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Reaction-based dual signaling of fluoride ions by resorufin sulfonates†

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We developed new reaction-based probes for the dual signaling of fluoride ions. Selective fluoride-assisted deprotection of resorufin nosylate to generate resorufin fluorochrome was used for signaling. Resorufin nosylate exhibited selective colorimetric and fluorogenic signaling of fluoride ions in acetonitrile. The response from sulfide ions was effectively masked by using the TPEN–Cu^{2+} complex as a source of Cu^{2+} ions for masking sulfide. Selective optical signaling of fluoride was possible in the presence of commonly encountered anions with a detection limit of 1.9×10^{-6} M.

Introduction

Anionic species play important roles in many chemical and biological processes. A number of optical chemosensors for selectively detecting anionic substrates of different shapes and charges have been reported.[1,2] Of the many important anionic targets, fluoride ions have attracted much research interest owing to their importance in many aspects of chemical, biological, clinical, and environmental sciences.[3] In particular, fluoride anions play an essential role in dental care, osteoporosis treatment, and water fluoridation.[4]

There are a variety of sophisticated fluoride sensors.[5] Representative fluoride sensors operating in organic solvents use hydrogen bonding between fluoride ions and a variety of sensor functional groups, such as phenol, urea, thiourea, amide, pyrrolic, and indolic NHs. The sensors are made of various molecular skeletons, including unmodified fluorescein,[6] bisurea of anthracene,[7] pyrrolylquinoxalines containing pyrene antenna moieties,[8] calix[4]pyrrole,[9] and calix[4]-arene.[10] Chelating and cationic boranes,[11,12] well-known boron–dipyrromethene dyes,[13] and the axial-substituted subphthalocyanine moiety[14] have also been successfully devised for selective fluoride signaling. Recently, chemodosimetric probes for fluoride anions have also attracted much research interest.[15] These probes are based on the specific reactivities of compounds with fluoride ions. Notable examples are dual chromogenic and fluorescent chemodosimeters based on fluoride-induced Si–O bond cleavage of silyloxybenzyl-protected resorufin and naphthalimide,[16,17] and the silyl ether derivative of dicyanomethylene-4*H*-chromene and fluorescein.[18,19] Another interesting system reported by Kim and Swager is a turn-on type dosimeter that uses fluoride-triggered coumarin dye formation by the unique chemical reactivity of fluoride with bulky silyl-protecting groups.[20]

Resorufin is one of the most attractive fluorochromes used to construct advanced optical signaling systems because of its characteristically large fluorescence enhancement and pronounced colorimetric possibilities.[21] The deprotection of sulfonic esters has been successfully used to design a variety of important chemical species. Typical examples are pentafluorobenzenesulfonyl-fluorescein for hydrogen peroxide,[22] bis-(dinitrobenzenesulfonyl)-fluorescein for superoxide,[23] dinitrobenzenesulfonyl-merocyanine and BODIPY for thiols,[24] dinitrobenzenesulfonyl-fluorescein for sulfide,[25] and dinitrobenzenesulfonyl-resorufin for acetyl-cholinesterase assay.[26] The deprotection of phenol function in trifluoromethanesulfonate and toluenesulfonate by fluoride ions has been demonstrated in organic synthesis (Scheme 1).[27] Using this transformation, we developed a new fluoride-selective probe by the selective deprotection of resorufin nitrobenzenesulfonate. The designed compound showed selective and sensitive chromogenic and fluorescence turn-on type signaling for fluoride ions in acetonitrile.

Results and discussion

Resorufin nosylate **1**, dinitrobenzenesulfonate **2**, and tosylate **3** were prepared by reacting sodium salt of resorufin with

Scheme 1 Deprotection of aryl sulfonates by fluoride ion.

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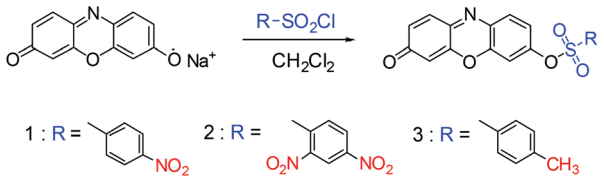


Scheme 2 Preparation of resorufin sulfonates for fluoride signaling.

