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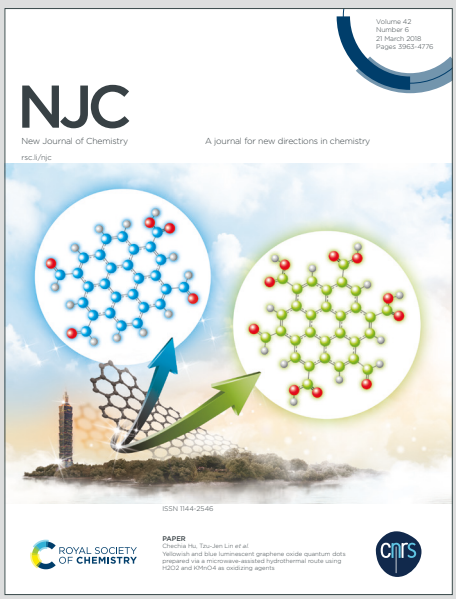

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ARTICLE

A novel NIR fluorescent probe for double-site and ratiometric detection of SO_2 derivatives and its application

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A feasible double-site near-infrared (NIR) fluorescent probe **Q5** based on xanthenes was developed. Probe **Q5** exhibited clearly HSO_3^- induced changes in the fluorescent ratio of two well-separated NIR and VIS peaks, showing excellent selectivity compared with other analytes. And the detection limit of probe for HSO_3^- was found to be 89 nM. Furthermore, fluorescence imaging experiments of HSO_3^- in CEM cells revealed the probe has potential application value in biological systems.

Introduction

SO_2 and its derivatives play an important physiological role in maintaining normal cardiovascular function. SO_2 has some peculiar biological activities, such as vasodilation and anti-oxidation.[1-3] SO_2 is widely used as antibacterials, enzyme inhibitors and antioxidants in foods, drinks and beverages.[4,5] However, beyond a certain concentration, SO_2 can cause damage to the skin, respiratory tract and gastrointestinal tract. Inhalation of SO_2 causes respiratory diseases and cancer and has been extensively studied in toxicology.[6,7] Therefore, there is a great need to develop reliable detection methods for monitoring SO_2 and its derivatives. The main chemical state of SO_2 in aqueous environments is the precursor of bisulfite (HSO_3^-) and sulfite (SO_3^{2-}).[8] Up to now, various analytical means have been designed and fluorescent analysis methods have received considerable attention because of their advantages of simple operation, high sensitivity and real-time sensing capability.[9-11] Fluorescence analysis, as an important analytical method, is currently widely used in biological research.[12-15]

Currently, the fluorescent probes of SO_2 designed and synthesized in the reported literature have been mainly based on the nucleophilic nature of SO_2.[16-31] However, there are still many problems need to be solved, such as background fluorescence interference, unsatisfactory detection limit, long response time, and suffering interference from other active sulfur molecules.[32-42] In order to reduce the interference of background fluorescence and auto-fluorescence, some ratio probes, which based on FRET or TBET were developed. But the synthesis route of these probe is long or complex, due to two fluorophores needed.

NIR fluorescent probes have become a research hotspot in the field of fluorescent probes, due to the advantages of strong tissue permeability and less damage to tissues or cells.[43-47] So far, many NIR fluorescent probes for the detection of HSO_3^- have been developed.[48-51] Nevertheless, few probes have been reported for double-site detection of HSO_3^-. Herein, a new xanthene-based NIR ratio fluorescence probe **Q5** which could be used for detecting HSO_3^- in double-sites under neutral and alkaline conditions was developed and synthesized. Ratio fluorescence imaging experiments in CEM cells has revealed its potential application in biological systems.

