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Synthesis and Evaluation of Sulfoxide-Functionalized BODIPYs as Chemosensors for Thiols

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BODIPY-based fluorescent chemosensors bearing sulfoxide function were designed and evaluated. Thiols triggered sulfoxide→sulfide transduction in these probes leads to an obvious red-shift in absorption and dramatic fluorescence enhancement with distinctly ratiometric features, enabling the accurate assay of thiols in living cells.

Keywords sulfoxide→sulfide transfer, Cysteine, ratiometric, living cells, reduction

Introduction

Biological thiols, including cysteine (Cys), homocysteine (Hcy) and glutathione (GSH), play a prominent role in variations of physical and pathological processes.[1] Importantly, these thiols exert anti-oxidation protection in cells.[2] Nevertheless, abnormal levels of thiols lead to a variety of pathologies.[3] It has been known that aberrant levels of these sulfhydryl compounds produce serious diseases, such as cancer, Alzheimer and even cardiovascular diseases.[4] Phenomenon of interesting is that Cys, Hcy and GSH perform somehow completely different functions even though they have similar chemical structures.[5] Although Cys and Hcy differ by a single methylene unit in their side chains, Cys is one of the most important biothiols as basic building block for proteins, while high levels of Hcy are associated with an increased risk of stroke and heart disease.[6] Therefore, it is of significant importance to develop novel probes for discriminating these important biothiols.

Generally, the sulfhydryl group in thiols bears strong nucleophilicity, which has been employed for rational design of diverse probes for thiol sensing, including Michael addition,[7] cyclization with aldehydes,[8] conjugate addition–cyclization reactions,[9] cleavage of sulfonamide and sulfonate esters,[10] and thiol–halogen nucleophilic substitution.[11] Furthermore, the sulfhydryl group endows thiols a reductive feature, which is mainly invovled in biological systems. Nevertheless, few design strategies have been adopted to construct probes via such promising character. Thus, we decide to develop new fluorescence probes for biothiols utilizing their intrinsic reducibility. We have previously reported BODIPY-based sulfoxide, which can be selectively transfered to BODIPY-based thioether by benzenethiols, accompanied with drastic ratiometric photophysical changes.[12] However, these compounds show no photophysical responses to Cys, Hcy and GSH. We reason that the steric effects mainly influence such sulfoxide→sulfide transduction. To test this hypothesis, we herein report the design, synthesis, and biological evaluations of two new sulfoxide-functionalized BODIPYs. Detailed studies show that Cys can selectively induce sulfoxide→sulfide transduction in these probes, while there is no obvious interference from Hcy and GSH. These probes are aslo proved the capability in ratiometric measurement of Cys in living cells.

Experimental

Synthesis of BSFI-1

The reaction mixture of **1** (0.358 g, 1 mmol), methyl thioglycolate (0.127 g, 1.2 mmol) and DMAP (0.122 g, 1 mmol) in 20 mL CH_3CN was stirred overnight at 25 ℃. Then CH_3CN was removed under vacuum. The resulted crude product was purified by flash chromatography (silica gel) to afford **BSFI-1** (0.315 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49－7.44 (m, 3H), 7.32－7.27 (m, 2H), 6.34 (d, J＝4 Hz, 1H), 6.28 (d, J＝4 Hz, 1H), 3.77 (s, 2H), 3.74 (s, 3H), 2.61 (s, 3H), 2.34 (q, J＝8 Hz, 2H), 1.42 (s, 3H), 1.01 (t, J＝8 Hz, 3H).

Synthesis of BSFO-1

0.99 equivalents of 75% *m*-CPBA (0.115 g, 0.49 mmol) was added to a solution of **BSFI-1** (0.216 g, 0.5 mmol) in 20 mL dichloromethane and stirred for 2 h at 0 ℃. Excessive acids were neutralized by Na_2CO_3 and the reaction mixture was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4 and evaporated in vacuo.

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The crude product was further purified by flash chromatography (silica gel) to afford **BSFO-1** (0.154 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54—7.49 (m, 3H), 7.36—7.33 (m, 2H), 6.96 (d, J=4 Hz, 1H), 6.35 (d, J=4 Hz, 1H), 4.23 (d, J=12 Hz, 1H), 3.92 (d, J=16 Hz, 1H), 3.81 (s, 3H), 2.64 (s, 3H), 2.37 (q, J=8 Hz, 2H), 1.48 (s, 3H), 1.03 (t, J=8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.19, 165.43, 148.65, 143.96, 141.54, 138.11, 136.97, 135.12, 133.28, 129.73, 128.76, 128.73, 128.65, 128.61, 124.04, 114.82, 60.45, 52.83, 29.70, 17.16, 14.03, 12.55; HRMS (ESI$^+$) calcd for $C_{22}H_{23}N_2BF_2SO_3Na$ [M+Na]$^+$: 467.1388; found 467.1387.