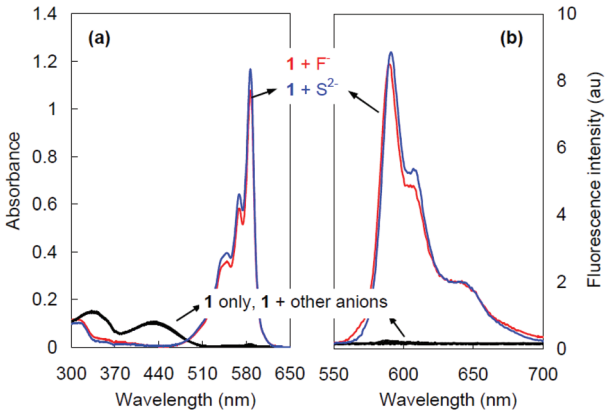


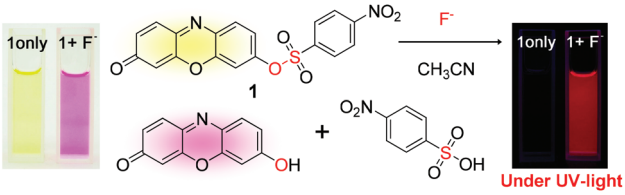
Fig. 1 UV–vis spectra (a) and fluorescence spectra (b) of **1** in the presence of various anions. (a) [**1**] = 1.0 × 10^{-5} M, [A^{n-}] in TBA salt = 1.0 × 10^{-4} M. (b) [**1**] = 5.0 × 10^{-6} M, [A^{n-}] in TBA salt = 5.0 × 10^{-5} M in CH_3CN. λ_{ex} = 485 nm.

p-nitrobenzenesulfonyl chloride, 2,4-dinitrobenzenesulfonyl chloride, or *p*-toluenesulfonyl chloride, respectively, in dichloromethane (Scheme 2). The chromogenic and fluorescence signaling of sulfonates toward fluoride ions were investigated in acetonitrile where the most pronounced signaling selectivity and efficiency were observed.

The UV–vis absorption spectrum of **1** was characterized by two moderate intensity bands at 335 and 433 nm (Fig. 1a). Treating **1** with 10 equiv. of fluoride or sulfide in TBA salt resulted in a pronounced change in the UV–vis absorption spectrum. The absorption bands of **1** at 335 and 433 nm disappeared and new strong bands appeared at 550, 569, and 587 nm that are ascribed to resorufin fluorochrome. The solution color changed markedly from yellow to pink, which allowed detection of fluoride and sulfide ions with the naked eye. Other representative anions tested (Cl^-, Br^-, I^-, AcO^-, NO_3^-, N_3^-, ClO_4^-, and HSO_4^-) showed almost no responses. In these cases, a large change in the wavelength of the absorption maximum provides a possibility of ratiometric analysis of fluoride and sulfide signaling. The absorbance ratio at 587 and 433 nm (A_{587}/A_{433}) was used for ratiometry. The change was very large for fluoride (from 0.01 to 179) and sulfide (from 0.01 to 187), while the other tested anions revealed nearly constant responses between 0.01 for Br^- and 0.13 for AcO^- (Fig. S1, ESI†). The response of **1** toward sulfide ions is disappointing for applications in fluoride-selective signaling. As mentioned earlier, sulfide signaling by the dinitrobenzenesulfonate of fluorescein has already been reported.[25] However, the sulfide response of **1** could be effectively suppressed by using the TPEN–Cu^{2+} complex as a source of Cu^{2+} masking ions, which allowed the desired fluoride-selective signaling of **1** (*vide infra*).

Fluorescence signaling of fluoride and sulfide ions by **1** was also pronounced (Fig. 1b). Nosylate **1** showed very weak emission above 550 nm in acetonitrile, as did other *O*-derivatized resorufins. However, upon treatment with 10 equiv. of fluoride or sulfide ions, intense fluorescence was observed at 591 nm. The fluorescence intensity ratio at 591 nm in the presence and absence of added analyte I/I_o was 58.9 for fluoride and 62.2 for sulfide ions (Fig. S2, ESI†). Concomitantly, a deep pink fluorescence developed under illumination with a UV-lamp. Other anions revealed no significant response and the I/I_o at 591 nm changed within a narrow range between 1.11 for Br^- and 1.60 for AcO^-. These observations clearly demonstrate the fluoride- and sulfide-selective chromogenic and fluorescent signaling behavior of nosylate **1**.

