fig. 16, a clear fluorescence enhancement is observed with addition of Al^{3+}, but other metal ions such as Fe^{3+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ca^{2+}, Mn^{2+}, Mg^{2+}, Ag^{+}, Na^{+}, Cu^{2+} and K^{+} produce little fluorescence intensity changes, indicating 3HF can be served as a selective fluorescent chemosensor for Al^{3+} without interference from other metal ions.

To further test the feasibility of 3HF as a specific sensor for Al^{3+}, competition experiments were carried out. As shown in Fig. 17, except Fe^{3+} and Cu^{2+}, other metal ions exhibit no interference with the detection of Al^{3+}. Thus, 3HF can be used as a selective fluorescent sensor for Al^{3+} in the presence of other competing metal ions.

Conclusion

In summary, anion to cation relay recognition has been presented and further displayed in the highly selective sensing of

HSO_3^- and Al^{3+}. There is a clear fluorescence enhancement (14-fold) at about 524 nm with addition of HSO_3^- to 3HFF. Then, a blue-shifted emission band is observed from 524 nm to 453 nm with addition of Al^{3+} to 3HFF + HSO_3^- system. The corresponding detection limits are 1.97 μM and 0.521 μM, respectively. In the course of our research, 3HF was also successfully used as a reference substance to prove the process of relay recognition. A novel relay recognition probe has realized sensing of HSO_3^- and Al^{3+} with sequence specificity and more applications of this efficient strategy might be found based on this concept.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2015.04.072.

