## **Electronic Supplementary Information for**

## A novel fluorescence off-on probe for the sensitive and selective detection of fluoride ions

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Scheme S1. Synthetic route of probe 1.



**Fig. S1.** <sup>1</sup>H NMR spectrum of probe **1** (400 MHz, 298 K, CDCl<sub>3</sub>).



Fig. S2.  $^{13}$ C NMR spectrum of probe 1 (100 MHz, 298 K, CDCl<sub>3</sub>).



Fig. S3. High resolution ESI-MS of probe 1.



Fig. S4. Absorption and fluorescence emission spectra of coumarin (10  $\mu$ M) in a mixture of DMSO and Tris buffer solution (pH 8.0).



**Fig. S5.** High resolution ESI-MS of the reaction solution of probe **1** (50  $\mu$ M) with F<sup>-</sup> (500  $\mu$ M). The peak at m/z = 161.0243 reflects the formation of the fluorophore coumarin.



Fig. S6. Plots of fluorescence intensity *vs*. the reaction time of probe 1 (10  $\mu$ M) with varied concentrations of F<sup>-</sup> (0-200  $\mu$ M). The measurements were performed in a mixture of DMSO and Tris buffer solution (pH 8.0) at room temperature.  $\lambda_{ex/em} = 385/455$  nm.



**Fig. S7.** Effect of pH on the fluorescence ( $\lambda_{ex/em} = 385/455$  nm) of probe **1** (10  $\mu$ M) reacting with F<sup>-</sup> (200  $\mu$ M). The results are the mean  $\pm$  standard deviation (SD) of three separate measurements.



**Fig. S8.** Fluorescence images of test strips for detecting  $F^-$  in aqueous solution with varied  $F^-$  concentrations (0, 5, 10, 15, 20, and 30  $\mu$ M). The test strips were excited at 365 nm by a hand-held UV lamp.



**Fig. S9.** Fluorescence images of test strips in the presence of various anions (200  $\mu$ M). The test papers were excited at 365 nm by a hand-held UV lamp.



**Fig. S10.** Fluorescence response of probe **1** (10  $\mu$ M) to F in real samples. (A) Tap water: samples No. 1-3 from bottom to up; (B) Yingze Lake water: samples No. 1-3 from bottom to up; (C) Toothpaste: samples No. 1-3 from up to bottom.  $\lambda_{ex/em} = 385/455$  nm.

| Mechanism                      | Detection limit | Wavelength                          | Detection media                               | Literature  |
|--------------------------------|-----------------|-------------------------------------|---|---|
| P-O cleavage                   | 0.29 μM         | $\lambda_{\rm em} = 455 \ \rm nm$   | DMSO/Tris buffer<br>(7:3, v/v)                | This work   |
| H-bond interaction             | Not mentioned   | $\lambda_{\rm em} = 495 \ \rm nm$   | CH₃CN   | Zhou <i>et al.</i> ,<br><i>Spectrochim. Acta A</i> ,<br>2018, <b>204</b> , 777    |
| H-bond<br>interaction          | 3.2 µM          | $\lambda_{\rm em} = 510 \ \rm nm$   | toluene                                       | Lu <i>et al., Sens.</i><br><i>Actuators B</i> , 2018, <b>270</b> ,<br>291         |
| Deprotonation<br>of N-H proton | 0.28 μM         | $\lambda_{\rm em} = 598 \ \rm nm$   | DMSO  | Yang <i>et al., Sens.</i><br><i>Actuators B</i> , 2015, <b>210</b> ,<br>784       |
| Si-O cleavage                  | 0.59 μΜ         | $\lambda_{\rm em} = 564 \ \rm nm$   | CH <sub>3</sub> CN/HEPES<br>buffer (8:2, v/v) | Yoo <i>et al., RSC Adv.,</i><br>2016, <b>6</b> , 19910                            |
| Si-O cleavage                  | 3.5 μΜ          | $\lambda_{\rm em} = 480 \ \rm nm$   | ethanol                                       | Zhang et al., Anal.<br>Bioanal. Chem., 2017,<br><b>409</b> , 2075                 |
| Si-O cleavage                  | 1.03 μM         | $\lambda_{\rm em} = 523 \text{ nm}$ | DMSO  | Roy et al., Chem.<br>Coummun., 2014, <b>50</b> ,<br>5510                          |
| Si-O cleavage                  | 0.17 μΜ         | $\lambda_{\rm em} = 485 \ \rm nm$   | CH <sub>3</sub> CN                            | Zhang <i>et al.</i> , <i>Chem.</i><br><i>Commun.</i> , 2014, <b>50</b> ,<br>14021 |

Table S1. Comparison of probe 1 with other recently reported fluorescent probes for F

| Si-O cleavage | Not mentioned | $\lambda_{\rm em} = 589 \ \rm nm$ | CH <sub>3</sub> CN/H <sub>2</sub> O (1:1,<br>v/v) or CH <sub>3</sub> CN | Kim <i>et al.</i> , <i>Org. Lett.</i> , 2007, <b>9</b> , 3109                   |
|---------------|---------------|-----------------------------------|---|---|
| Si-O cleavage | 85 nM         | $\lambda_{\rm em} = 718 \ \rm nm$ | DMSO/H <sub>2</sub> O (95:5, v/v)                                       | Cao et al., Tetrahedron<br>Lett., 2012, <b>53</b> , 2107                        |
| Si-O cleavage | 0.1 μΜ        | $\lambda_{\rm em} = 682 \ \rm nm$ | CH <sub>3</sub> CN  | Xie <i>et al., J. Fluoresc.,</i> 2016, <b>26</b> , 1737                         |
| Si-O cleavage | 0.12 μΜ       | $\lambda_{\rm em} = 676 \ \rm nm$ | CH <sub>2</sub> Cl <sub>2</sub>   | Cao <i>et al., RSC Adv.,</i> 2012, <b>2</b> , 418                               |
| Si-O cleavage | 17.2 μΜ       | $\lambda_{\rm em} = 493 \ \rm nm$ | DMF/HEPES buffer (7:3, v/v)   | Zhou <i>et al.</i> , <i>Dyes</i><br><i>Pigments</i> , 2018, <b>158</b> ,<br>277 |
| P-O cleavage  | 9.8 nM        | $\lambda_{\rm em} = 536 \ \rm nm$ | DMSO/Tris buffer<br>(7:3, v/v)  | Kim et al., Dyes<br>Pigments, 2015, <b>112</b> ,<br>170                         |
| P-O cleavage  | 48 nM         | $\lambda_{\rm em} = 669 \ \rm nm$ | DMSO/Tris buffer<br>(7:3, v/v)  | Du <i>et al., Anal. Chim.</i><br>Acta, 2018, <b>1030</b> , 172.                 |