Organic & Biomolecular Chemistry

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Dual signaling of hydrazine by selective deprotection of dichlorofluorescein and resorufin acetates†‡

Cite this: *Org. Biomol. Chem.*, 2013, **11**, 2961

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Received 16th January 2013,
Accepted 26th February 2013

DOI: 10.1039/c3ob40091c

www.rsc.org/obc

The highly selective chemosignaling behaviors for hydrazine by a reaction-based probe of dichlorofluorescein and resorufin acetates were investigated. Hydrazinolysis of latent dichlorofluorescein and resorufin acetate fluorochromes caused prominent chromogenic and fluorescent turn-on type signals. The probes selectively detected hydrazine in the presence of commonly encountered metal ions and anions as background. Dichlorofluorescein and resorufin acetates selectively detected hydrazine with detection limits of 9.0×10^{-8} M and 8.2×10^{-7} M, respectively. Furthermore, hydrazine was selectively detected over other closely related compounds, such as hydroxylamine, ethylenediamine, and ammonia. As a possible application of the acetate probes, hydrazine signaling in tap water was tested.

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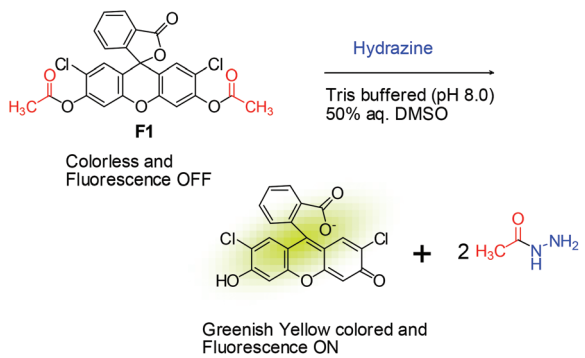
Introduction

The search for selective and efficient signaling and imaging systems to detect various chemically and biologically pertinent species is an important area of supramolecular research.[1] A variety of sophisticated systems based on optically responsive molecular frameworks have been designed to selectively detect or visualize target species.[2] One common strategy is using analyte triggered selective transformations of latent dye derivatives to yield signaling fluorochromes based on versatile dyes of fluorescein, rhodamine, and resorufin.[3–5]

Hydrazine has been used as a propellant fuel in rockets and spacecraft.[6] In industrial applications, hydrazine is used as an oxygen scavenger to prevent corrosion damage in water boilers for feed and heating systems.[7] Hydrazine is also a key starting material in the organic synthesis of pharmaceuticals,[8] such as 3-amino-1,2,4-triazole, maleic hydrazide, and isoniazid, as well as pesticides, explosives, and dyes. Hydrazine and its water solutions, however, are highly toxic to humans and animals.[9] Human occupational data and laboratory animal studies suggest that hydrazines may cause adverse systemic health effects including infections of the respiratory tract and damage to the lungs, liver, and kidneys.[10] Moreover, the United States Environmental Protection Agency and the World Health Organization have classified hydrazines as possible cancer-causing environmental contaminants.[11]

Hydrazine is routinely determined by electrochemical analysis[12] and chromatography,[13] including gas chromatography,[14] HPLC,[15] and capillary electrophoresis.[16] Spectrophotometry using colored derivatives, such as *p*-dimethylaminobenzaldehyde[17] and chlorosalicylaldehyde,[18] is also used to detect hydrazine. Other colorimetric systems have been discussed in a recent report.[19] However, few fluorometric analysis systems have been reported despite their sensitivity and specificity.[20] Fluorescence signaling that uses disruption of the internal hydrogen bonding of carbazolopyridinophane,[21] fluorescence enhancement of poly(phenylene ethynylene)-type conjugated polymers,[22] and intramolecular charge transfer of coumarin-like fluorophores[23] have been reported.