Signaling occurs due to deprotection of the nosylate group on the phenolic hydroxyl group of resorufin by fluoride ions (Scheme 3), which is a useful protocol in synthetic organic chemistry.[28] ^{1}H NMR, UV–vis, and fluorescence measurements were used to follow the depicted deprotection process. The ^{1}H NMR spectrum of probe **1** in the presence of 5 equiv. of fluoride ions transformed to that of resorufin (Fig. 2). The six resonances of **1** in the 6.3–8.0 ppm region were transformed to three well-defined signals of resorufin at 5.91, 6.29, and 7.21 ppm. UV–vis and fluorescence spectra of **1** in the presence of 10 equiv. of fluoride ions were also identical to those of resorufin (Fig. S3 and S4, ESI†). The signaling speed of fluoride by **1** was



Scheme 3 Signaling of fluoride ions by deprotection of resorufin nosylate.

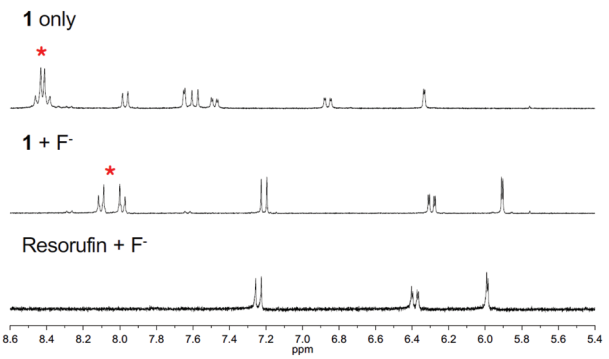


Fig. 2 Partial ^{1}H NMR spectra of **1**, **1** + F^-, and resorufin + F^-. [**1**] = [Resorufin] = 5.0 × 10^{-3} M. [F^-] in TBA salt = 2.5 × 10^{-2} M in DMSO-d_6. Red starred peaks are due to the aromatic resonances of the nosyl group.

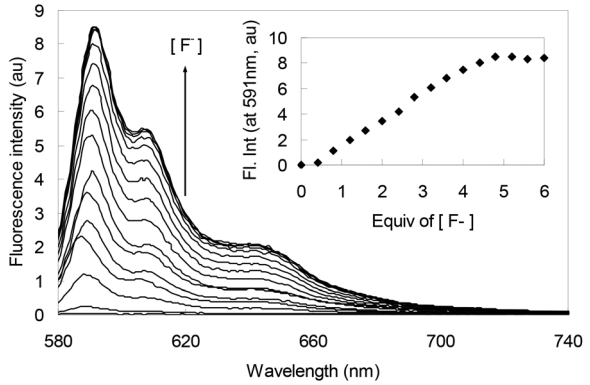


Fig. 3 Concentration dependent fluorescence signaling behavior of **1** for fluoride ions. [**1**] = 5.0×10^{-6} M, [F^-] in TBA salt = from 0 to 3.0×10^{-5} M in CH_3CN. Inset: fluorescence intensity at 591 nm as a function of fluoride concentration. λ_{ex} = 485 nm.

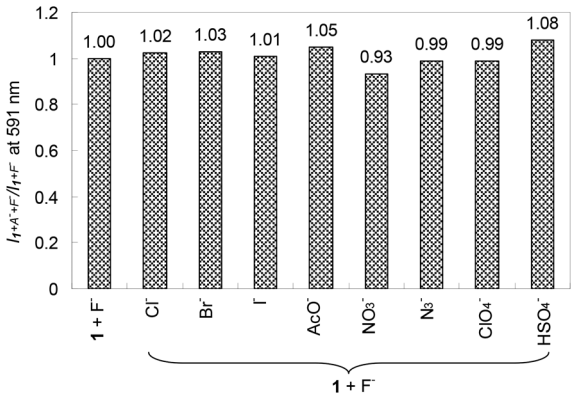


Fig. 4 Signaling of fluoride ions by **1** in the presence of various anions as the background. [**1**] = 5.0×10^{-6} M, [F^-] = [A^-] in TBA salt = 5.0×10^{-5} M in CH_3CN. λ_{ex} = 485 nm.

fast and completed within 5 min after sample preparation (Fig. S5, ESI†).

