

Electronic Supplementary Information

Fluorescent turning on detection of Sn²⁺ in living eukaryotic and prokaryotic cells

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Synthesis of the sensors

Synthesis OF R5

Rhodamine B hydrochloride (5.0 g, 10.4 mmol) and ethylenediamine (12.5 g, 208.8 mmol) were dissolved in EtOH (50 mL) and refluxed for 12 h. Most of solvent was removed by evaporation, and the residue was dispersed in water. The pink precipitate was recovered by filtration, washed thoroughly with water and finally washed with petroleum ether, dried in vacuo. **R5** was obtained as a pink powder (3.6 g, 72% yield): ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 2.3 Hz, 1H), 7.45 (d, *J* = 2.5 Hz, 2H), 7.14 – 7.05 (m, 1H), 6.44 (s, 1H), 6.42 (s, 1H), 6.37 (d, *J* = 2.3 Hz, 2H), 6.28 (d, *J* = 2.3 Hz, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 3.33 (q, *J* = 7.0 Hz, 9H), 3.19 (t, *J* = 6.6 Hz, 2H), 2.40 (t, *J* = 6.6 Hz, 2H), 1.62 (s, 5H), 1.16 (t, *J* = 7.0 Hz, 13H).

Synthesis of R1

Oxirane (0.44 g, 10.0 mmol) was added to a cooled solution of **R5** (0.48 g, 0.1 mmol) in dichloromethane (10 mL, -5°C). The solution was stirred for 4 h at -5°C and then overnight at room temperature before being concentrated under reduced pressure. The resulted mixture was purified by column chromatography using dichloromethane/ methanol (10/1, v/v) as an eluent to give **R1** as a white solid (0.2 g, 40% yield): ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 2.9 Hz, 1H), 7.46 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.13 – 7.06 (m, 1H), 6.46 (s, 1H), 6.44 (s, 1H), 6.39 (d, *J* = 2.4 Hz, 2H), 6.30 (d, *J* = 2.5 Hz, 1H), 6.28 (d, *J* = 2.5 Hz, 1H), 3.54 – 3.45 (m, 4H), 3.34 (q, *J* = 7.0 Hz, 9H), 3.22 (t, *J* = 5.7 Hz, 2H), 2.55 (t, *J* = 7.5 Hz, 4H), 2.23 (t, *J* = 5.0 Hz, 2H), 1.89 (s, 2H), 1.17 (t, *J* = 7.0 Hz, 13H). ¹³C NMR (125 MHz, CDCl₃) δ 153.96, 150.99, 148.86,

133.12, 129.67, 129.32, 128.31, 124.24, 123.41, 107.85, 104.52, 97.76, 44.10, 27.81, 12.59. HRMS calc. for $C_{34}H_{45}N_4O_4$ ($M+H^+$): 573.3435, found: 573.3463.

Synthesis of M2

Hydrazine monohydrate (5.2 g, 100.0 mmol) was stirred in 20 mL of isopropanol at 0 °C for 15 min, and treated dropwise with a solution of Boc_2O (10.0 g, 45.8 mmol) in 10 mL of isopropanol. The reaction slurry was naturally warmed to room temperature and continually stirred for 20 min. The solvent was removed by rotary evaporation and the residue was dissolved in CH_2Cl_2 and dried over $MgSO_4$. After most of the solvent was removed by rotary evaporation, the remaining liquid was distilled under reduced pressure to give *t*-butyl carbazate (**M2**) as a white solid, 1H NMR (400 MHz, $CDCl_3$) δ 6.42 (s, 1H), 3.60 (s, 2H), 1.37 (s, 9H).

Synthesis of R2

A solution of rhodamine B (442 mg, 1 mmol) in Cl_2SO (10 mL) was kept at room temperature overnight. The reaction mixture was evaporated under vacuum and the solid was abstracted by anhydrous CH_2Cl_2 (3×15 mL) and evaporated to give rhodamine B acid chloride (**R4**). The crude acid chloride was dissolved in anhydrous CH_2Cl_2 (10 mL) and added dropwise to a solution of Boc-NH-NH₂ (132 mg, 1 mmol) and Et_3N (200 mL, 2 mmol) in anhydrous CH_2Cl_2 (15 mL). The reaction mixture was kept at room temperature for 10 min. Evaporation of the solvent yielded a crude that was purified by column chromatography using petroleum ether/ethyl acetate (3/1, v/v) as an eluent to give **R2** as a white solid (0.26 g, 50% yield). 1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, $J = 7.6$ Hz, 1H), 7.57 – 7.44 (m, 2H), 7.16 (d, $J = 7.5$ Hz, 1H), 6.52 (s, 2H), 6.38 (d, $J = 1.8$ Hz, 2H), 6.28 (d, $J = 8.4$ Hz, 2H), 3.34 (q, $J = 7.0$ Hz, 8H), 1.61 (s, 4H), 1.26 (s, 9H), 1.16 (d, $J = 14.1$ Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.92, 153.56, 152.87, 148.92, 132.58, 131.45, 129.05, 128.32, 123.80, 123.09, 108.24, 105.41, 97.68, 59.49, 57.65, 54.48, 44.13, 39.49, 12.31. HRMS calc. for $C_{33}H_{41}N_4O_4^+$ ($M+H^+$): 557.3122, found: 557.3111.