We recently reported a hydrazine-selective probe based on hydrazine-induced deprotection of levulinated coumarin.[24] In this paper, new dual signaling probes were devised for hydrazine using selective hydrolysis of dichlorofluorescein and resorufin acetate derivatives (Scheme 1). Hydrazinolysis of phenol acetates is a well-established process,[25] thus we



Scheme 1 Signaling of hydrazine by fluorescein acetate **F1**.

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†Dedicated to Professor Andrew D. Hamilton on the occasion of his 60th birthday.

‡Electronic supplementary information (ESI) available: Additional chemosignaling behaviors of dichlorofluorescein and resorufin acetates and ^{1}H and ^{13}C NMR spectra of **F1**, **F2** and **R2**. See DOI: 10.1039/c3ob40091c

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postulated that hydrazine could readily remove the acetate moiety of the fluorochrome to yield a deprotected analogue. As expected, hydrazinolysis regenerated the phenolic moiety of fluorochromes of dichlorofluorescein and resorufin, and dual signaling was realized as in probes designed to visualize hydrogen peroxide or perborate.[26–28]

Results and discussion

Signaling by dichlorofluorescein acetates (F1 and F2)

Dichlorofluorescein was converted to its acetates to construct the latent probe (Fig. 1). Acetate and chloroacetate were tested as protecting groups because the hydrolysis of fluorescein acetates strongly depends on the substituents of the ester function.[29] First, we investigated hydrazine detection by dichlorofluorescein diacetates **F1** and **F2** by observing the absorbance at 512 nm *versus* time. Compounds **F1** and **F2** exhibited hydrazine-selective signaling in 50% aqueous DMSO (Fig. S1, ESI‡). Hydrazine hydrolyzed chloroacetate **F2** almost instantaneously resulting in a constant signal. However, spontaneous hydrolysis of probe **F2** was also significant. On the other hand, the diacetate **F1** selectively detected hydrazine within 10 min, and the stability of **F1** was sufficient for hydrazine signaling. Therefore, the hydrazine signaling behaviors were further investigated using relatively optimized structure **F1** in terms of signaling speed and stability of the probe itself.

In the UV-vis spectrum of **F1**, there was no appreciable absorption above 450 nm in 50% aqueous DMSO (Fig. 2a). Treating **F1** with 100 equiv. of hydrazine created a strong absorption band at 512 nm, characteristic of 2′,7′-dichlorofluorescein, with a concomitant change in color from colorless to greenish yellow (inset of Fig. 2a). The absorbance at 512 nm changed almost 250-fold in the presence of hydrazine. Conversely, various metal ions and anions did not affect the absorption spectrum. The absorbance ratio A/A_o at 512 nm ranged from 0.78 (Li^+) to 2.8 (Cu^{2+}) for metal ions and from 0.99 ($P_2O_7^{4-}$) to 1.9 (N_3^-) for anions (Fig. S2, ESI‡). This indicates that under signaling conditions, the possible interference of ester hydrolysis assisted by common metal ions or anions is not a practical problem in hydrazine sensing by **F1**.

The fluorescence detection of hydrazine by **F1** was also pronounced. Diacetate **F1** showed very weak emission over 490 nm due to the closed spirolactone form of fluorescein

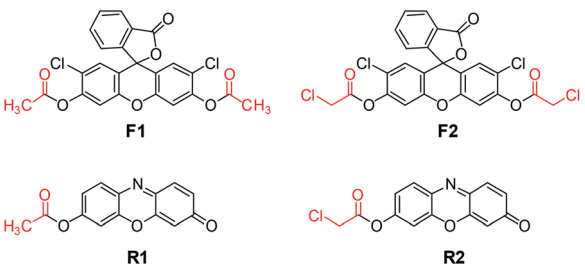

Fig. 1 Structures of dichlorofluorescein and resorufin acetates used for a hydrazine probe.