The quantitative fluoride signaling behavior of **1** was investigated by fluorescence titration (Fig. 3). As fluoride concentration increased, the fluorescence intensity at 591 nm increased steadily and showed a concentration-dependent calibration up to 2.5×10^{-5} M of fluoride ions. From this concentration-dependent signaling profile, the detection limit for the determination of fluoride ions in acetonitrile was estimated as 1.9×10^{-6} M.[29] UV–vis titration also provided a useful calibration plot by ratiometric analysis using the ratio of two absorbances of **1** at 433 and 587 nm (Fig. S6, ESI†). The detection limit obtained by UV–vis measurements was 6.2×10^{-6} M, which is fairly larger than that obtained by fluorescence measurements.

The possible interferences in the fluoride signaling of **1** from other coexisting anions were checked. Fluoride-selective fluorescence signaling behavior of **1** was not significantly affected by the presence of commonly encountered anions (Fig. 4 and Fig. S7, ESI†). The variation in fluorescence intensity at 591 nm of the **1**–F^- system in the presence and absence of coexisting anions (A^-) $I_{\mathbf{1}+F+A}/I_{\mathbf{1}+F}$ under competitive conditions fluctuated in a narrow range between 0.93 for NO_3^- and 1.08 for HSO_4^- ions. The UV–vis spectral behavior also confirmed that the fluoride-selective signaling was not significantly affected by commonly encountered anions as the background (Fig. S8, ESI†).

The signaling behaviors of resorufin dinitrobenzenesulfonate **2** and tosylate **3** were also tested, expecting more improved fluoride signaling. For dinitrobenzenesulfonate **2**, the signaling sensitivity for fluoride ions was high and the signaling speed was fast (Fig. S9 and S10, ESI†) due to the increased electron withdrawing nature of the dinitro substituent on the sulfonate benzene ring. However, the selectivity toward fluoride ions was inferior to that of nosylate **1** (Fig. S11 and S12, ESI†). In addition to fluoride (A_{587}/A_{433} = 25), acetate (A_{587}/A_{433} = 3.0) and azide ions (A_{587}/A_{433} = 15) were also significantly responsive. On the other hand, tosylate **3** having an electron donating *p*-methyl substituent exhibited satisfactory fluoride selectivity, but the signaling speed and sensitivity for fluoride ions were much less favorable (Fig. S13 and S14, ESI†). Complete fluoride signaling with **3** required several hours.

As mentioned earlier, probe **1** exhibited significant signaling toward sulfide ions comparable to that of fluoride ions under the same measurement conditions. Compounds **2** and **3** also exhibited substantial responses toward sulfide ions (Fig. S15, ESI†). To obtain the sole fluoride selectivity of **1**, interference from sulfide ions was suppressed by adding metal ions that form very insoluble metal sulfides, such as Cu^{2+} or Zn^{2+}. The addition of Cu^{2+} or Zn^{2+} ions effectively suppressed signaling by sulfide; however, fluoride signaling was also significantly affected by the interaction of added metal ions with fluoride ions. The undesirable interaction of fluoride with added metal ions was successfully controlled by using TPEN, which forms stable complexes with transition metal cations, as an auxiliary complexing agent (Fig. 5). Because the solubility product, K_{sp}, of CuS(s)[30] is 8×10^{-37} and the association constant, K_{assoc}, for the complex between Cu^{2+} and TPEN[31] is 3.47

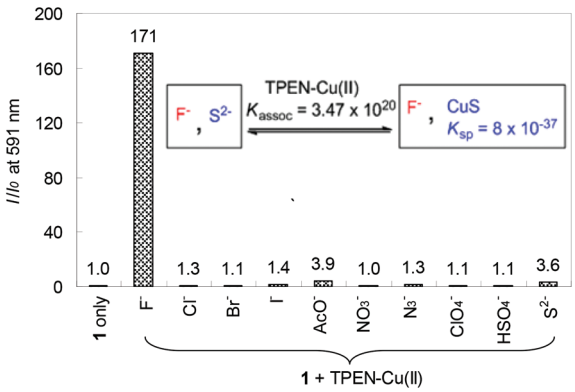


Fig. 5 Changes in fluorescence intensity I/I_o of **1** at 591 nm in the presence of various anions in CH_3CN. The sulfide signaling of **1** was suppressed by the TPEN–Cu^{2+} complex. [**1**] = 5.0×10^{-6} M, [A^{n-}] in TBA salt = 5.0×10^{-5} M, [TPEN] = 9.0×10^{-5} M, [Cu^{2+}] = 7.5×10^{-5} M in acetonitrile. λ_{ex} = 485 nm.