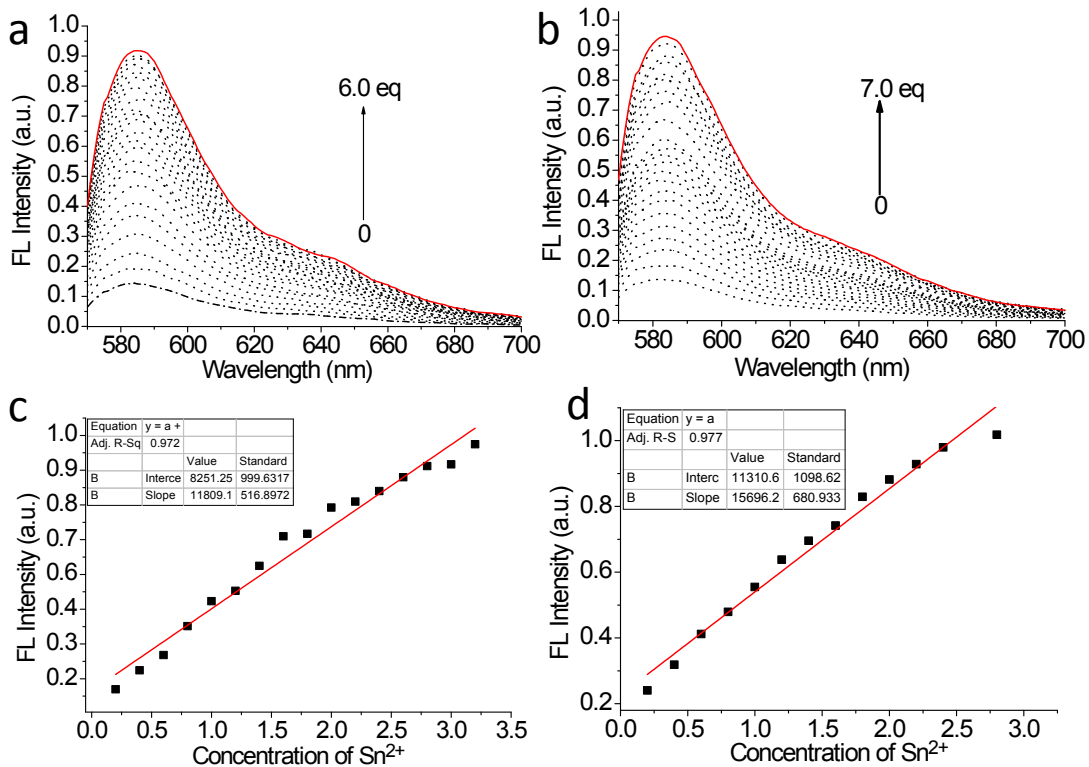


Fig. S1 Normalized fluorescence intensity change of **R1** and **R2** (1.0×10^{-5} M) at 580 nm with addition of different equivalents of Sn^{2+} . Detection limit of **R1** and **R2** was calculated as $3\sigma/\text{slope}$.

Association constant

$$K = \frac{[\text{SnR}]_e}{[\text{Sn}^{2+}]_e [\text{R}]_e} = \frac{[\text{SnR}]_e}{([\text{Sn}^{2+}]_0 - [\text{SnR}]_e) ([\text{R}]_0 - [\text{SnR}]_e)} \quad \text{Eq. S1}$$

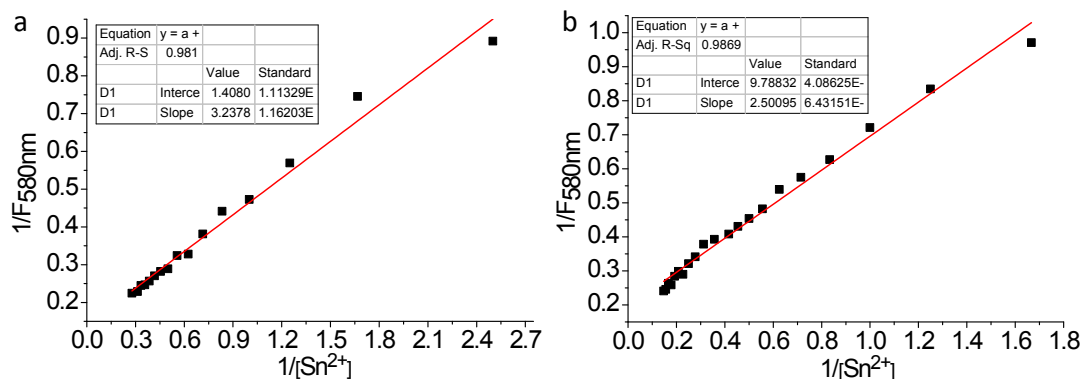


Fig S2 Reciprocal of fluorescent intensity of **R1** and **R2** (1.0×10^{-5} M) at 580 nm with addition of different equivalents of Sn^{2+} ion.