Experimental

chemicals and instruments

Cyclohexanone, 3-(diethylamino)phenol, 1,4-Phthalaldehyde and other reagents were purchased from regular sales channels, without special explanation, and were directly used in the experiments. The reagents used in the analysis were all pure analytical grade, and can be directly used without any treatment. The deionized water was purified by Milli-Q. The analytes ofbiothiols (Cys, Hcy, and GSH), anions (HSO_3^-, HS^-, F^-, Cl^-, Br^-, I^-, PO_4^{3-}, HPO_4^{2-},CO_3^{2-}, HCO_3^-, NO_2^-, NO_3^-, SO_4^{2-}, $S_2O_8^{2-}$, $S_2O_5^{2-}$, OAc^-, S^{2-}, SCN^-, $S_2O_3^{2-}$,$S_2O_4^{2-}$,), ROS (HClO, ClO_4^-, H_2O_2, KO_2) and potassium or sodium salts of anions were prepared as 10.00 mM in water solution, which were used to sense objects of **Q5**.

Absorption spectra were accurately measured on a Lambda 35 UV/VIS spectrometer, Perkin Elmer precisely. Fluorescence spectra were measured on the F-4500 FL Spectrophotometer, and The EXSlit and EM Slit were both set at 10.0 nm. The pH was measured by a Model pHs-3Cmetr (Shanghai, China). ^1H NMR and ^{13}C NMR spectra were measured on a Bruker DTX-400 spectrometer using TMS as internal reference. ESI mass spectra were performed on a HPLC Q-Tof HR-MS spectrometer

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by using methanol as mobile phase. Cells were imaged on a LEICA TCS SP8 laser scanning confocal microscope.

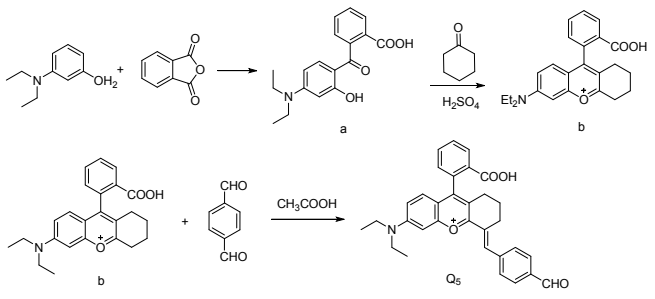
Synthesis of probe Q5

Compound a. 3-(diethylamino)phenol (6.27 g, 38 mmol) and phthalic anhydride (5.6 g, 38 mmol) were dissolved in toluene, and the reaction mixture was refluxed for 5-6 h. After the reaction was completed, it was filtered, washed with methanol. The obtained solid was not further purified and used for the next reaction.

Compound b. Cyclohexanone (0.66 ml, 6.37 mmol) was added dropwise to concentrated sulfuric acid (7 mL) at 0 °C, then compound a (1.0 g, 3.2 mmol) was added to the vigorously stirring mixture solution. The mixture was then heated to 90 °C and the temperature was maintained for 1-1.5 h. After the reaction finished, the reaction mixture was cooled to room temperature, and the reaction mixture was poured into a suspension containing 30 g of ice water with stirring, and 0.7 mL of 70% perchloric acid was added under stirring, resulting in a large amount of red precipitation immediately. The solid was washed with 20 mL ice water and dried to obtain red solid for further reaction.

Compound Q5. Compound b (376 mg, 1 mmol) and terephthalaldehyde (402 mg, 3 mmol) were dissolved in acetic acid (19 mL), and the reaction mixture was heated to 90-100 °C and further stirred at 90-100 °C for 2-5 h, before cooling to room temperature. Decompression was performed to remove the solvent to obtain the crude product, which was purified by silica gel flash chromatography using CH_2Cl_2/ MeOH (40:1) as eluent to obtain compounds Q5 as purple solid (394 mg, 80.1%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 1.17 (t, 6 H, *J* = 7.04 Hz), 1.66 (m, 3 H), 2.07 (m, 1 H), 2.65 (m, 1 H), 2.79 (m, 1 H), 3.36 (q, 4 H, *J* = 7.08 Hz), 6.35 (dd, 1 H), 6.42 (d, 1 H, *J* = 2.48 Hz), 6.48 (d, 1 H, *J* = 8.92 Hz), 7.22 (d, 1 H, *J* = 7.64 Hz), 7.42 (s, 1 H), 7.56 (t, 3 H, *J* = 8 Hz), 7.65 (t, 1 H, *J* = 7.44 Hz), 7.88 (d, 2 H, *J* = 8.2 Hz), 7.95 (d, 2 H, *J* = 7.6 Hz), 10.02 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 12.7, 22.4, 23.0, 27.4, 44.4, 86.3, 97.2, 104.6, 108.8, 109.4, 123.5, 124.0, 125.0, 127.5, 128.6, 129.3, 129.6, 130.0, 133.2, 134.6, 134.7, 143.7, 146.4, 149.4, 152.1, 152.5, 170.0, 191.8; HR-MS *m/z*: Calcd for $C_{32}H_{30}NO_4^+$ [M] 492.2169, found 492.2175. (Supporting Information, Fig. S1-S3)



