Supplementary Information

Reaction-based dual signaling of fluoride ions by resorufin sulfonates

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**Fig. S1.** Changes in absorbance ratio $A_{587}/A_{433}$ of 1 in the presence of various anions. [1] = $1.0 \times 10^{-5}$ M, [A$^-$] in TBA salt = $1.0 \times 10^{-4}$ M in CH$_3$CN.

![Absorbance Ratio Graph](image)

**Fig. S2.** Fluorescence intensity ratio $I/I_0$ at 591 nm of 1 in the presence of various anions. [1] = $5.0 \times 10^{-6}$ M, [A$^-$] in TBA salt = $5.0 \times 10^{-5}$ M in CH$_3$CN. $\lambda_{ex}$ = 485 nm.

![Fluorescence Intensity Ratio Graph](image)
Fig. S3. UV-vis spectra of 1, 1 + tetrabutylammonium fluoride, resorufin + tetrabutylammonium fluoride. [1] = [Resorufin] = 1.0 × 10^{-5} M, [TBA^+F^-] = 1.0 × 10^{-4} M in CH3CN.

Fig. S4. Fluorescence spectra of 1, 1 + tetrabutylammonium fluoride, resorufin + tetrabutylammonium fluoride. [1] = [Resorufin] = 5.0 × 10^{-6} M, [TBA^+F^-] = 5.0 × 10^{-5} M in CH3CN. \( \lambda_{ex} = 485 \text{ nm} \).
**Fig. S5.** Time trace for the changes in UV-vis absorbance of 1 at 587 nm in the presence of fluoride ions. [1] = 1.0 × 10^{-5} M, [TBA^+F^-] = 1.0 × 10^{-4} M in CH_3CN.

**Fig. S6.** UV-vis spectral changes of 1 upon titration with fluoride ions. [1] = 1.0 × 10^{-5} M, [TBA^+F^-] = from 0 to 5.5 × 10^{-5} M in CH_3CN.
**Fig. S7.** Competitive signaling of fluoride ions by 1 in the presence of common anions as background. [1] = 5.0 × 10⁻⁶ M, [F⁻] = [A⁻] in TBA salt = 5.0 × 10⁻⁵ M in CH₃CN. \( \lambda_{\text{ex}} = 485 \text{ nm} \). Other anions = Cl⁻, Br⁻, I⁻, AcO⁻, NO₃⁻, N₃⁻, ClO₄⁻, and HSO₄⁻.

**Fig. S8.** UV-vis spectral changes of 1-F⁻ in the presence of common anions as background. [1] = 1.0 × 10⁻⁵ M, [F⁻] = [A⁻] in TBA salt = 1.0 × 10⁻⁴ M in CH₃CN. Other anions = Cl⁻, Br⁻, I⁻, AcO⁻, NO₃⁻, N₃⁻, ClO₄⁻, and HSO₄⁻.
Fig. S9. Time trace for the changes in UV-vis absorbance of 2 at 587 nm in the presence of fluoride ions. [2] = 1.0 × 10⁻⁵ M, [TBA⁺F⁻] = 1.0 × 10⁻⁴ M in CH₃CN.

Fig. S10. Concentration-dependent fluorescence signaling behavior of 2 for fluoride ions. [2] = 5.0 × 10⁻⁶ M, [TBA⁺F⁻] = 0 ~ 1.2 × 10⁻⁵ M in CH₃CN. λₑₓ = 485 nm.
**Fig. S11.** Changes in UV-vis spectra of 2 in the presence of various anions. $[2] = 1.0 \times 10^{-5}$ M, $[A^-]$ in TBA salt = $1.0 \times 10^{-4}$ M in CH$_3$CN.

**Fig. S12.** Changes in absorption intensity ratio $A_{587}/A_{433}$ of 2 in the presence of various anions. $[2] = 1.0 \times 10^{-5}$ M, $[A^-]$ in TBA salt = $1.0 \times 10^{-4}$ M in CH$_3$CN.
**Fig. S13.** Time trace for the changes in UV-vis absorbance of 3 at 587 nm in the presence of fluoride ions. \([3] = 1.0 \times 10^{-5} \text{ M}, [\text{TBA}^-\text{F}^-] = 1.0 \times 10^{-4} \text{ M}\) in CH\(_3\)CN.

**Fig. S14.** Concentration dependent fluorescence signaling behavior of 3 for fluoride ions. \([3] = 5.0 \times 10^{-6} \text{ M}, [\text{TBA}^-\text{F}^-] = 0 \sim 7.0 \times 10^{-4} \text{ M}\) in CH\(_3\)CN. \(\lambda_{\text{ex}} = 485 \text{ nm}\).
**Fig. S15.** Changes in fluorescence intensity ratio ($I/I_o$) at 591 nm of 1, 2, and 3 in the presence of fluoride and sulfide ions. [1] = [2] = [3] = $5.0 \times 10^{-6}$ M, [TBA$^+$/F$^-$/] = [(TBA$^-$)$_2$S$_2^-$] = $5.0 \times 10^{-5}$ M in CH$_3$CN. $\lambda_{ex} = 485$ nm.

**Fig. S16.** Changes in fluorescence intensity ratio ($I/I_o$) at 591 nm of 1 and 1 + fluoride as a function of water content in CH$_3$CN. [1] = $5.0 \times 10^{-6}$ M, [TBA$^+$/F$^-$/] = $5.0 \times 10^{-5}$ M in aqueous acetonitrile (water content: from 0 to 5%). $\lambda_{ex} = 485$ nm.
**Fig. S17.** Fluorescence intensity ratio $I/I_0$ at 591 nm of 1 in the presence of various anions. [1] = 1.0 × 10^{-5} M, [A^{-}] in TBA salt = 1.0 × 10^{-4} M in 1% aqueous acetonitrile solution. $\lambda_{ex}$ = 485 nm.

![Graph showing fluorescence intensity ratios](image)

**Fig. S18.** $^1$H NMR spectrum of 1 in DMSO-d$_6$.  

![NMR spectrum image](image)
Fig. S19. $^{13}$C NMR spectrum of 1 in DMSO-d$_6$.

Fig. S20. $^1$H NMR spectrum of 3 in DMSO-d$_6$. 
Fig. S21. $^{13}$C NMR spectrum of 3 in DMSO-d$_6$. 

![NMR Spectrum](image)