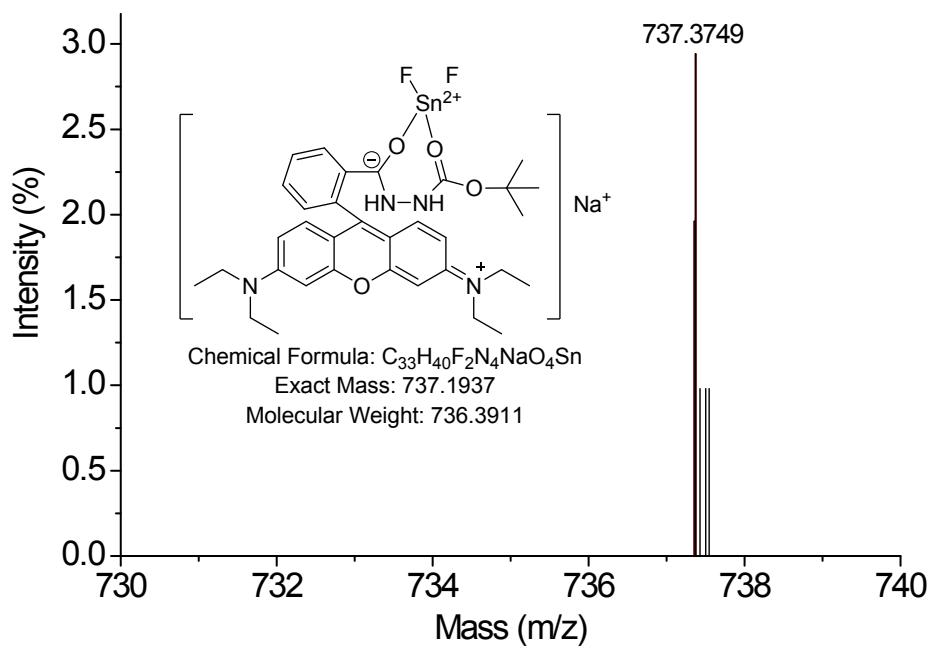
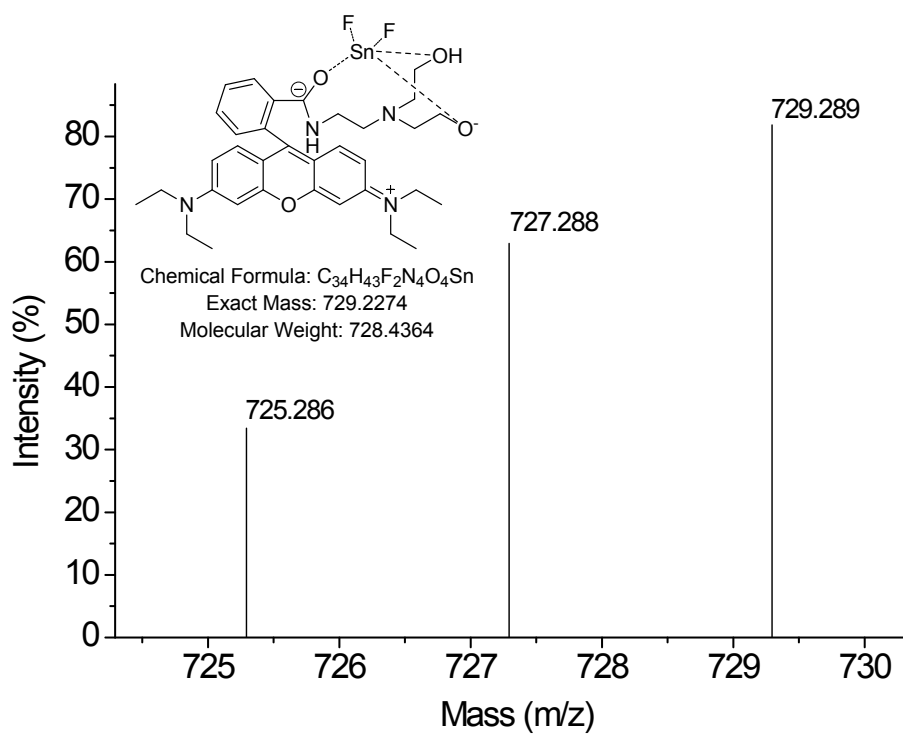


Fig. S3 Maldi-Tof-MS spectra of the complexes