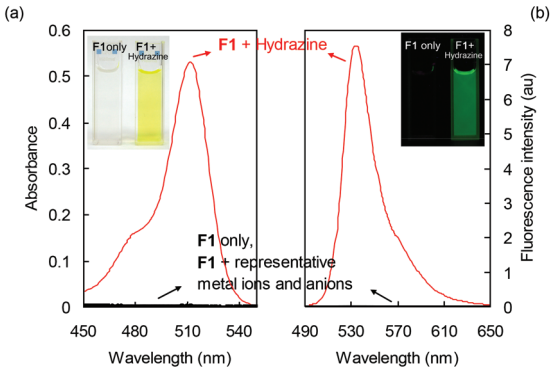

Fig. 2 UV-vis (a) and fluorescence spectra (b) of **F1** and **F1** in the presence of hydrazine or representative metal ions and anions. [**F1**] = 5.0 × 10^{-6} M, [Hydrazine] = [M^{n+}] = [A^{n-}] = 5.0 × 10^{-4} M. In a mixture of DMSO and tris buffer solution (pH 8.0, 10 mM) (1 : 1, v/v). λ_{ex} = 480 nm.

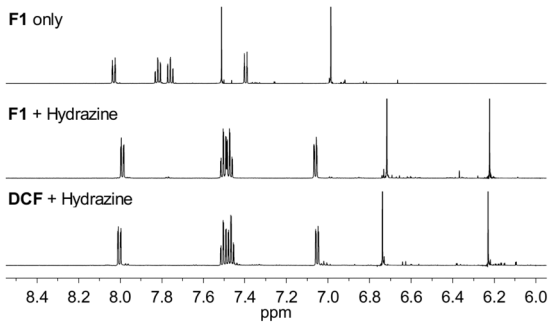

Fig. 3 Partial ^{1}H NMR spectra of **F1** in the absence and presence of hydrazine. [**F1**] = [DCF] = 1.0 × 10^{-2} M, [Hydrazine] = 5.0 × 10^{-2} M in D_2O–DMSO-d_6 (1 : 1, v/v). DCF: 2′,7′-dichlorofluorescein.

(Fig. 2b). Treatment with 100 equiv. of hydrazine created a prominent emission at 534 nm due to the ring-opened fluorescein structure. Concomitantly, the fluorescence color of the solution changed from dark to green under UV illumination (inset of Fig. 2b). The fluorescence intensity ratio of **F1** at 534 nm (I/I_o) in the presence and absence of hydrazine was larger than 920 (Fig. S3, ESI‡). Other metal ions and anions showed relatively small and constant I/I_o ratios at 534 nm, between 0.66 (Fe^{3+}) and 3.6 (Co^{2+}) for metal ions and between 0.89 (SO_3^{2-}) and 2.9 (N_3^-) for anions.

Hydrazine was detected by hydrazinolysis of the phenol acetate moiety of **F1** (Scheme 1). This reaction generated 2′,7′-dichlorofluorescein, which exhibited its characteristic chromogenic and fluorescent behaviors. The **F1** transformation to 2′,7′-dichlorofluorescein was evidenced by ^{1}H NMR, UV-vis, and fluorescence measurements. The ^{1}H NMR spectrum of the product obtained by treating **F1** with 5 equiv. of hydrazine in 50% deuterated aqueous DMSO-d_6 was identical to that of 2′,7′-dichlorofluorescein in the presence of the same amount of hydrazine (Fig. 3). Treating **F1** with hydrazine shifted the singlet resonances for 1′,8′-protons and 4′,5′-protons at 7.52 and 6.99 ppm to 6.74 and 6.24 ppm, respectively. Concomitantly, resonance for the methyl protons of acetate at 2.31 ppm

