Electronic Supporting Information

Rhodamine-based "off-on" fluorescent chemosensor for selective detection of Fe^{3+} in aqueous media and its application in bioimaging

Singming Chan,[a] Qinghua Li,[a] Hoyin Tse,[a] Albert W. M. Lee,[a] N. K. Mak,[b] H. L. Lung[b] and Wing-Hong Chan[a,c*]

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruka Advance-III spectrometer (at 400 and 100 MHz, respectively) in $CDCl_3$. High-resolution mass spectra were recorded on a Bruka Autoflex mass spectrometer (MALDI-TOF). Fluorescent emission spectra and UV-vis spectra were collected on a PE LS50B and a Cary UV-100 spectrometer, respectively. All fine chemicals were used as received. **CaSHII** was synthesized using our published method [1].

Reference:

[1] Q. Li, W-. Y. Wong,; W-. H. Chan, A. W. M. Lee, *Adv. Synth. Catal*. 2010, **352**, 2142-2146 and references therein.

Synthesis of **FIS1**:

A solution of Rhodamine B (0.30 g, 0.62 mmol) in $POCl_3$ (5 mL) was refluxed for 5 h. The reaction mixture was then cooled and concentrated by evaporation. The obtained acid chloride which was dissolved in $ClCH_2CH_2Cl$ (20 mL) together with **CaSHII** (0.14 g, 0.58 mmol) and triethylamine (0.7 mL). The mixture was stirred at room temperature for 12 h and was then concentrated by evaporation. The crude product was purified by silica gel column chromatography with EtOAc/*n*-hexane (1/3, v/v) to afford **FIS1** as a pink solid (m.p. 225-227^{0}C, 0.12 g, yield 33%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.91(1H, d, J = 7.6 Hz), 7.57-7.49 (2H, m), 7.20 (1H, d, J = 7.6 Hz), 6.57 (1H, d, J = 8.8 Hz),

6.42-6.25 (5H, m), 4.54-4.51 (1H, m), 3.40-3.24 (9 H, m), 3.15 (1H, d, J = 13.6 Hz), 1.79-1.75 (1H, m), 1.66-1.63 (2H, m), 1.46-1.44 (1H, m), 1.41-1.35 (1H, m), 1.15-1.11 (12H, m), 1.04-0.94 (5H, m), 0.82 (1H, s), 0.66-0.61(1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 154.6, 150.3, 149.2, 148.9, 133.2, 130.9, 129.9, 129.1, 128.3, 124.5, 123.0, 108.3, 108.1, 107.0, 98.6, 98.0, 66.8, 66.4, 50.0, 48.0, 46.2, 44.6, 44.4, 36.0, 34.2, 26.2, 21.6, 19.7, 12.6, 12.4, 12.2 ppm.

HRMS (ESI): m/z calcd for $C_{48}H_{47}N_4O_4S$ $[M+H]^+$: 655.3313; found, 655.3295.

$[\alpha]_D^{20}$ = -26.88 (c=0.42, $CHCl_3$)