$\times 10^{20}$, interfering sulfide ions in the presence of the TPEN–Cu^{2+} complex can be effectively sequestered by forming insoluble CuS(s). Conversely, fluoride ions could remain intact from the undesirable interaction of Cu^{2+} ions which are tightly complexed by TPEN. Although the cited constants (K_{sp} of CuS(s) and K_{assoc} of TPEN–Cu^{2+}) are not directly accountable for the significantly different situation of the present measuring conditions of acetonitrile, a qualitative interpretation might be plausible.

Finally, the practical applicability of **1** for the fluoride-selective signaling in mixed aqueous medium was tested. As water content in the aqueous acetonitrile solution increased, the signaling became drastically less effective as in other fluoride probes that operated in organic solutions (Fig. S16, ESI†).[32] In the present resorufin nosylate system, a satisfactory fluoride-selective signaling is not plausible in acetonitrile solution that contains more than 2% water (Fig. S17, ESI†).

Conclusions

We investigated new reaction-based fluoride signaling system based on the sulfonates of resorufin fluorochrome. Resorufin nosylate was smoothly deprotected by fluoride ions in acetonitrile. The deprotection resulted in selective colorimetric and fluorescence turn-on type fluoride signaling behavior. Conversely, dinitrobenzenesulfonate of resorufin exhibited low selectivity toward fluoride ions, while tosylate derivative demonstrated slow fluoride signaling speed. The interference from sulfide was successfully suppressed by using the TPEN–Cu^{2+} complex as a source of Cu^{2+} masking ions. Signaling was not affected by the presence of common anions. The designed resorufin nosylate system could be useful in constructing other supramolecular systems targeted for fluoride ions.

Experimental section

General

Resorufin sodium salt, 4-nitrobenzenesulfonyl chloride, 2,4-dinitrobenzenesulfonyl chloride, *p*-toluenesulfonyl chloride, *N*,*N*,*N*′*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN), and tetrabutylammonium (TBA) salts of various anions were purchased from commercial suppliers and used without further purification. All other chemicals and solvents were used as received. UV–vis and fluorescence experiments were performed using HPLC grade acetonitrile. ^{1}H NMR and ^{13}C NMR spectra were recorded at 600 MHz and 150 MHz, respectively, and referenced to the residual solvent signal. Mass spectra were obtained on a FAB-Double focusing mass spectrometer. Column chromatography was performed with silica gel (240 mesh).

Synthesis of 1

4-Nitrobenzenesulfonyl chloride (0.26 g, 1.2 mmol) in 10 mL dichloromethane was added to a suspension of resorufin sodium salt (0.30 g, 1.3 mmol) and triethylamine (0.54 mL, 3.9 mmol) in 40 mL dichloromethane. The reaction mixture was stirred at room temperature for 12 h, and the resulting solution was treated with water. The organic phase was separated, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane–ethyl acetate = 1 : 1) to afford nosylate **1** (0.27 g, 58%) as an orange colored solid. Mp = 199–200 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.45–8.36 (m, 4H), 7.94 (d, J = 8.7 Hz, 1H), 7.60 (d, J = 2.4 Hz, 1H), 7.56 (d, J = 9.8 Hz, 1H), 7.46 (dd, J = 8.7 Hz and 2.4 Hz, 1H), 6.84 (dd, J = 9.8 Hz and 2.0 Hz, 1H), 6.30 (d, J = 2.0 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 186.1, 151.7, 150.7, 149.7, 149.6, 144.6, 139.5, 135.6, 135.5, 132.6, 131.9, 130.6, 125.6, 119.7, 110.9, 106.7; HRMS (FAB); *m*/*z* calcd for $C_{18}H_{11}N_2O_7S$ $[M + H]^+$: 399.0281, found 399.0287.