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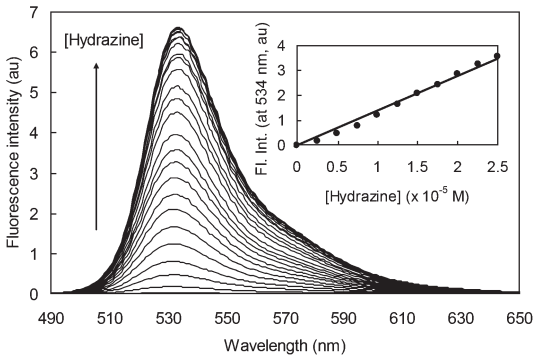

Fig. 4 Concentration-dependence of hydrazine detection by **F1**. [**F1**] = 5.0 × 10^{-6} M, [Hydrazine] = from 0 to 2.5 × 10^{-5} M, in a mixture of DMSO and tris buffer solution (pH 8.0, 10 mM) (1 : 1, v/v). λ_{ex} = 480 nm.

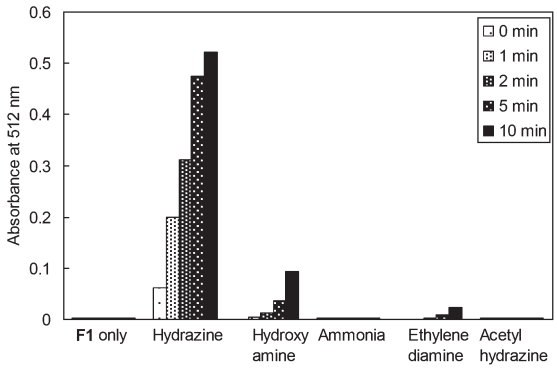

Fig. 5 Time-dependent changes in absorbance of **F1** at 512 nm in the presence of hydrazine and related compounds. [**F1**] = 5.0 × 10^{-6} M, [Hydrazine] = [Hydroxylamine] = [Ammonia] = [Ethylenediamine] = [Acetylhydrazine] = 5.0 × 10^{-4} M in a mixture of DMSO and tris buffer solution (pH = 8.0, 10 mM) (1 : 1, v/v).

disappeared. Another resonance at 1.73 ppm developed and is ascribed to the methyl protons of the acetylhydrazine byproduct (Fig. S4, ESI‡). In addition to this, the UV-vis and fluorescence spectra of **F1** in the presence of 20 equiv. of hydrazine were identical to those of 2′,7′-dichlorofluorescein (Fig. S5 and S6, ESI‡). An interesting observation is that acetylhydrazine, the product of the reaction between **F1** and hydrazine, was not able to cleave the acetate group under the experimental conditions (Fig. S7, ESI‡).

Diacetate **F1** selectively detected hydrazine in the presence of common metal ions and anions (Fig. S8, ESI‡). With metal ions or anions as background, the ratio of fluorescence signaling of **F1** at 534 nm, $I_{(\mathbf{F1}+\text{Hydrazine}+\text{ions})}/I_{(\mathbf{F1}+\text{Hydrazine})}$, ranged between 0.93 and 1.02. Only Cu^{2+} ions significantly reduced signaling ($I_{(\mathbf{F1}+\text{Hydrazine}+\text{Cu(II)})}/I_{(\mathbf{F1}+\text{Hydrazine})}$ at 534 nm = 0.73), which might be due to the interaction of Cu^{2+} ions with hydrazine.[30]

The concentration dependence of hydrazine detection by **F1** was assessed by fluorescence titration (Fig. 4). As shown in the inset of Fig. 4, the fluorescence intensity of diacetate **F1** at 534 nm was hydrazine concentration-dependent. The relationship was nearly linear up to 2.5 × 10^{-5} M hydrazine. The detection limit of **F1** for hydrazine was estimated by three times of standard deviation of the blank signal,[31] and was 9.0 × 10^{-8} M (2.9 ppb), which is sensitive enough for common chemical and industrial uses.