Scheme 1. Synthetic route of **Q5**.

Results and discussion

Spectroscopic responses of probe Q5 to HSO_3^-

First, ultraviolet spectrometer was used to determine the UV absorption curve of the single probe and the UV selectivity curve of the probe for various analytes. Fig. 1 showed **Q5** (10 μM) had clearly specific response to HSO_3^- with 26 other analytes (F^-, Cl^-, Br^-, I^-, PO_4^{3-}, HPO_4^{2-},CO_3^{2-}, HCO_3^-, NO_2^-, NO_3^-, SO_4^{2-}, $S_2O_8^{2-}$, $S_2O_5^{2-}$, OAc^-, HClO, ClO_4^-, H_2O_2, KO_2,Cys, Hcy, GSH, HS^-, S^{2-}, SCN^-, $S_2O_3^{2-}$ and $S_2O_4^{2-}$). The single probe **Q5** showed a major absorption peak at 575 nm, because of the structural conjugation. In addition, **Q5** also had some absorption peaks between 250-400 nm. After addition of HSO_3^- (100 μM), the absorption peak of **Q5** at 575 nm and 290-340 nm were obvious decreased, the absorption peak at 375 nm and 260 nm was increased significantly. This is because that the 1,4 - addition reaction occurred between **Q5** and HSO_3^-. **Q5** was broken into two parts, so that there were two obvious absorption peaks after that, allowing colorimetric detection of HSO_3^-. Meanwhile, HSO_3^- might also happen nucleophilic addition reaction with the aldehyde group of **Q5**. The color change of probe solution can be recognized by naked eyes (Fig. 1 inset). However, when other analytes were added, there were almost no obvious change in the UV absorption curve of the probe **Q5**. The results of data analysis showed that the **Q5** could identify HSO_3^- specifically in PBS (pH = 7.40, 10 mM, containing 30% MeOH), and could achieve the effect of naked eye recognition.

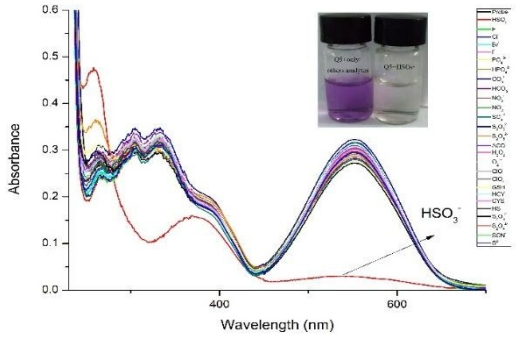


Fig. 1.UV-vis absorbance spectra of **Q5** (10 μM) in the absence and addition of 10 eq. other analyses in PBS (pH = 7.40, 10 mM, containing 30% MeOH). Inset: solution from purple to colorless before and after the addition of HSO_3^- to **Q5** observed by the naked eye.