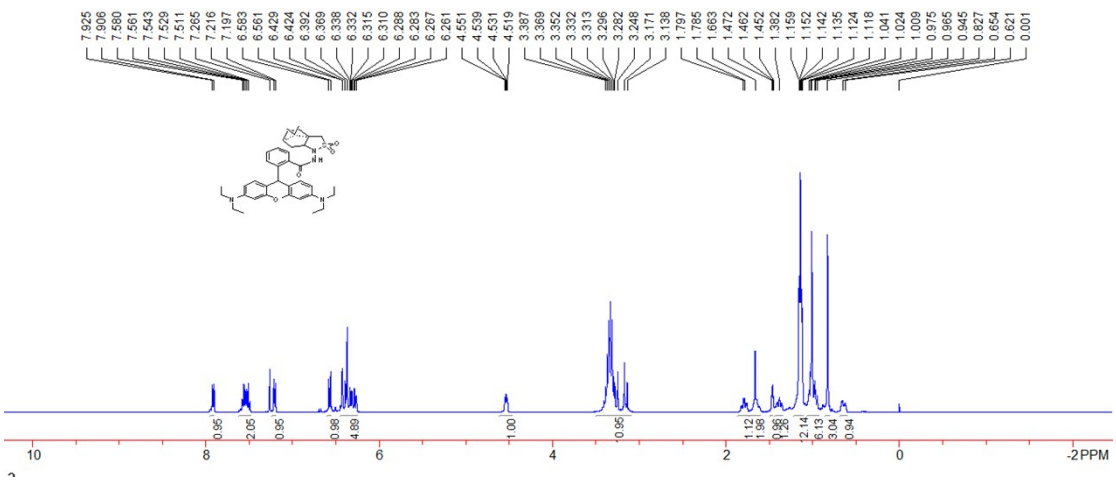


Fig. S1 ^{1}H NMR spectrum of **FIS1**

DEPT-135

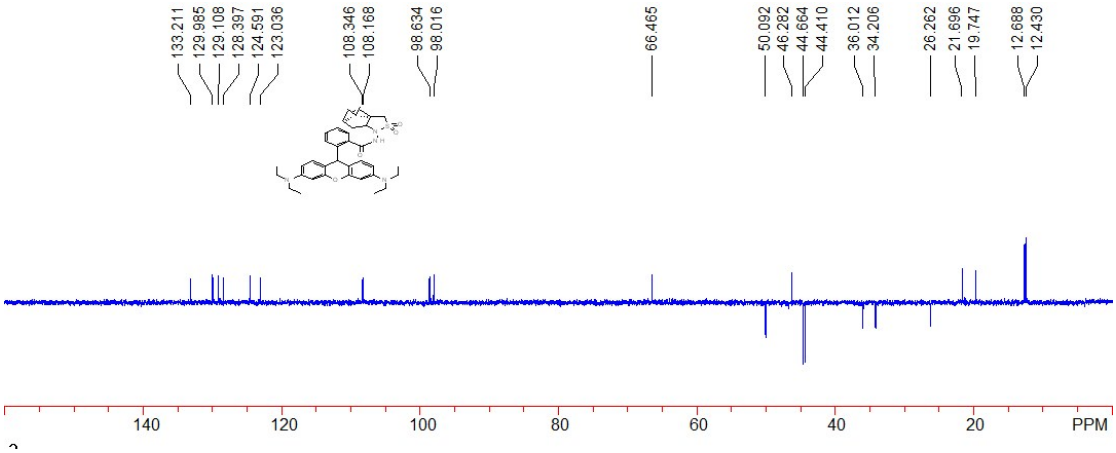


Fig. S2 ^{13}C NMR (DEPT-135 mode) spectrum of **FIS1**

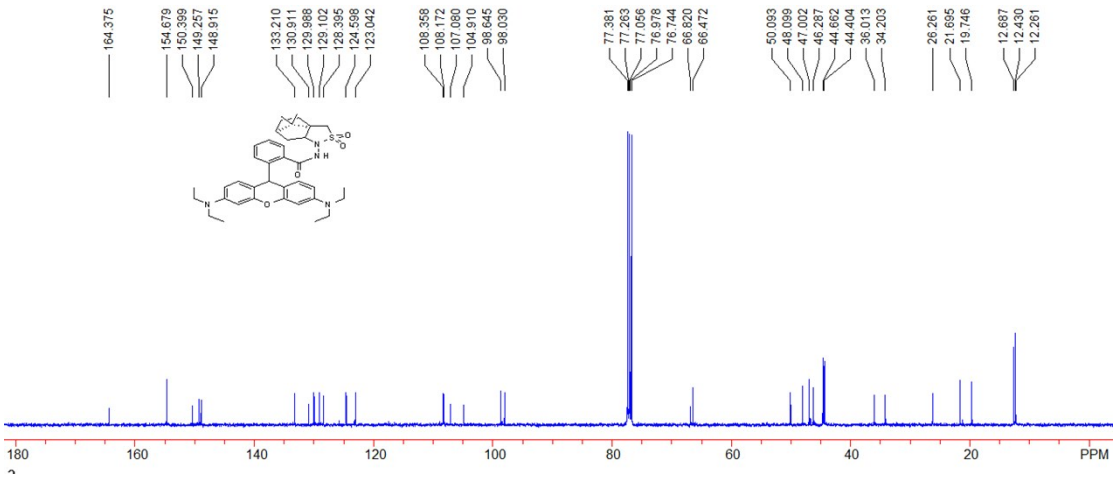