The hydrazine selectivity of **F1** over other closely related compounds was measured (Fig. 5). Hydroxylamine, one of the most significant materials that interferes with hydrazine analysis,[15] was tested, along with ethylenediamine and ammonia. Only hydroxylamine interfered considerably with hydrazine detection by probe **F1**. The absorbance ratio at 512 nm, $A_{\text{hydroxylamine}}/A_{\text{hydrazine}}$, was 0.18 for hydroxylamine, 0.05 for ethylenediamine, 0.003 for ammonia, and 0.003 for acetylhydrazine.

Signaling by resorufin acetates (R1 and R2)

Hydrazine was also selectively detected by the hydrolysis of an acetate probe based on another versatile fluorophore, resorufin (Fig. 1). As in the case of fluorescein, acetate **R1** and

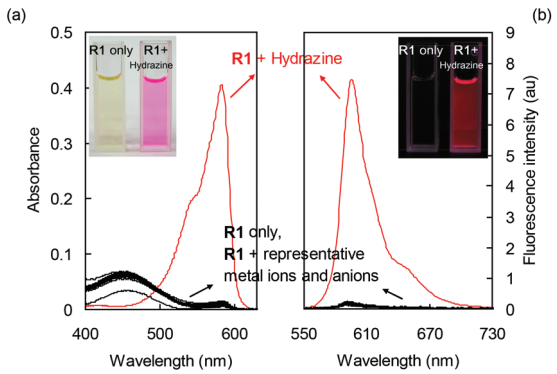

Fig. 6 UV-vis (a) and fluorescence spectra (b) of **R1** and **R1** in the presence of hydrazine or representative metal ions and anions. [**R1**] = 5.0 × 10^{-6} M, [Hydrazine] = [M^{n+}] = [A^{n-}] = 5.0 × 10^{-4} M. In a mixture of DMSO and tris buffer solution (pH 8.0, 10 mM) (1 : 1, v/v). λ_{ex} = 492 nm.

chloroacetate **R2** derivatives of resorufin were prepared and their signaling behavior was tested. As expected, spontaneous hydrolysis of chloroacetate **R2** was much faster than acetate **R1** (Fig. S9, ESI‡). In fact, while **R1** exhibited some spontaneous hydrolysis, the hydrolysis observed at 30 min was minor and did not significantly affect hydrazine detection. Therefore, the signaling behavior toward hydrazine was investigated using the relatively optimized structure **R1** in terms of probe stability and signaling speed.

Chromogenic signaling of **R1** was monitored by UV-vis measurements (Fig. 6a). The acetate derivative **R1** had a maximum absorption at 453 nm in 50% aqueous DMSO (tris buffered at pH 8.0). Upon interaction with hydrazine, a pronounced chromogenic behavior characteristic of resorufin was observed with a color change from yellow to pink, which is naked-eye detectable (inset of Fig. 6a). That is due to the hydrazine-assisted deprotection of the acetate of **R1** to resorufin. Other metal ions and anions caused almost no change in the **R1** absorption profile (Fig. S10, ESI‡). On the other hand, similar to other hydroxyl-protected resorufin derivatives, the

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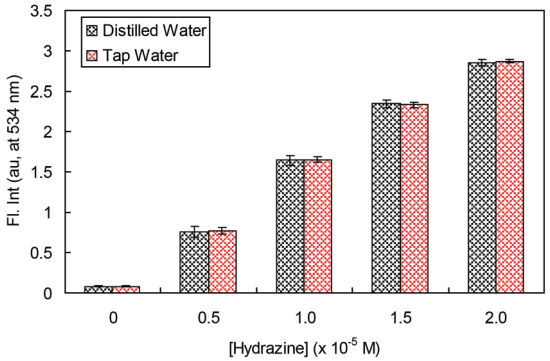

Fig. 7 Fluorescence detection of hydrazine in distilled water and tap water by **F1**. [**F1**] = 5.0 × 10^{-6} M, [Hydrazine] = from 0 to 2.0 × 10^{-5} M, in a mixture of DMSO and tris buffer solution (pH = 8.0, 10 mM) (1 : 1, v/v). λ_{ex} = 480 nm.

fluorescence spectrum of **R1** was weak and emission above 595 nm was not noticeable in 50% aqueous DMSO (tris buffered at pH 8.0). Treating **R1** with 100 equiv. hydrazine enhanced the fluorescence intensity at 595 nm by 47-fold (Fig. 6b). Concomitantly, the fluorescence color of the solution under UV illumination changed from dark to pink (inset of Fig. 6b). Responses of other coexisting metal ions and anions were negligible (Fig. S11, ESI‡).