References

[1] K.P. Carter, A.M. Young, A.E. Palmer, Fluorescent sensors for measuring metal ions in living systems, Chem. Rev. 114 (2014) 4564–4601.
[2] J.-m. An, M.-h. Yan, Z.-y. Yang, T.-r. Li, Q.-x. Zhou, A turn-on fluorescent sensor for Zn(II) based on fluorescein-coumarin conjugate, Dyes Pigm. 99 (2013) 1–5.
[3] L.C. de Azevedo, M.M. Reis, L.F. Motta, GOd Rocha, L.A. Silva, J.B. de Andrade, Evaluation of the formation and stability of hydroxyalkylsulfonic acids in wines, J. Agric. Food Chem. 55 (2007) 8670–8680.
[4] L. Decnop-Weever, J. Kraak, Determination of sulphite in wines by gas-diffusion flow injection analysis utilizing spectrophotometric pH-detection, Anal. Chim. Acta 337 (1997) 125–131.
[5] A. Isaac, A.J. Wain, R.G. Compton, C. Livingstone, J. Davis, A novel electroreduction strategy for the determination of sulfite, Analyst 130 (2005) 1343–1344.
[6] S.K. Verma, M.K. Deb, Single-drop and nanogram level determination of sulfite (SO_3^{2-}) in alcoholic and nonalcoholic beverage samples based on diffuse reflectance fourier transform infrared spectroscopic (DRS-FTIR) analysis on KBr matrix, J. Agric. Food Chem. 55 (2007) 8319–8324.
[7] X.-F. Yang, X.-Q. Guo, Y.-B. Zhao, Novel spectrofluorimetric method for the determination of sulfite with rhodamine B hydrazide in a micellar medium, Anal. Chim. Acta 456 (2002) 121–128.
[8] Y.-Q. Sun, P. Wang, J. Liu, J. Zhang, W. Guo, A fluorescent turn-on probe for bisulfite based on hydrogen bond-inhibited C=N isomerization mechanism, Analyst 137 (2012) 3430–3433.
[9] D. áBrynn Hibbert, J. áJustin Gooding, A sulfite biosensor fabricated using electrodeposited polytyramine: application to wine analysis, in: Analyst 124 (1999) 1775–1779.
[10] J. Lee, H. Kim, S. Kim, J.Y. Noh, E.J. Song, C. Kim, et al., Fluorescent dye containing phenol-pyridyl for selective detection of aluminum ions, Dyes Pigm. 96 (2013) 590–594.
[11] S.V. Verstraeten, L. Aimo, P.I. Oteiza, Aluminium and lead: molecular mechanisms of brain toxicity, Arch. Toxicol. 82 (2008) 789–802.
[12] Z.-C. Liao, Z.-Y. Yang, Y. Li, B.-D. Wang, Q.-X. Zhou, A simple structure fluorescent chemosensor for high selectivity and sensitivity of aluminum ions, Dyes Pigm. 97 (2013) 124–128.
[13] X. Cheng, H. Jia, J. Feng, J. Qin, Z. Li, "Reactive" probe for hydrogen sulfite: Good ratiometric response and bioimaging application, Sens. Actuators, B 184 (2013) 274–280.
[14] A.P. Davis, Anion binding and transport by steroid-based receptors, Coord. Chem. Rev. 250 (2006) 2939–2951.
[15] V. Amendola, L. Fabbrizzi, Anion receptors that contain metals as structural units, Chem. Commun. (2009) 513–531.
[16] S. Erdemir, S. Malkondu, A simple triazole-based "turn on" fluorescent sensor for Al^{3+} ion in MeCN–H_2O and F^- ion in MeCN, J. Lumin. 158 (2015) 401–406.
[17] J. Yoon, S.K. Kim, N.J. Singh, K.S. Kim, Imidazolium receptors for the recognition of anions, Chem. Soc. Rev. 35 (2006) 355–360.
[18] M. Eun Jun, B. Roy, K. Han Ahn, "Turn-on" fluorescent sensing with "reactive" probes, Chem. Commun. 47 (2011) 7583–7601.
[19] X. Qian, Y. Xiao, Y. Xu, X. Guo, J. Qian, W. Zhu, "Alive" dyes as fluorescent sensors: fluorophore, mechanism, receptor and images in living cells, Chem. Commun. 46 (2010) 6418–6436.
[20] D.P. Kjell, B.J. Slattery, M.J. Semo, A novel, nonaqueous method for regeneration of aldehydes from bisulfite adducts, J. Org. Chem. 64 (1999) 5722–5724.
[21] X.-F. Yang, M. Zhao, G. Wang, A rhodamine-based fluorescent probe selective for bisulfite anion in aqueous ethanol media, Sens. Actuators, B 152 (2011) 8–13.
[22] G.J. Mohr, A chromoreactand for the selective detection of HSO_3^- based on the reversible bisulfite addition reaction in polymer membranes, Chem. Commun. (2002) 2646–2647.
[23] C. Yu, M. Luo, F. Zeng, S. Wu, A fast-responding fluorescent turn-on sensor for sensitive and selective detection of sulfite anions, Anal Methods 4 (2012) 2638–2640.
[24] X. Fang, S. Zhang, G. Zhao, W. Zhang, J. Xu, A. Ren, C. Wu, W. Yang, The solvent-dependent binding modes of a rhodamine-azacrown based fluorescent probe for Al^{3+} and Fe^{3+}, Dyes Pigm. 101 (2014) 58–66.
[25] Y.-Y. Guo, L.-Z. Yang, J.-X. Ru, X. Yao, J. Wu, W. Dou, W.-W. Qin, G.-L. Zhang, X.-L. Tang, W.-S. Liu, An, "OFF–ON" fluorescent chemosensor for highly selective and sensitive detection of Al (III) in aqueous solution, Dyes Pigm. 99 (2013) 693–698.
[26] Y.K. Jang, U.C. Nam, H.L. Kwon, I.H. Hwang, C. Kim, A selective colorimetric and fluorescent chemosensor based-on naphthol for detection of Al^{3+} and Cu^{2+}, Dyes Pigm. 99 (2013) 6–13.
[27] S. Malkondu, A highly selective and sensitive perylenebisimide-based fluorescent PET sensor for Al^{3+} determination in MeCN, Tetrahedron 70 (2014) 5580–5584.
[28] J.Y. Noh, S. Kim, I.H. Hwang, G.Y. Lee, J. Kang, S.H. Kim, J. Min, S. Park, C. Kim, J. Kim, Solvent-dependent selective fluorescence assay of aluminum and gallium ions using julolidine-based probe, Dyes Pigm. 99 (2013) 1016–1021.
[29] Y.A. Davila, M.I. Sancho, M.C. Almandoz, S.E. Blanco, Structural and spectroscopic study of Al(III)–3-hydroxyflavone complex: determination of the stability constants in water–methanol mixtures, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 95 (2012) 1–7.
[30] A. Kurzwernhart, W. Kandioller, S. Bächler, C. Bartel, S. Martic, M. Buczkowska, et al., Structure-activity relationships of targeted RuII(η6-p-Cymene) anticancer complexes with flavonol-derived ligands, J. Med. Chem. 55 (2012) 10512–10522.
[31] A. Hachem, Y. Le Floc'h, R. Gree, Y. Rolland, S. Simonet, T. Verbeuren, Synthesis of novel aromatic analogues of 12-HETE, Tetrahedron Lett. 43 (2002) 5217–5219.
[32] P.K. Mandal, A. Samanta, Evidence of ground-state proton-transfer reaction of 3-hydroxyflavone in neutral alcoholic solvents, J. Phys. Chem. A 107 (2003) 6334–6339.
[33] P.K. Sengupta, M. Kasha, Excited state proton-transfer spectroscopy of 3-hytdroxyflavone and quercetin, Chem. Phys. Lett. 68 (1979) 382–385.
[34] G.A. Reynolds, K.H. Drexhage, New coumarin dyes with rigidized structure for flashlamp-pumped dye lasers, Opt. Commun. 13 (1975) 222–225.