Synthesis of BSFI-2

A mixture of DMF (3 mL) and $POCl_3$ (3 mL) was stirred for 10 min at 0 ℃ and for another 30 min at room temperature, then a solution of **BSFI-1** (0.428 g, 1 mmol) in 20 mL dichloroethane was added to the mixture. The resulting reaction mixture was stirred for 3 h at 50 ℃. $POCl_3$ was then neutralized with saturated aqueous $NaHCO_3$ under ice-cold conditions and the reaction mixture was extracted with CH_2Cl_2, washed with water and dried by anhydrous Na_2SO_4. The solvents were evaporated in vacuo. The crude product was further purified using column chromatography to give **BSFI-2** (0.298 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.01 (s, 1H), 7.55—7.49 (m, 3H), 7.35—7.31 (m, 2H), 6.68 (s, 1H), 3.79 (s, 2H), 3.66 (s, 3H), 2.71 (s, 3H), 2.39 (q, J=8 Hz, 2H), 1.49 (s, 3H), 1.05 (t, J=8 Hz, 3H).

Synthesis of BSFO-2

0.99 equivalents of 75% *m*-CPBA (0.115 g, 0.49 mmol) was added to a solution of **BSFI-2** (0.229 g, 0.5 mmol) in 20 mL dichloromethane and stirred for 2 h at 0 ℃. Excessive acids were neutralized with Na_2CO_3 and extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4. The solvents were evaporated in vacuo. The crude product was further purified by flash chromatography (silica gel) to afford **BSFO-2** (0.169 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (s, 1H), 7.56—7.51 (m, 3H), 7.34—7.31 (m, 2H), 6.21 (s, 1H), 3.91 (s, 3H), 2.72 (s, 3H), 2.39 (q, J=8 Hz, 2H), 1.48 (s, 3H), 1.05 (t, J=8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.98, 162.00, 152.29, 144.56, 141.79, 140.79, 140.75, 139.10, 137.80, 136.25, 132.88, 129.96, 129.43, 128.98, 128.88, 128.58, 128.55, 116.55, 52.63, 29.70, 17.22, 13.91, 12.68; HRMS (ESI$^+$) calcd for $C_{23}H_{22}N_2BF_2SO_3$ [M+H]$^+$: 455.1412; found 455.1410.

Results and Discussion

The preparation of the target probes **BSFO-1** and **BSFO-2**, together with the model compound **BSFO** was depicted in Scheme 1. Nucleophilic aromatic substitution reaction (S_NAr) proceeded readily with methyl thioglycolate or *p*-thiocresol to generate the corresponding sulfide compounds.[13] The follow-up oxidation with *m*-CPBA furnished the final BODIPY-based sulfoxides. Particularly, the oxidation of **BSFI-2** bearing formaldehyde moiety at the nearest 4-position led to the production of aromatic fused BODIPY, which can be an alternative strategy to the classical method for obtaining aromatic ring-fused BODIPYs. All the chemical structures were analyzed by ^{1}H NMR, ^{13}C NMR and HRMS.

With these compounds in hand, we then evaluated the photophysical responses to biothiols. As expected, upon incubation of Cys, Hcy and GSH with **BSFO** in acetonitrile/PBS buffer (1∶1, *V*/*V*, 25 mmol•L^{-1}, pH 7.4, Figure S1), minimal changes in absorption and fluorescence spectra were observed. We reason that the steric effects mainly influence the sulfhydryl group triggered reduction of sulfoxide to sulfide. Generally, such sulfoxide→sulfide transfer results in the changing in the electronic nature of the substituents on the core, which would lead to red/blue optical transition in absorption and emission wavelengths. All these features enable the design of ratiometric probes based on sulfoxide→sulfide transfer in case of feasible reduction by thiols. On the base of these considerations, **BSFO-1** with a flexible chain (Scheme 1) to reduce the steric effect was then employed to testify the reaction properties with biothiols.

