Electronic Supporting Information (ESI) for

Rapid and selective detection of fluoride in aqueous solution by a new hemicyanine-based colorimetric and fluorescent chemodosimeter

Shengjun Yang,‡ Yao Liu‡ and Guoqiang Feng*

Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P.R. China, gf256@mail.ccnu.edu.cn

Synthesis of 4-(tert-butyldiphenylsilyloxy)benzaldehyde 4

![Chemical structure of 4](image)

Compound 4 was prepared according to a previously published procedure¹: to a solution of p-hydroxybenzaldehyde (1.22 g, 10 mmol) and imidazole (816 mg, 12 mmol) in dry DMF (20 mL), tert-butyldichlorodiphenylsilane (2.75 g, 10 mmol) was dropped under ice-water bath. After stirring 12 h at room temperature, the volatiles were evaporated under reduced pressure to oil. The residue was purified by flash chromatography (silica gel column) using petroleum ether and ethyl acetate (v/v = 10/1) to afford 4 as a white solid in 65% yield. Mp: 94-97°C; ¹H NMR (400 MHz, CDCl₃): 1.11 (9H, s, t-Bu), 6.86 (2H, t, ArH), 7.36-7.46 (6H, m, ArH), 7.63-7.71 (6H, m, ArH), 7.41 (2H, s, ArH), 9.80 (1H, s, CHO). ¹³C NMR (100 MHz, CDCl₃): 19.4,
26.3, 120.2, 127.9, 130.2, 131.7, 131.8, 135.3, 161.1, 190.8. IR (KBr, cm\(^{-1}\)): 2951, 2857, 1696, 1599, 1511, 1276, 1163, 1114, 904, 746; MS (EI): Calcd for C\(_{23}\)H\(_{24}\)O\(_2\)Si\(^+\) (M\(^+\)) 360.15; Found 360.03.

**Synthesis of compound 5**

![Synthesis of compound 5](image)

Compound 5 was prepared as a light purple solid from 2,3,3-trimethylindolenine and iodomethane by a previously reported method.\(^2\) Mp: > 300°C. \(^1\)H NMR (600 MHz, DMSO-d\(_6\)): 1.53 (6H, s, 2CH\(_3\)), 2.80 (3H, s, CH\(_3\)), 3.99 (3H, s, CH\(_3\)), 7.61 (2H, m, ArH), 7.84 (1H, t, \(J = 6.0\) Hz, ArH), 7.92 (1H, t, ArH); \(^1\)C NMR (150 MHz, DMSO-d\(_6\)): 196.0, 142.1, 141.6, 129.3, 128.8, 123.4, 115.2, 54.0, 35.0, 21.7, 14.5; IR (KBr, cm\(^{-1}\)): 3448, 2964, 1630, 1608, 1481, 1457, 1020, 778; MS (EI): Calcd for C\(_{12}\)H\(_{16}\)N\(^+\) [M – I\(^+\)] 174.13; Found 173.14.

**Synthesis of the reference sample of 2**

![Synthesis of the reference sample of 2](image)

The reference sample of 2 was prepared according to a previously published procedure.\(^3\) To a solution of 5 (301 mg, 1 mmol) in ethanol (10 mL), 4-hydroxybenzaldehyde (122 mg, 1 mmol) and piperidine (10 \(\mu\)L) was added. The reaction mixture was heated to reflux for 1 h with stirring and then cooled to room temperature. A red solid precipitated and filtered to give the desired product in 58% yield. Mp: 255-257 °C. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)): 1.77 (6H, s, 2CH\(_3\)), 4.08 (3H, s, NCH\(_3\)), 6.96 (2H, d, \(J = 8.4\) Hz, ArH), 7.46 (1H, d, \(J = 16\) Hz, CH), 7.59 (2H, t, \(J = 7.6\) Hz, ArH), 7.84 (2H, d, \(J = 7.2\) Hz, ArH), 8.12 (2H, d, \(J = 8.0\) Hz, ArH), 8.36 (1H,
d, $J = 16$ Hz, CH), 10.85 (1H, s, OH). $^{13}$C NMR (100 MHz, DMSO-d$_6$): 181.3, 163.1, 153.6, 143.1, 141.8, 133.6, 128.8, 125.9, 122.7, 116.3, 114.6, 109.3, 51.7, 34.3, 25.7. MS (EI): Calcd. for C$_{19}$H$_{20}$NO [M – HI] 277.36; Found 277.28.

References:

**Fig. S1** Absorption and colour changes of chemodosimeter 1 (5 µM) upon addition of F$^-$ (40 mM) in PBS (20 mM, pH 7.4) solution (ethanol/water = 3/7, v/v) at 25°C. The UV-vis spectrum (red line) was obtained 5 min after F$^-$ addition.
**Fig. S2** Time-dependent of absorption kinetics spectra of chemodosimeter \(1 \ (5 \ \mu M)\) upon addition of different concentrations of \(F^-\) in PBS (20 mM, pH 7.4) solution (ethanol/water = 3/7, v/v) at 25°C. The reaction is monitored at 535 nm. \([F^-]\) from a to g: 0, 0.1, 0.5, 1, 2, 6 and 20 mM, respectively.

**Fig. S3** A comparison of kinetics of chemodosimeter 1 (5 \(\mu M\)) upon addition of 40 mM \(F^-\) in PBS (20 mM, pH 7.4) solution (ethanol/water = 3/7, v/v) at 25°C measured by absorbance intensity changes at 535 nm (●) and fluorescent intensity changes at 558 nm (■). Both absorbance intensity and fluorescent intensity are normalized to make a clear comparison.
**Fig. S4** The reversible colour changes of the reaction mixture (1 + F⁻) upon subsequent addition of HCl acid and aqueous NaOH.

**Fig. S5** HR-MS spectrum of the reaction product of chemodosimeter 1 with F⁻.

**Fig. S6** Comparison of the ¹H NMR spectra between the reference sample of 2 and the reaction product of chemodosimeter 1 with F⁻.
Fig. S7 Colour changes of test paper containing chemodosimeter 1 with different concentration of $\text{F}^-$ in water.

NMR and MS spectra for the following compounds:
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Fig. S8 $^1$H NMR and $^{13}$C NMR spectra of compound 4 recorded in CDCl$_3$.

Fig. S9 $^1$H NMR and $^{13}$C NMR spectra of compound 5 recorded in DMSO-d$_6$. 
Fig. S10 $^1$H NMR and $^{13}$C NMR spectra of compound 1 recorded in CDCl$_3$ and DMSO-d$_6$, respectively.

Fig. S11 HR-MS spectrum of chemodosimeter 1