UV-vis titration of **R1** with hydrazine was performed in 50% aqueous DMSO (pH 8.0 buffer, 10 mM Tris). As the hydrazine concentration increased, the absorbance of **R1** at 453 nm steadily decreased, while the absorbance at 583 nm increased (Fig. S12, ESI‡). Thus, the concentration dependence of **R1** signaling was analyzed by ratiometry using the ratio of the absorbance at 453 and 583 nm. A plot of A_{583}/A_{453} as a function of the hydrazine concentration suggests that it could be used as a calibration curve to determine the hydrazine concentration, up to 3.0 × 10^{-5} M. The detection limit of **R1** for hydrazine was estimated to be 8.2 × 10^{-7} M,[31] which is comparable to the dichlorofluorescein based probe, **F1**.

Hydrazine detection in tap water

Fluorescein-based probe **F1** was used to analyze hydrazine in aqueous solution. Because hydrazine is a suspected carcinogen and is widely used in various industrial processes, hydrazine detection in aqueous samples is of interest. We analyzed hydrazine in tap water and distilled water. An aliquot of hydrazine was added to water and the recoveries obtained by **F1** signals were compared in tap water and distilled water (Fig. 7). The analysis of hydrazine in both solutions agreed well at hydrazine concentrations up to 2.0 × 10^{-5} M.

Conclusions

We developed new, simple structured probes to detect hydrazine in aqueous environments and investigated their applications as colorimetric probes. Signaling was effected by hydrazinolysis of the phenol acetate moiety to its phenolic analogue. The fluorophores used were 2′,7′-dichlorofluorescein and resorufin. Pronounced chromogenic and fluorogenic signaling of hydrazine was possible with detection limits of 9.0 × 10^{-8} M for 2′,7′-dichlorofluorescein and 8.2 × 10^{-7} M for resorufin, respectively. Both probes were selective for hydrazine over other common metal ions and anions. Furthermore, hydrazine was selectively detected over other closely related compounds, such as hydroxylamine, ethylenediamine, and ammonia. The probes could be applied to colorimetric sensing of hydrazine in various laboratory and industrial applications.

Experimental section

General

2′,7′-Dichlorofluorescein, resorufin sodium salt, acetyl chloride, and chloroacetyl chloride were purchased from Aldrich Chemical Co. Acetylhydrazine, hydroxylamine, ammonia water, and ethylenediamine were obtained from TCI. All solvents used for spectroscopic measurements were purchased from Aldrich Chemical Co. as 'spectroscopic grade'. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were obtained on a Varian VNS spectrometer and referenced to the residual solvent signal. UV-vis spectra were recorded using a Jasco V-550 spectrophotometer equipped with a Peltier temperature controller. Fluorescence spectra were measured with a PTI QuantaMaster steady-state spectrofluorometer. Mass spectra were obtained on a Micromass Autospec mass spectrometer. Column chromatography was performed with silica gel (240 mesh).

Preparation of F1 and F2

Acetyl chloride (0.21 mL, 3.0 mmol) or chloroacetyl chloride (0.24 mL, 3.0 mmol) was added to a suspension of 2′,7′-dichlorofluorescein (0.40 g, 1.0 mmol) and cesium carbonate (0.98 g, 3.0 mmol) in DMF (10 mL). The reaction mixture was stirred at room temperature for 1 h, diluted with water, and extracted with dichloromethane. The organic phase was separated and washed with 0.1 N NaOH solution and water, and then evaporated to obtain a white solid residue. The product was purified by column chromatography (silica gel, CH_2Cl_2).