We first evaluated the photophysical response of **BSFO-1** to Cys in a PBS buffer solution (pH 7.4, 50% acetonitrile as co-solvent). As can be seen in Figure 1, time-dependent absorption and fluorescence spectra changes were collected in the presence of Cys. In the absence of cysteine, **BSFO-1** showed an intense absorption band at 480 nm with a corresponding emission

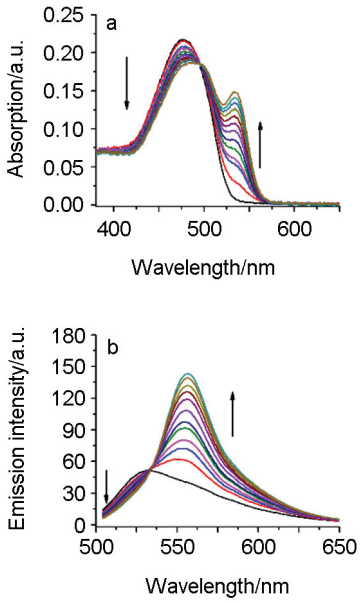

Figure 1 Time-dependent (a) absorption and (b) fluorescence responses of **BSFO-1** (10 μmol•L^{-1}) to 1 mmol•L^{-1} Cys. Spectra were recorded 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 min after Cys addition at 37 ℃ in acetonitrile/PBS buffer (1∶1, *V*/*V*, 25 mmol•L^{-1}, pH 7.4), λ_{ex} =480 nm.

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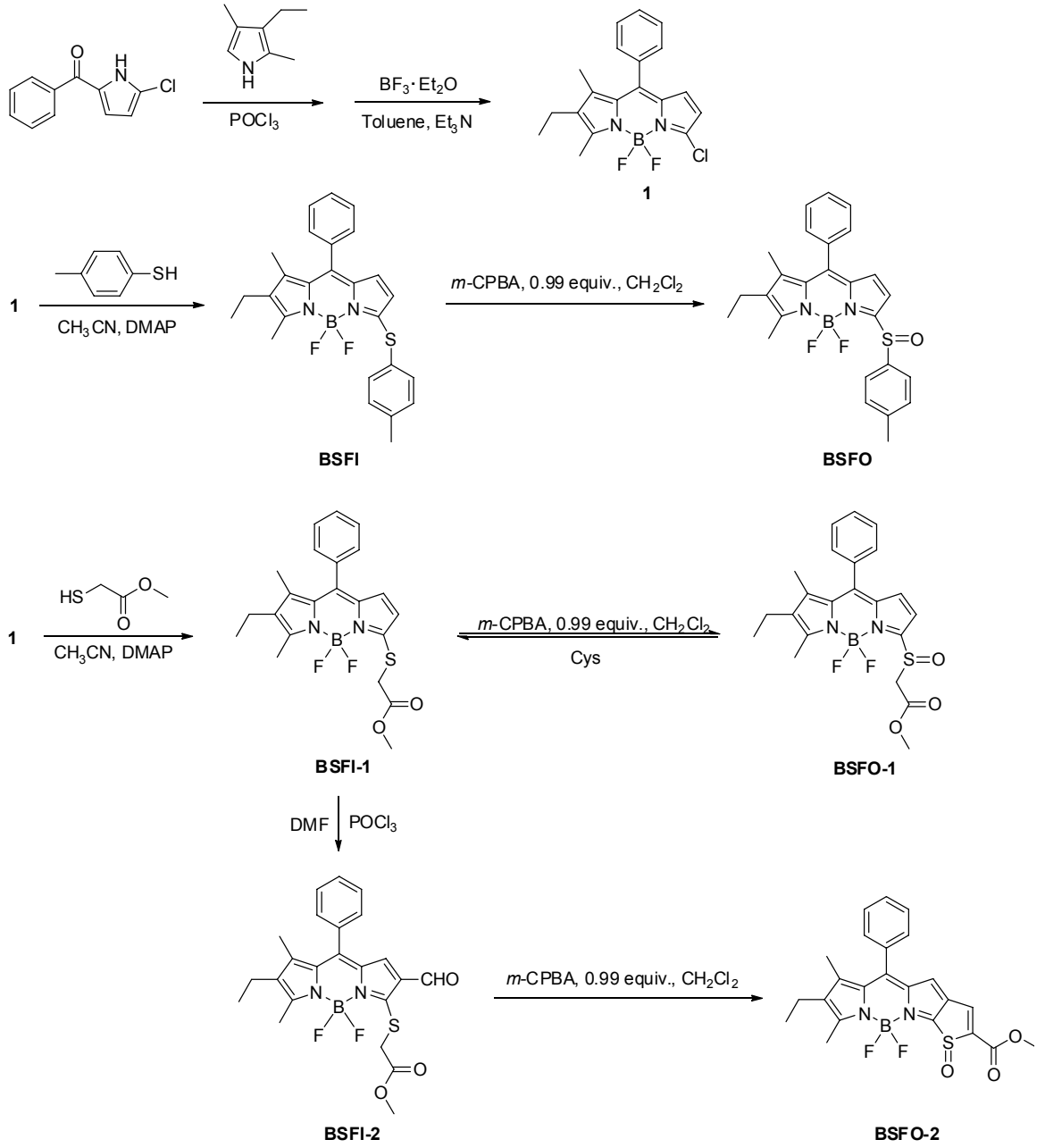
Scheme 1 Synthesis of target probes **BSFO-1**, **BSFO-2** and the model **BSFO**