To further make an investigation on the relationship between HSO_3^- and **Q5**, an ultraviolet titration experiment was performed (Fig. S4)**.** When the concentration of HSO_3^- was increased, a new 375 nm-centered absorption peak was emerged and the 575 nm-centered one was disappeared, which could be attributed to the HSO_3^- induced the destruction of the π-conjugated structure of probe **Q5** through Michael addition. There was a good linear relationship between UV peak of **Q5** at 550 nm and HSO_3^-consistence (Fig. S4 inset).

According to the UV absorption changes of the probe **Q5**, 410 nm and 580 nm as the excitation wavelengths was used in fluorescence spectroscopy, respectively. The fluorescence selectivity of **Q5** to various analytes was further explored. Fig. 2 demonstrated the single probe **Q5** showed an emission peak at 650 nm ascribe to the entire conjugate structure of **Q5** and another one at 464 nm ascribe to xanthene moiety in the PBS (pH = 7.40, 10 mM, containing 30% MeOH). A significant

increment of particular fluorescence of xanthene fluorophore moiety was appeared at 485 nm (about 6 times enhanced) with 10 eq.HSO_3^-, and the fluorescence emission peaks at 650 nm was obvious decreased. As a result of the 1,4-addition reaction was occurred between probe **Q5** and HSO_3^-, the fluorescence of xanthene moiety was released. It was remarkable that the difference between the two emission wavelength is quite large (almost 165 nm), caused a large ratiometric value. Simultaneously, under the same condition, no significant changes could be observed after adding the same number of other analyses. The fluorescence emission peak at 650 nm of **Q5** could be seen more clearly when excited at 580 nm (Fig. S5). According to the above results, probe **Q5** could specific identify HSO_3^- as a ratio probe.

In addition, Fig. 3 showed that the free probe **Q5** exhibited very low fluorescence intensity ratiometric value in the present of background analytes, while this value was significantly enhanced (about 10 times enhanced) with 10 eq. HSO_3^-. Therefore, other analytes had low interference for HSO_3^- in PBS (pH = 7.40, 10 mM, containing 30% MeOH). These results indicated that probe **Q5** had an excellent selectivity for HSO_3^- in the presence of exogenous analyses of these tests.

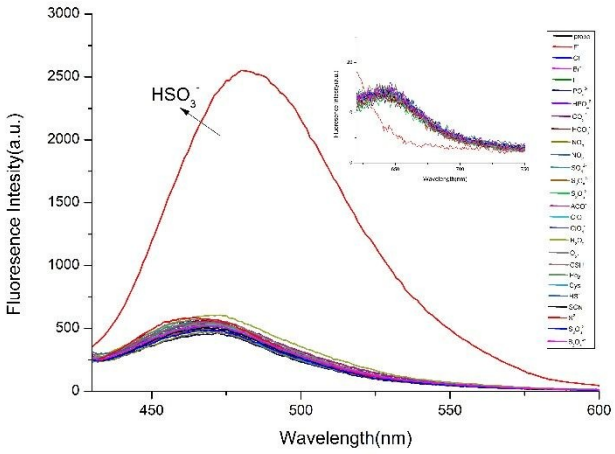


Fig. 2. Fluorescence intensity of **Q5** (10μM) after the addition of 10 eq. various analytes in PBS (pH = 7.40, 10 mM, containing 30% MeOH). (λ_{ex}= 410 nm, scan range 430–750 nm).