Fig. S3 ^{13}C NMR spectrum of **FIS1**

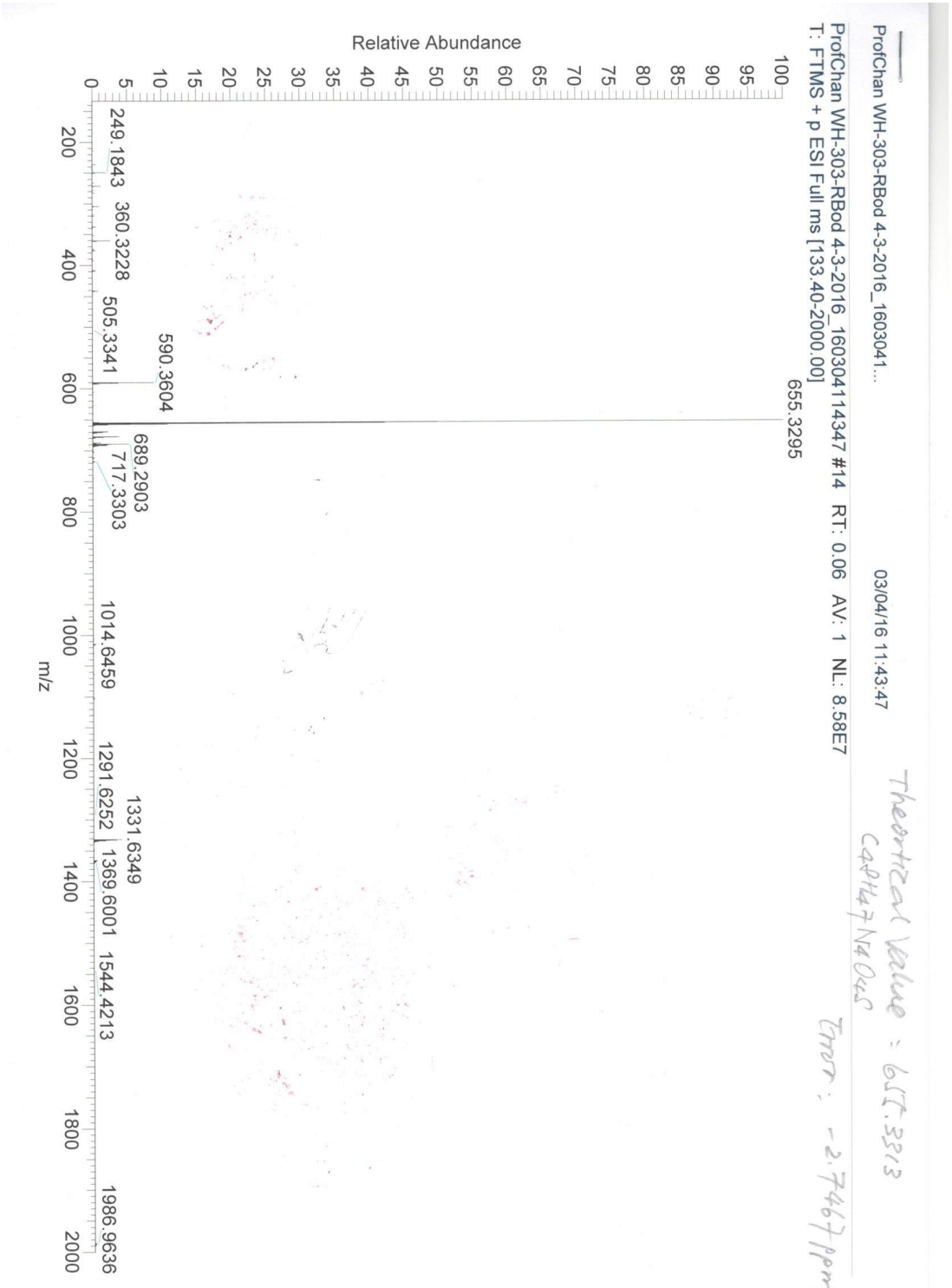


Fig. S4 HRMS (ESI mode) of **FIS1**

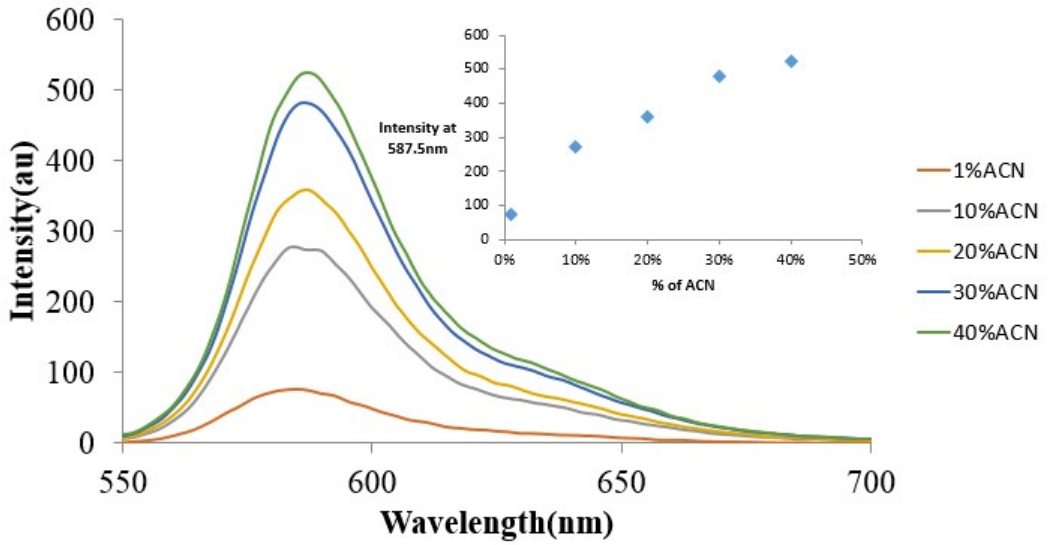


Fig. S5 Fluorescent spectra of **FIS1** (10 μM) upon addition of 