



## Original article

Chromogenic and fluorescent “turn-on” chemodosimeter for fluoride based on F<sup>-</sup>-sensitive self-immolative linkerXin-Yu Wang, Feng-Jie Guan, Bin Li, Hua Zhang<sup>\*</sup>, Hong-Wei Wu, Kai Ji, Chuan-Xiang Liu<sup>\*</sup>

School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China

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## ABSTRACT

A new chromogenic and fluorescent “turn-on” chemodosimeter **3** was designed and synthesized by using a fluoride-sensitive self-immolative linker, in combination with the fluorescent dyes 7-hydroxy-4-trifluoromethyl coumarin. The chemodosimeter exhibited high selectivity and sensitivity toward fluoride anions through “turn-on” chromogenic and fluorogenic dual modes.

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## 1. Introduction

The development of chromogenic and fluorogenic sensors for anions is well-established field in supramolecular chemistry because of their roles in chemical and biological processes [1]. Among inorganic anions, F<sup>-</sup> ions are usually used for the prevention of dental caries and treatment of osteoporosis [2–5]. Over-intake of fluoride can cause fluorosis and lead to nephrotoxic changes and urolithiasis in humans [6,7]. Therefore, the interest in developing of novel chemosensors for the selective detection of fluoride ions has grown in the last few years.

The conventional approaches for fluoride sensing are mainly based on the fluoride ionic electrode, fluoride-hydrogen bonding or deprotonation [8,9]. Recently, the most popular strategy is to utilize the high affinity of fluoride to silica for the construction of sensors with Si–O, or Si–C bonds [6,10–13]. The approaches involve the direct linkage of a Si–O protected fragment to chromophore/fluorophore, or the insertion of a conjugated system between a Si–O group and chromophore/fluorophore followed by a unique F<sup>-</sup>-triggered cascade reaction. The reported mechanism is mainly to release the F<sup>-</sup>-silica-protected group and the signal subunit with delocalized oxygen negative charge. However, realization of novel chromogenic and fluorogenic sensors for fluoride ions is still a challenge, especially with respect to different mechanisms, novel chromophore with high sensitivity.

Recently, aryl phthalate esters were reported as self-immolative linkers for potential fluoride sensors. The fluoride-sensitive self-immolative linker, such as 2-(trimethylsilyl)ethyl ether group, was explored by conjugating the phthalic anhydride with the fluorescent dyes 7-hydroxycoumarin (previous probe, Fig. 1) [14]. To improve the sensitivity and operational ability of the above systems, the more sensitive fluorophore containing electron-withdrawing group (such as CF<sub>3</sub> group) should be used to design the sensor. In this study, using the novel the fluorescent dyes 7-hydroxy-4-trifluoromethyl coumarin, we developed a new probe **3** to investigate the potential signal changes (Fig. 1).

## 2. Experimental

NMR spectra were recorded on Bruker AVANCE III 500 MHz and chemical shifts were reported in parts per million (ppm,  $\delta$ ) downfield from internal standard Me<sub>4</sub>Si (TMS). HRMS were recorded on solanX 70 FT-MS spectrometer with methanol and water (v/v = 1:1) as solvent. IR were recorded on Bruker VERTEX70. Flash chromatography was carried out on silica gel (200–300 mesh). The intermediate **1** and **2** was synthesized as described in the literature (Figs. S1 and S2 in the Supporting information) [14–16].

Synthesis of probe **3** (Scheme 1): 2-(Trimethylsilyl) ethyl hydrogen phthalate (**1**, 1.29 g, 4.83 mmol) [14,15], 7-hydroxy-4-(trifluoromethyl)-coumarin (**2**, 1.11 g, 4.83 mmol) [16], and 4-dimethylaminopyridine (0.65 g, 5.3 mmol) were dissolved in a mixture of anhydrous methylene chloride (15 mL) and anhydrous

<sup>\*</sup> Corresponding authors.

E-mail addresses: [zhanghua@sit.edu.cn](mailto:zhanghua@sit.edu.cn) (H. Zhang), [cxliu@sit.edu.cn](mailto:cxliu@sit.edu.cn) (C.-X. Liu).

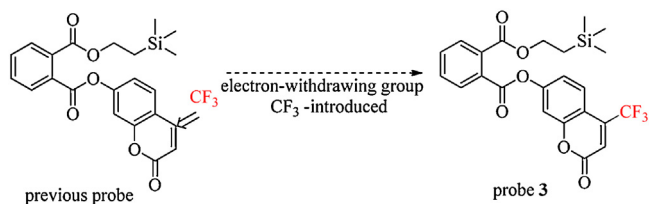
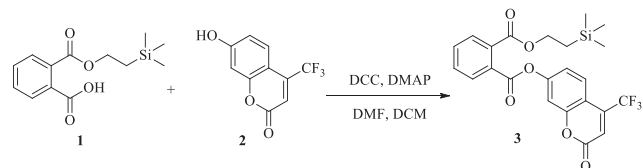


Fig. 1. The designed probe **3**.



Scheme 1. Synthesis of probe **3**.