maximum at 528 nm. Upon addition of Cys, a distinct reduction of the absorption band at 480 nm was observed, along with an increase of the absorption at 535 nm and occurrence of the obvious isosbestic point at 495 nm. Importantly, the fluorescence spectra also endowed ratiometric changes in the presence of Cys. The fluorescence intensity at 528 nm decreased gradually, and that at 556 nm enhanced simultaneously, resulting in a distinct ratio change of I_{556}/I_{528} from 0.8 to 2.4 (Figure 2), indicative of the capability of accurate analysis of Cys. The ratiometric change of fluorescence is time-dependent and the observed rate constant was determined to be 0.0158 min^{-1} under the pseudo-first-order conditions. Also, Cys triggered distinct color changes of the solution (Figure S2).

The response behavior of **BSFO-1** toward other thiol-containing amino acids was further determined. It was found that Hcy and GSH elicited minimal photophysical responses under the same physiological conditions (Figure S3). This distinct selectivity was contributed to the dynamics of reactions between probe and thiols. From the experimental data, the pseudo-first-order reaction rate was determined to be 0.0033 min^{-1} for Hcy, and that of GSH was 2.9×10^{-4} min^{-1} (Figure S3). Obviously, these rates are much slower than that for Cys, indicative of the high selectivity of **BSFO-1** toward Cys over Hcy and GSH. The selectivity of **BSFO-1** towards Cys over relevant thiol-lacking amino acids and hydrogen sulfide was then evaluated by measuring the changes in the fluorescence spectra upon

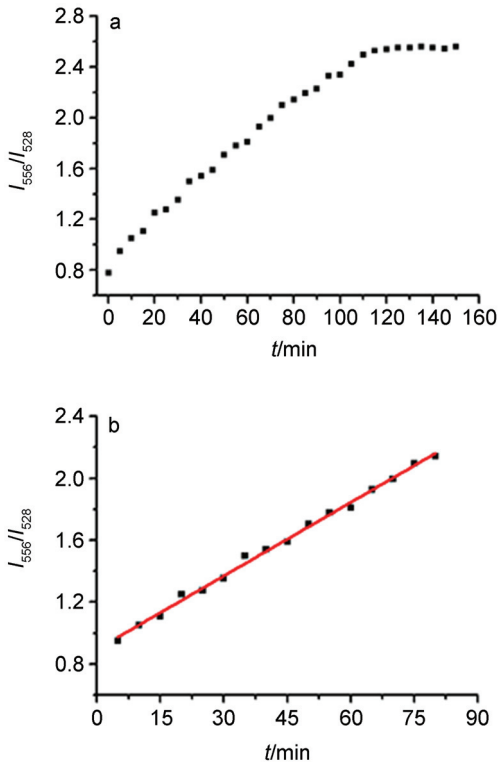


Figure 2 (a) Time-dependent fluorescence intensity ratio (I_{556}/I_{528}) changes of **BSFO-1** (10 μmol•L^{-1}) toward 1 mmol•L^{-1} Cys at 37 ℃, in acetonitrile/PBS buffer (1∶1, *V*/*V*, 25 mmol•L^{-1}, pH 7.4), λ_{ex} =480 nm; (b) Pseudo first-order kinetic plots of the reaction of **BSFO-1** (10 μmol•L^{-1}) with 1 mmol•L^{-1} Cys at 37 ℃.