3.5 equivalent of Fe^{3+} in aqueous solution of acetonitrile of different composition (H_2O: ACN, v/v = 99:1; 90:10; 80:20; 70:30; 60:40; 50:50).

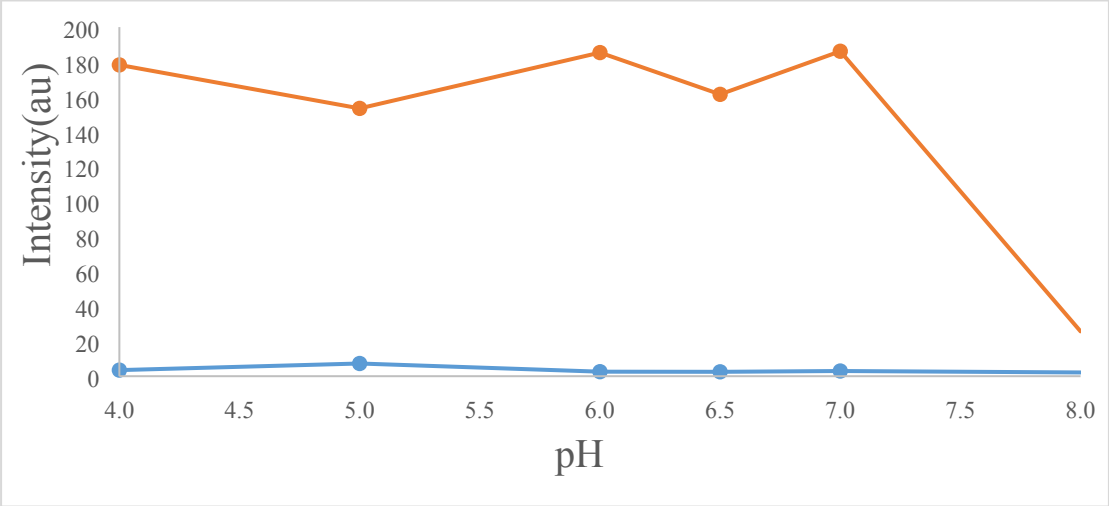
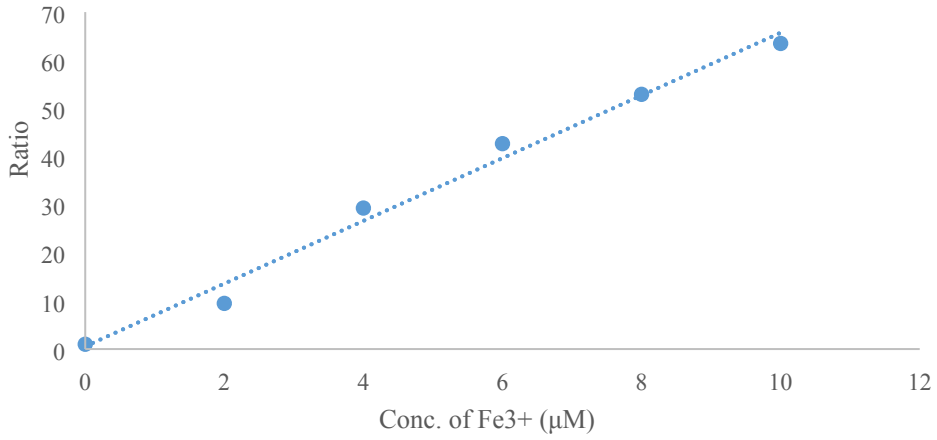