Synthesis of 2

Compound **2** was prepared by reacting resorufin sodium salt with 2,4-dinitrobenzenesulfonyl chloride following the reported procedure.[26] The crude product was purified by flash column chromatography (silica gel, hexane–ethyl acetate = 1 : 1) to yield dinitrobenzenesulfonate **2** (53%) as an orange colored solid.

Synthesis of 3

Resorufin tosylate **3** was prepared by the reaction of resorufin sodium salt with *p*-toluenesulfonyl chloride following the procedure described above. Crude product **3** was purified by flash column chromatography (silica gel, hexane–ethyl acetate = 1 : 1) to give tosylate **3** (60%) as a yellowish green solid. Mp = 195–196 °C. ^{1}H NMR (600 MHz, DMSO-d_6) 7.83 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 9.8 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 2.5 Hz, 1H), 7.07 (dd, J = 8.7 Hz and 2.5 Hz, 1H), 6.82 (dd, J = 9.8 Hz and 2.1 Hz, 1H), 6.28 (d, J = 2.1 Hz, 1H), 2.41 (s, 3H) ^{13}C NMR (150 MHz, DMSO-d_6) δ 186.1, 151.2, 149.7, 149.4, 146.7, 144.5, 135.6, 135.4, 132.3, 131.7, 131.4, 130.9, 128.8, 119.7, 110.6, 106.7, 21.7; HRMS (FAB); *m*/*z* calcd for $C_{19}H_{14}NO_5S$ $[M + H]^+$: 368.0587, found 368.0591.

Preparation of stock solutions

A stock solution of **1** (5.0×10^{-4} M) was prepared in acetonitrile. Stock solutions (1.0×10^{-2} M) of the TBA salt of F^-, Cl^-, Br^-, I^-, AcO^-, NO_3^-, N_3^-, ClO_4^-, HSO_4^-, and S^{2-} were prepared in CH_3CN. TBA sulfide was prepared by treating TBA hydroxide with ammonium sulfide. A stock solution of the TPEN–Cu^{2+} complex was prepared by dissolving 25.4 mg (0.060 mmol) of TPEN and 18.5 mg (0.050 mmol) of copper perchlorate hexahydrate in CH_3CN (5.0 mL). To protect fluoride ions from interaction with added metal ions, 1.2 equiv. of TPEN with respect to Cu^{2+} ions was used. The final concentrations of TPEN and Cu^{2+} were 0.012 M and 0.01 M, respectively.

Measurement of signaling behaviors

The UV–vis and fluorescence signaling behaviors of **1** toward analytes in TBA salts were measured in acetonitrile. Measuring solutions were prepared by successively placing 60 μL (for UV–vis measurements) or 30 μL (for fluorescence measurements) of stock solution of **1**, and 30 μL (for UV–vis measurements) or 15 μL (for fluorescence measurements) of a TBA salt solution (1.0×10^{-2} M) in a vial. The resulting solutions were diluted to 3.0 mL with acetonitrile. The final concentrations of **1** and TBA salt were 1.0×10^{-5} M and 1.0×10^{-4} M for UV–vis, and 5.0×10^{-6} M and 5.0×10^{-5} M for fluorescence measurements, respectively. The excitation wavelength was 485 nm for fluorescence measurements. The detection limit was estimated by plotting changes in the fluorescence intensities of **1** at 591 nm as a function of $\log[F^-]$ following the reported procedure.[29] A linear regression curve was fitted to the intermediate values of the sigmoidal plot. The point at which this line crossed the ordinate axis was taken as the detection limit.

Masking of sulfide interference

To remove interference from sulfide ions, the analyte was treated with the TPEN–Cu^{2+} complex solution as a masking agent. To each sample solution containing different anions, 22.5 μL of the TPEN–Cu^{2+} stock solution was added, followed by probe **1** under the same conditions. The final concentrations of probe **1**, anions, TPEN, and Cu^{2+} for fluorescence measurements were 5.0×10^{-6} M, 5.0×10^{-5} M, 9.0×10^{-5} M, and 7.5×10^{-5} M, respectively.

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