DMF (9 mL). *N,N*-Dicyclohexylcarbodiimide was quickly added to the reaction mixture, which was stirred under  $N_2$  overnight. Dicyclohexyl urea was filtered off, and the filtrate was diluted in 10 mL of methylene chloride. The solution was washed with brine and then dried over anhydrous  $Na_2SO_4$ . The crude product was collected by evaporation under reduced pressure and then purified by flash chromatography on silica gel (PE/EA = 30:1) to yield **3** (0.92 g, 45%) as a white solid. Compounds **3** were characterized by  $^1H$  NMR,  $^{13}C$  NMR and ESI-HRMS analyses (Figs. S3–S5 in Supporting information).  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.93–7.87 (m, 1H), 7.87–7.78 (m, 2H), 7.69–7.62 (m, 2H), 7.45 (d, 1H,  $J = 2.5$  Hz), 7.38 (dd, 1H,  $J = 9.0, 2.5$  Hz), 6.80 (s, 1H), 4.46–4.37 (m, 2H), 1.12–1.08 (m, 2H), 0.05 (s, 9H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  166.71, 165.75, 158.51, 155.11, 154.29, 131.84, 131.69, 131.56, 131.39, 129.37, 128.96, 126.35, 118.99, 111.10, 64.40, 17.37, –1.53; ESI-HRMS ( $m/z$ ): Calcd. for  $[C_{23}H_{21}F_3O_6Si + Na]^+$  501.09572 ( $[M + Na]^+$ ), found 501.09485.

All UV–vis spectroscopy were recorded after the addition of tetrabutylammonium salts in  $CH_3CN$ , while keeping the ligand concentration constant ( $5 \times 10^{-3}$  mol/L) on a SHIMADZU UV-1800

spectrophotometer [17]. The solutions of the anions were prepared from the tetrabutylammonium salts of anions ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $ClO_4^-$ ,  $NO_3^-$ ,  $AcO^-$ ,  $H_2PO_4^-$ ,  $BF_4^-$ ,  $HSO_4^-$ ).

All fluorescence spectroscopy were recorded after the addition of tetrabutylammonium salts in  $CH_3CN$ , while keeping the ligand concentration constant ( $5 \times 10^{-3}$  mol/L), on a Hitachi F-4600 spectrofluorometer. The solutions of the anions were prepared from the tetrabutylammonium salts of anions.

For  $^1H$  NMR titrations, probe **3** was dissolved in  $DMSO-d_6$ , which was mixed with different equiv. of fluoride ions in NMR tubes. The spectra were performed at 298 K [18].

### 3. Results and discussion

First, the chromogenic behavior of probe **3** in acetonitrile was investigated upon the addition of different anions (Fig. 2a) [9]. When tetrabutylammonium fluoride (TBAF) was added, a new red-shifted peak at 434 nm was observed in the UV–visible spectrum of probe **3**. This can be attributed to complete fluoride deprotection as a consequence of the release of chromenolate anion [16]. An instantaneous colorimetric change from colorless to yellow (Fig. 2b, top, naked-eye detection) was observed. However, the addition of other anions such as  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $ClO_4^-$ ,  $NO_3^-$ ,  $AcO^-$ ,  $H_2PO_4^-$ ,  $BF_4^-$ ,  $HSO_4^-$  ions (as their tetrabutylammonium salts) did not lead to any color change (Fig. 2b, bottom, naked-eye detection), indicating the highly selective nature of probe **3** for fluoride ions. This excellent selectivity was further highlighted by the interference experiments (Fig. 2c), in which a consistent turn-on color response was observed upon the addition of 20 equiv. of  $F^-$  ions to the solutions of **3** containing equal concentrations of potentially competing anions. Next, the addition of increasing concentrations of fluoride ions resulted in a dramatic color change from colorless to yellow, because of a gradual growth in the absorbance peak at 252 nm and 434 nm and the simultaneous decrease of new peaks at 282 nm and 314 nm with two clear isosbestic points at 265 and 348 nm in acetonitrile (Fig. 2d).

Most remarkable changes were observed in the fluorescence titration studies [19]. Upon the addition of fluoride ions, the fluorescence emission intensity of probe **3** increased drastically

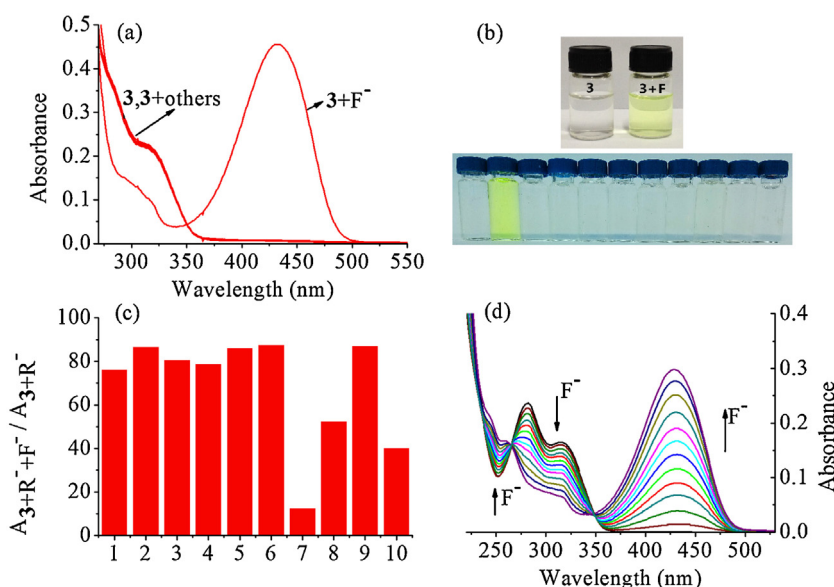


Fig. 2. (a) UV–visible spectra of compound **3** (20  $\mu$ mol/L) in presence of 20 equiv. of various anion in  $CH_3CN$  solution; (b) color changes of receptor compound **3** in  $CH_3CN$  solution upon addition of various anions; (c) UV–visible spectra of compound **3** in presence of various anion in  $CH_3CN$  solution. The red bars represent the absorbance enhancement at 434 nm of **3** in the presence of 20 equiv. of the anion of interest after addition of 20 equiv. of fluoride ions and (d) UV–visible spectral changes of **3** (20  $\mu$ mol/L) in  $CH_3CN$  upon the titration with TBAF (0 to 20 equiv.)

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