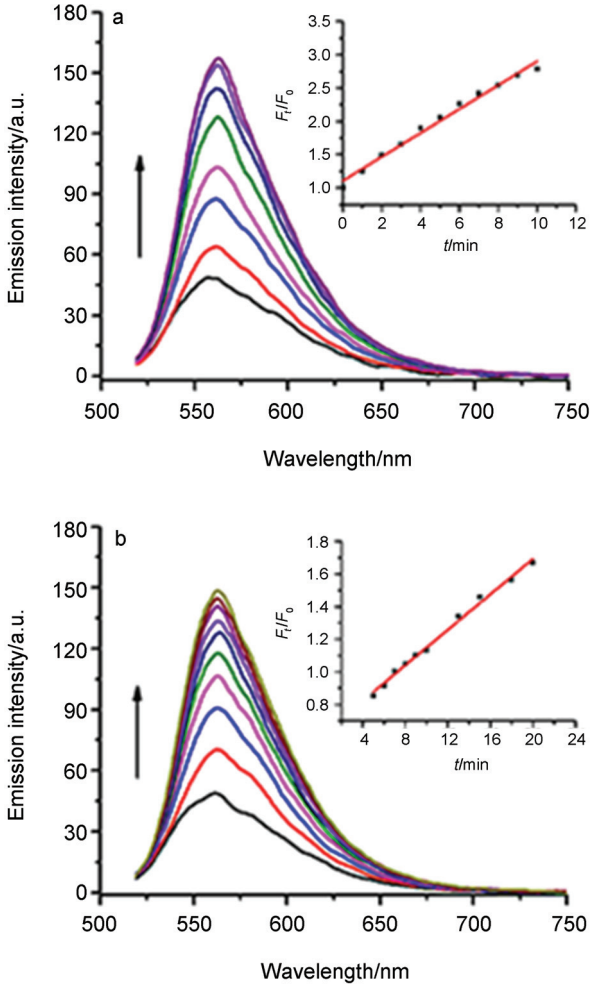


Figure 3 (a) Fluorescence responses of **BSFO-2** (10 μmol•L^{-1}) to 1 mmol•L^{-1} Cys. Spectra were acquired 0, 1, 3, 5, 7, 9, 11, 13 min after the addition of Cys in 25 mmol•L^{-1} sodium phosphate at 37 ℃, pH 7.4, λ_{ex}=500 nm. Inset is pseudo first-order kinetic plots of **BSFO-2** (10 μmol•L^{-1}) with 1 mmol•L^{-1} Cys at 37 ℃, F_0 represents the emission intensity at 564 nm in the absence of Cys, F_t represents time-dependent emission intensity at 564 nm in the presence of Cys. (b) Fluorescence responses of **BSFO-2** (10 μmol•L^{-1}) to 1 mmol•L^{-1} Hcy. Spectra were acquired 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 min after the addition of Hcy. Inset is pseudo first-order kinetic plots of **BSFO-2** (10 μmol•L^{-1}) with 1 mmol•L^{-1} Hcy at 37 ℃, F_0 represents the emission intensity at 564 nm in the absence of Hcy, F_t represents time-dependent emission intensity at 564 nm in the presence of Hcy.

addition of excess amount of various amino acids within the analytical time of 2 h. The ratiometric fluorescent change can only be introduced by Cys (Figure S3). By contrast, other relevant analytes led to no obvious ratiometric change, indicating that **BSFO-1** is a highly selective probe and can monitor Cys with minimum interference from other relevant analytes.

The reaction mechanism of **BSFO-1** with Cys was then studied. When **BSFO-1** (5 mmol•L^{-1}) and cysteine (500 mmol•L^{-1}) were stirred for 2 h in acetonitrile/PBS buffer (1∶1, *V*/*V*, 25 mmol•L^{-1}, pH 7.4) at 37 ℃, an obvious color change of the solution from yellow to red was noted and a stable fluorescent product was observed clearly on the TLC plate. The reaction product was purified and identified by NMR and mass spectra. HRMS manifested a peak at *m*/*z*=451.1437, which is identical to that of **BSFI-1**. ^{1}H NMR spectra also matched well with that of **BSFI-1** (Figure S4). All these data suggest that the sulfoxide function was eventually reduced to sulfide by sulfhydryl group in Cys.