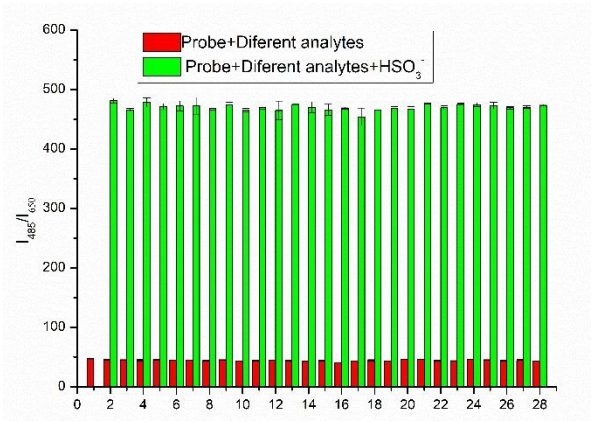


Fig. 3. Fluorescence intensity ratio (F_{485}/F_{650}) of **Q5** (10 μM) after the addition of HSO_3^- (100 μM) and background analytes (100 μM) in PBS (pH = 7.40, 10 mM, containing 30% MeOH). (λ_{ex} = 410 nm,λ_{em}= 485 nm ， 650 nm).(1) Probe, (2) HSO_3^-, (3) F^-, (4) Cl^-, (5) Br^-, (6) I^-, (7) PO_4^{3-}, (8) HPO_4^{2-}, (9) CO_3^{2-}, (10) HCO_3^-, (11) NO_3^-, (12) NO_2^-, (13) SO_4^{2-}, (14) $S_2O_8^{2-}$, (15) $S_2O_5^{2-}$, (16) ACO^-, (17) ClO^-,(18) ClO_4^-, (19) H_2O_2,(20) $O_2^{\cdot-}$,(21) GSH, (22) Hcy,(23) CYS, (24) HS^-, (25) S^{2-}, (26) SCN^-, (27) $S_2O_3^{2-}$, (28) $S_2O_4^{2-}$.

To further verify the quantitative relationship of the interaction between the probe Q5 and HSO_3^-, and the DL of this new probe for HSO_3^-, two fluorescence titration experiments at different excitation wavelengths (410 nm, 580 nm) were studied, respectively. The concentration of **Q5** was kept constant and the increasing concentration of HSO_3^- (0-150 μM) was added continually. As shown in Fig. 4, with the increase of the concentration of HSO_3^- (λ_{ex} = 410 nm), the fluorescence emission peaks at 465 nm was gradually shift to 485 nm due to 1,4-addition reaction between probe **Q5** and HSO_3^-, and the fluorescence intensity was constantly enhanced. The fluorescence emission intensity at 650 nm was gradually decreased. The fluorescence intensity ratiometric value (F_{485}/F_{650}) was found to be increased linearly with the concentration of HSO_3^- and the DL (3σ/slope) of HSO_3^- was calculated to be 89 nM (Fig. 4 inset). Comparison of reported fluorescence probe for HSO_3^- with Q5 (Table S1), Q5 has more excellent sensitivity to HSO_3^-. Therefore, these results indicated that the probe **Q5** can act as a fluorescent sensor for high sensitivity and selectivity detection of HSO_3^-. The change of the fluorescence titration in the NIR region was clearer at the excitation wavelength of 580 nm (Fig. S6). When the concentration of HSO_3^- was increasing, it was clear that the fluorescence intensity at 650 nm was decreased, and there was a good decreased linear correlation between probe **Q5** and HSO_3^-(Fig. S6, inset).

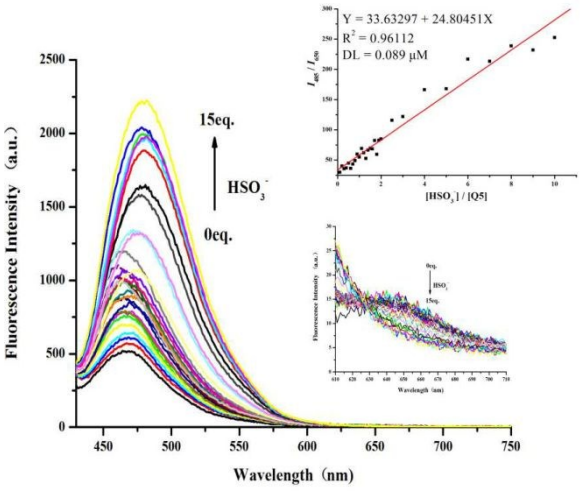


Fig. 4. Fluorescence emission spectra of **Q5**(10μM) after the addition of various concentrations of HSO_3^- (0-15 equiv) in PBS (pH = 7.40, 10 mM, containing 30% MeOH). Inset displayed the linear responses (F_{485}/F_{650}) of **Q5** with HSO_3^- concentrations (λ_{ex} = 410 nm,λ_{em}= 485 nm，650 nm) .