F1: Yield, 90%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (dd, J = 7.6 and 0.8 Hz, 1H), 7.77–7.72 (m, 1H), 7.71–7.67 (m, 1H), 7.20 (dd, J = 7.7 and 0.9 Hz, 1H), 7.15 (d, J = 0.4 Hz, 2H), 6.87 (d, J = 0.4 Hz, 2H), 2.36 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 167.9, 151.8, 149.7, 148.4, 135.8, 130.6, 128.9, 125.7, 125.6, 124.0, 122.7, 117.6, 112.7, 80.4, 20.6; HRMS (FAB); m/z calcd for $C_{24}H_{15}Cl_2O_7$ $[M + H]^+$: 485.0189, found 485.0193. Anal. Calcd for $C_{24}H_{14}Cl_2O_7$: C, 59.40; H, 2.91. Found: C, 59.44; H, 2.92.

F2: Yield, 85%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, J = 7.5 Hz, 1H), 7.77 (td, J = 7.5 and 1.2 Hz, 1H), 7.72 (td, J = 7.5 and 1.0 Hz, 1H), 7.25–7.18 (m, 3H), 6.90 (d, J = 0.4 Hz, 1H), 4.37 (s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 164.5, 151.7, 149.6, 147.8, 135.9, 130.8, 129.1, 125.8, 125.5, 123.9, 122.4, 118.3, 112.5, 80.1, 40.3; HRMS (FAB); m/z calcd for

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$C_{24}H_{13}Cl_4O_7$ $[M + H]^+$: 552.9410, found 552.9422. Anal. Calcd for $C_{24}H_{12}Cl_4O_7$: C, 52.02; H, 2.18. Found: C, 52.25; H, 2.26.

Preparation of R1

Resorufin acetate **R1** was prepared following the literature procedure.[32]

Preparation of R2

Resorufin chloroacetate **R2** was similarly prepared by reacting resorufin sodium salt (0.24 g, 1.0 mmol) with chloroacetyl chloride (0.24 mL, 3.0 mmol). The product was purified by column chromatography (silica gel, CH_2Cl_2). Yield, 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, J = 8.7 Hz, 1H), 7.43 (d, J = 9.8 Hz, 1H), 7.20 (d, J = 2.2 Hz, 1H), 7.17 (dd, J = 8.7 and 2.5 Hz, 1H), 6.86 (dd, J = 9.8 and 2.0 Hz, 1H), 6.33 (d, J = 2.0 Hz, 1H), 4.34 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.2, 165.1, 152.7, 149.1, 148.7, 144.3, 135.3, 134.8, 131.5, 131.3, 118.7, 109.4, 107.4, 40.7; HRMS (FAB); m/z calcd for $C_{14}H_9ClNO_4$ $[M + H]^+$: 290.0215, found 290.0220. Anal. Calcd for $C_{14}H_8ClNO_4$: C, 58.05; H, 2.78; N, 4.84. Found: C, 58.27; H, 2.81; N, 4.74.

Analysis of hydrazine in tap water

A stock solution of hydrazine (1.0 mM) was prepared in tap water. Stock solutions of **F1** (5.0×10^{-4} M) in DMSO and tris buffer (1.0 M in tap water) were also prepared. A calculated amount of hydrazine, **F1**, and tris buffer was added to a vial and the resulting solution was diluted to 3.0 mL with distilled water and DMSO to make a final composition of 1 : 1, v/v. The final **F1** and tris buffer concentrations were 5.0×10^{-6} M and 1.0×10^{-2} M, respectively. All measurements were performed in triplicate.

Acknowledgements

This work was supported by a fund from the Korea Research Foundation of the Korean government (2012-0002403).

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