The linear relationship between the fluorescence response[14] and concentration of Cys is important for accurate measurement of Cys. In the titration experiments, it was clear that the fluorescence response is Cys concentration dependent with Cys concentrations from 0 to 500 μmol•L^{-1}. The detection limit was then calculated to be 5.62×10^{-6} mol•L^{-1} (Figure S5).

Collectively, a ratiometric probe for thiols was obtained via simply regulating the reactivity of sulfoxide susceptible to reduction by sulfhydryl group in thiols. Obviously, diminishing the steric effect is a suitable design strategy to furnish the sulfoxide→sulfide transfer.

To further demonstrate this trend, another BODIPY-based sulfoxide, **BSFO-2** was explored to evaluate the responses to these thiols. **BSFO-2** bears rigid conjugate plane which makes sulfoxide exposure to reducing agents. Furthermore, the rigidity of the aromatic ring should accelerate the reduction by thiols. As expected,

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BSFO-2 showed much faster reaction toward Cys. Under the pseudo-first-order conditions, the observed rate constant was found to be 0.18 min^{-1} (Figure 3), which is 10 times that for **BSFO-1**. Since the elevating reactivity, **BSFO-2** showed poor selectivity toward thiol-containing amino acids. **BSFO-2** also gave distinct fluorescence turn-on response to Hcy with an observed rate constant of 0.05 min^{-1}. Other related amino acids induced minimal fluorescence variations (Figure S6).

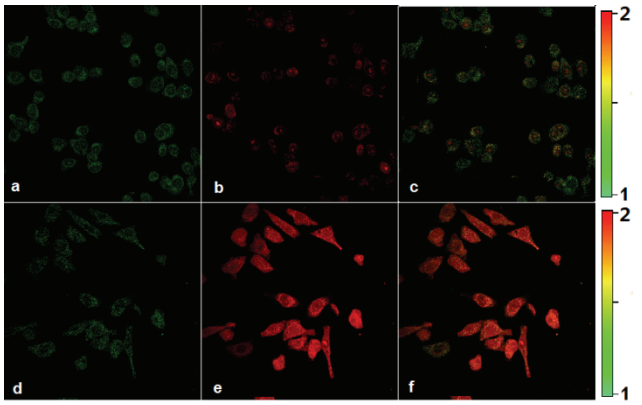

Figure 4 Fluorescent confocal images of HeLa cells (a—c) pretreated with 500 μmol•L^{-1} *N*-methylmaleimide for 20 min, further incubated with **BSFO-1** (5 μmol•L^{-1}) for 1 h, the excitation wavelength was 488 nm: (a) green channel at 500—530 nm, (b) red channel at 550—580 nm, (c) overlay image generated from (a) and (b); (d—f) cells pretreated with 500 μmol•L^{-1} *N*-methylmaleimide for 20 min, further incubated with Cys (500 μmol•L^{-1}) for 20 min, then loaded with **BSFO-1** (5 μmol•L^{-1}) for 1 h, the excitation wavelength was 488 nm: (d) green channel at 500—530 nm, (e) red channel at 550—580 nm, (f) overlay image generated from (d) and (e).

Finally, **BSFO-1** was employed for living cells imaging in a dual color manner (Figure 4). In these experiments, HeLa cells were pretreated with *N*-methylmaleimide (500 μmol•L^{-1}, a trapping reagent of thiols) for 20 min, then incubated with **BSFO-1** (5 μmol•L^{-1}) for 1 h. Bright fluorescence signals were observed in green channel (500—530 nm), while the red channel (550—580 nm) is dark. The ratio from red channel to green channel can be defined to be 1.0. In sharp contrast, pronounced fluorescence signals were observed in red channel when pretreated cells were loaded with Cys (500 μmol•L^{-1}) for 20 min before incubation with **BSFO-1** (5 μmol•L^{-1}) for 1 h, and the ratio was finally improved to be around 2.0, resulting in nearly 2-fold enhancement. These results indicated that **BSFO-1** is cell-permeable and can be a promising probe for ratiometric determination of Cys in living cells.

Conclusions

In summary, a new design strategy utilizing the intrinsic reductive characteristic of the sulfhydryl group in thiols was explored to generate fluorescent probes. Thus, BODIPY-based sulfoxides were designed and evaluated. These probes showed thiol-triggered sulfoxide→sulfide transfer, accompanied by ratiometric absorption and fluorescence changes. These features were further successfully used for imaging Cys in living cells.

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