In order to accurately detect analytes in different actual environments. The effect of the different acid conditions to the probe **Q5** and **Q5** toward HSO_3^- were investigated. Fig. S7 showed that the ratiometric value (F_{485}/F_{650}) of the free probe was not obviously changed and was relatively stable under the condition of pH<11 in PBS (10 mM, containing 30% MeOH), While, in the presence of HSO_3^-, the ratiometric value (F_{485}/F_{650}) was significantly enhanced between pH 7.0 and pH 12.0 (neutral and alkaline) due to the occurrences of the 1,4 - addition reaction and nucleophilic addition reaction between **Q5** and HSO_3^-. This pH span was conformed to the physiological environment in most organisms (pH=7.4). The results suggested that the probe **Q5** can detect HSO_3^- under physiological conditions.

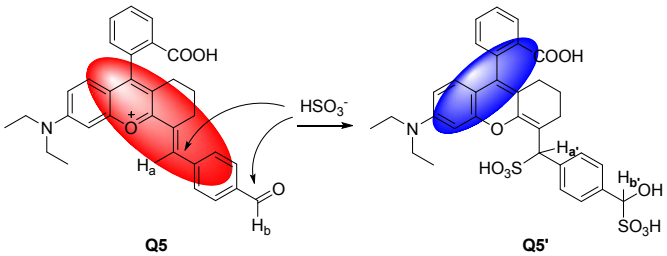
To examine the response time influence of the probe **Q5** to HSO_3^-, the kinetic experiments and the photostability of the probe **Q5** (λ_{ex} = 410 nm, λ_{em}= 485 nm, 650 nm) were investigated, respectively. At the same excitation wavelength, 10 eq. HSO_3^- was added, the fluorescence intensity changed with time at 485 nm and 650 nm, respectively. As shown in Fig. S8, compared with the fluorescence intensity ratio F_{485}/F_{650}, it could be seen that the photostability of the probe **Q5** was excellent in 1 h. After the addition of HSO_3^-, the ratio F_{485}/F_{650} was increased gradually. But there was no obvious maximum response platform in 1 h. With the same method, the photostability of the probe **Q5** and the response time to HSO_3^- at the maximum emission wavelength 650 nm was measured under the excitation wavelength of 580 nm (Fig. S9). When 10 eq. HSO_3^- was added, the fluorescence intensity achieved the minimum response platform within 0.5 h. The results showed that the probe **Q5** can act as a probe to detect HSO_3^- in real time.

The proposed mechanism of the probe Q5 towards HSO_3^-

We then explored the possible mechanism of the reaction between probe **Q5** and HSO_3^-. By consulting the relevant literature and the UV absorption spectra from Fig. 1. we speculated that 1,4-addition reaction of HSO_3^- with the double bond of probe **Q5** and a nucleophilic addition reaction of HSO_3^- with aldehyde group took place. The reactions caused the destruction of the conjugate structure and result in a change in the fluorescence ratio. According to our knowledge, a recognition mechanism of **Q5** to HSO_3^- was speculated in Scheme 2. In order to verify the mechanism, the ^{1}H NMR titration experiment of **Q5** with HSO_3^- in DMSO-d_6 (Fig. S10) were first investigated. The H_a of the double bond at δ7.42 ppm and the H_b of aldehyde group at δ10.02 ppm of free probe **Q5** could be found. After adding 1-10 equivalent HSO_3^- to **Q5**, both aldehyde hydrogen H_a and double bond hydrogen H_b were gradually disappearing. At the same time, two new peaks $H_{a'}$ and $H_{b'}$ were appearing gradually at δ5.03 and δ5.40, respectively. Then, the recognition mechanism of **Q5** was also verified by the HR-MS (Fig. S10). **Q5** exhibited a specific peak at *m/z* 492.2175 (Fig.S3). A mixture of **Q5** and HSO_3^- was added to HR-MS analysis and the peak at *m/z* 492.2175 was disappeared. A new significant peak at *m/z* 656.1622 distributed to **Q5'** was appeared (Fig.S11), which was basically consistent with the value of the theoretical calculation $[\mathbf{M}_{\mathbf{Q5'}}+H]^+$ (calcd = 656.1619). Both of the ^{1}H NMR titration experiment and HR-MS results certified the proposed mechanism shown in Scheme 2.

