# **Electronic Supplementary Information**

### A highly selective and sensitive fluorescence "turn-on" fluoride ion sensor

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## Contents

| Materials and instruments and General proceduresS2 |
|--|
| Figure S1  |
| Figure S2, Figure S3S4                             |
| Figure S4, Figure S5S5                             |
| Figure S6, Figure S7S6                             |
| Figure S8, Figure S9S7                             |
| Figure S10S8                                       |

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#### Materials and instruments and General procedures

#### Materials and instruments

All reagents and starting materials were obtained from commercial suppliers and used as received unless otherwise noted. F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, were used as the thetetrabutylammonium (TBA) salts and the SCN<sup>-</sup> and CN<sup>-</sup> ions were used as the sodium salts. Nuclear magnetic resonance (NMR) spectra were recorded on Varian Mercury 400. Mass spectra were recorded on a Bruker Esquire 6000 MS instrument. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer.

#### **General procedure**

#### 1. General procedure for UV-vis experiments

All the UV-vis experiments were carried out on a Shimadzu UV-2550 spectrometer. Any changes in the UV-vis spectra of the synthesized sensors were recorded on the addition of F<sup>-</sup> (measured 0.5 mL 0.1mol/L diluted to 0.01 mol/L). The host concentration was kept constant in all experiments.

#### 2. General procedure for fluorescence experiments

All the fluorescence experiments were carried out on a Shimadzu RF-5301PC spectrofluorophotometer. Any changes in the fluorescence spectra of the synthesized sensors were recorded on the addition of F<sup>-</sup> (measured 0.5 mL 0.1mol/L diluted to 0.01 mol/L). The host concentration was kept constant in all experiments.

#### 3. General procedure for <sup>1</sup>H NMR titration

For <sup>1</sup>H NMR titrations, two stock solutions were prepared in DMSO- $d_6$ : one of them contained the host only, the second one contained a certain concentration of F<sup>-</sup> (measured 0.5 mL 0.1mol/L diluted to 0.01 mol/L). Aliquots of the solutions were mixed directly in NMR tubes.



**Fig. S1.** <sup>1</sup>H NMR spectra of sensor **S** in DMSO- $d_6$ .



Figure S3. MS spectra of sensor S.



**Fig. S4.** Fluorescence spectra of sensor **S** ( $2.0 \times 10^{-5}$  mol/L) recorded before and after reaction with F<sup>-</sup> (0.01mol/L) (50 equiv). (Inset) Fluorescence changes of the probe **S** ( $2.0 \times 10^{-5}$  mol/L) in the presence of 50 equiv of F<sup>-</sup>.



Fig. S5. Linear portion of the curve of fluorescence intensity at 467 nm of sensor S  $(2.0 \times 10^{-5} \text{ mol/L})$  DMSO in the presence of F<sup>-</sup>.



Fig. S6. UV/vis absorption spectra of sensor S ( $2.0 \times 10^{-5}$  mol/L) in DMSO in the absence and presence of 50 equiv F<sup>-</sup>.



**Fig. S7.** Absorption spectra of sensor **S**  $(2.0 \times 10^{-5} \text{ mol/L})$  in DMSO upon addition of various (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, as the thetetrabutylammonium (TBA) salts CN<sup>-</sup> and SCN<sup>-</sup>; as the sodium salts, 50 equiv each) (0.01mol/L) in aqueous solution. (**Inset**) Color changes of the sensor **S**  $(2.0 \times 10^{-5} \text{ mol/L})$  in the

presence of 50 equiv of (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, CN<sup>-</sup> and SCN<sup>-</sup>).



**Fig. S8** Fluorescence intensity at 467 nm for **S** ( $2.0 \times 10^{-5}$  mol/L) in DMSO after addition of F<sup>-</sup> (0.01 M) in aqueous solution.



**Fig.S9** Photographs of **S** on test papers (Left) only **S**, (Mid) after immersion into solution with  $F^-$ , (Right) after immersion into solutions with others in absence of  $F^-$ (**A**) under irradiation at 365 nm (B) under nature light.



Fig. S10. <sup>1</sup>H NMR spectra of sensor S in  $D_2O$ .