Fig. S6 The pH effect of the probe (1 μM) in aqueous ACN solution (1:1, v/v) at different pH in response to 10 equivalent of Fe^{3+}.



1 μM **FIS1** vs 2 μM Fe^{3+} (2.0 equivalents)	Fluorescent Ratio Value
1^{st} trial	9.4871
2^{nd} trial	10.2155
3^{rd} trial	9.1269

Estimation of the LOD of the probe:

3 × standard deviation of the Fluorescent Ratio Value ÷ Slope of the Calibration

Curve

= 3 × 0.5546 ÷ 6.5153

= 0.2554 μM

Fig. S7 The estimation of the LOD of **FIS1** by fluorescent titration with Fe^{3+} by the probe.

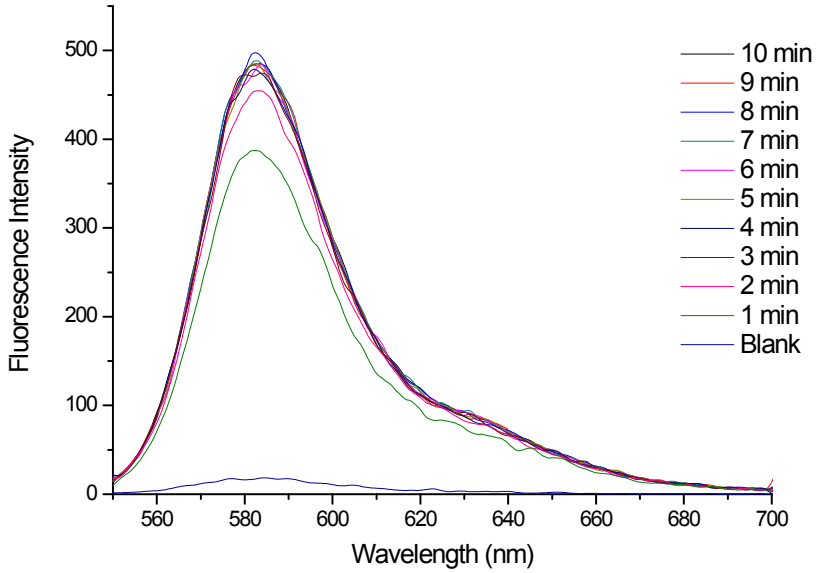


Fig. S8 Change of fluorescence spectra of the probe **FIS1** (2 μM) in response to 10 equiv. of Fe^{3+} over a period of 10 min (1:1 = H_2O:ACN, v/v).