Cellular imaging

Fluorescence imaging applications of probe **Q5** for monitoring of HSO_3^- in living biological cells had also been carried out. CEM cells were selected to co-cultured with probe **Q5**(10 μM) in PBS buffer for about 0.5 h at 37 ℃. Images were photographed under natural channel, blue channel and red channel of the confocal microscope, respectively. The cells were observed only with red fluorescence (Fig. 5c). After washing with PBS buffer three times, then 20 uL response ion HSO_3^- (100 μM) were supplemented to the cells co-cultured for about 0.5 h at 37 ℃. Images were photographed under natural channel, blue channel and red channel of the confocal microscope, respectively. The cells were observed to show blue fluorescence (Fig. 5e) and the red fluorescence disappeared (Fig. 5f). An image of cell incubated by **Q5** and HSO_3^-, under bright field, demonstrated that the cells were feasible in the whole experiments (Fig. 5a, 5d). The morphology of cells remained intact. These results of cell experiments demonstrated that probe **Q5** might successfully be used for detecting HSO_3^- and realized fluorescence imaging in living cells.



Scheme 2. The proposed mechanism of the response of **Q5** to HSO_3^-.

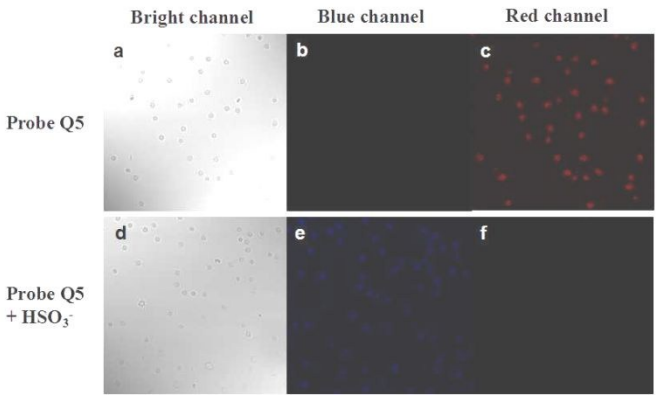


Fig.5 Fluorescence microscopic images of CEM cells. CEM cells treated with Q5 (10 μM) in PBS buffer for 0.5 h at 37 °C, (a)and (d), bright channel, (b)and(e), blue channel, (c)and (f), red channel.

Conclusions

In conclusion, a feasible double-site and ratiometric novel NIR fluorescent probe **Q5** based on xanthenes was developed. Probe **Q5** could effectively detect HSO_3^- in PBS solution

compared with other coexistent analytes, and provided a simple method with naked-eye recognition. The mechanism of double-site recognition for HSO_3^- was verified by ^1H NMR titration and HR-MS. In addition, it had been used in CEM cell imaging to demonstrate that it could act as a probe to monitor the level of HSO_3^- in living biological cells with the low toxicity.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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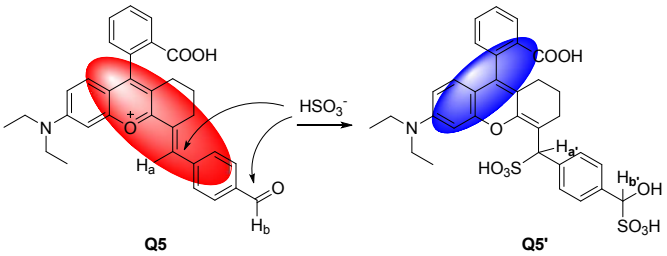

A "naked-eye" fluorescent probe based on xanthenes was obtained.