Supporting information

A BODIPY based indicator for Fluorogenic detection of salicylaldehyde with OFF-ON emission

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Experimental

Apparatus and materials

^{1}H NMR spectra were recorded in DMSO-d6 solution on the Inova 400 MHz instruments, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. HR MS were carried out on QTof-Micro YA 263 instruments. And fluorescent spectra were recorded on a Perkin Elmer LS55 Fluorescence Spectrophotometer.

Synthesis

Synthesis of compound 2

To a solutionof 2,4-dimethylpyrrole (2 equiv.) in absolute CH_2Cl_2 solution was added the 3,5-dinitrobenzoyl chloride (1 equiv.).The solution was stirred at room temperature for 24 hours, the color changing slowly from pale brown to deep red. Et_3N (6 equiv.) was then added, followed by a subsequent addition of BF_3-Et_2O (8 equiv.). The mixture was stirred for another 6 hours at room temperature. The reaction was stopped by the addition of saturated aqueous $NaHCO_3$ (100ml), and then was washed 3 times with saturated aqueous $NaHCO_3$.The organic layer was then dried over $MgSO_4$, filtered and the solvent removed. Chromatography on silica gel (CH_2Cl_2/cyclohexane, 1:1 as eluent) gave the pure compound 2.

Synthesis of compound 1

Compound 2 (0.7 g, 1.9 mmol) was dissolved in 50 mL of absolute THF and 50 mL of absolute MeOH. After purged with N_2, 5%Pd/C(1.0g) and 2.0 ml hydrazine were added. The

solution was stirred at reflux under N_2 for 5 hours. When TLC monitoring (silica gel; CH_2Cl_2) showed complete consumption of 2, the reaction mixture was filtered, and evaporated. The compound was purified by silica gel column chromatography (CH_2Cl_2 and CH_2Cl_2/MeOH as eluent) to give a red solid (83%). Recrystallized from CH_2Cl_2/n-hexane to afford orange crystals 1.

^{1}H NMR (DMSO-d6, 400 MHz): 6.13-6.18 (m, 2H), 5.89 (s, 1H), 5.67-5.68 (m, 2H), 4.95 (s, 4H), 2.41-2.48 (m, 6H), 1.68 (s, 6H).

HR-MS $C_{19}H_{21}BF_2N_4$, Anal. Calc. M+Na = 377.1723; Found 377.1734.

Which was consistent with the reported data.

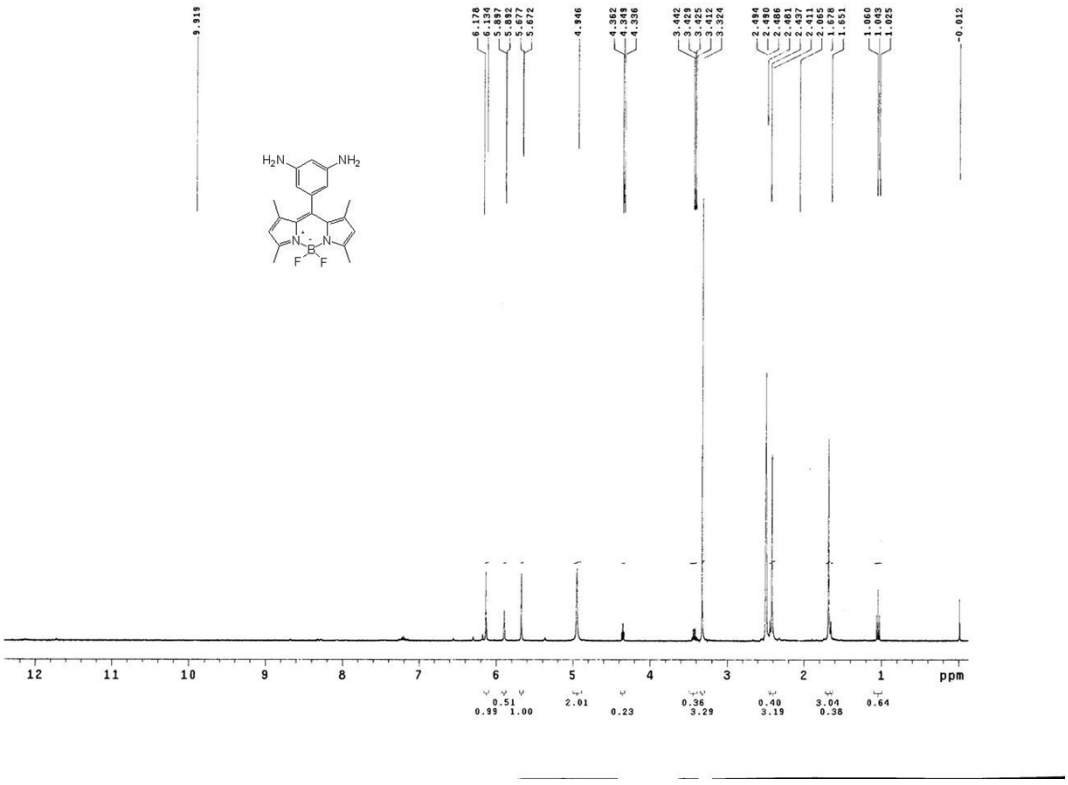

Fig. S1 ^{1}HN MR Spectra of probe 1.

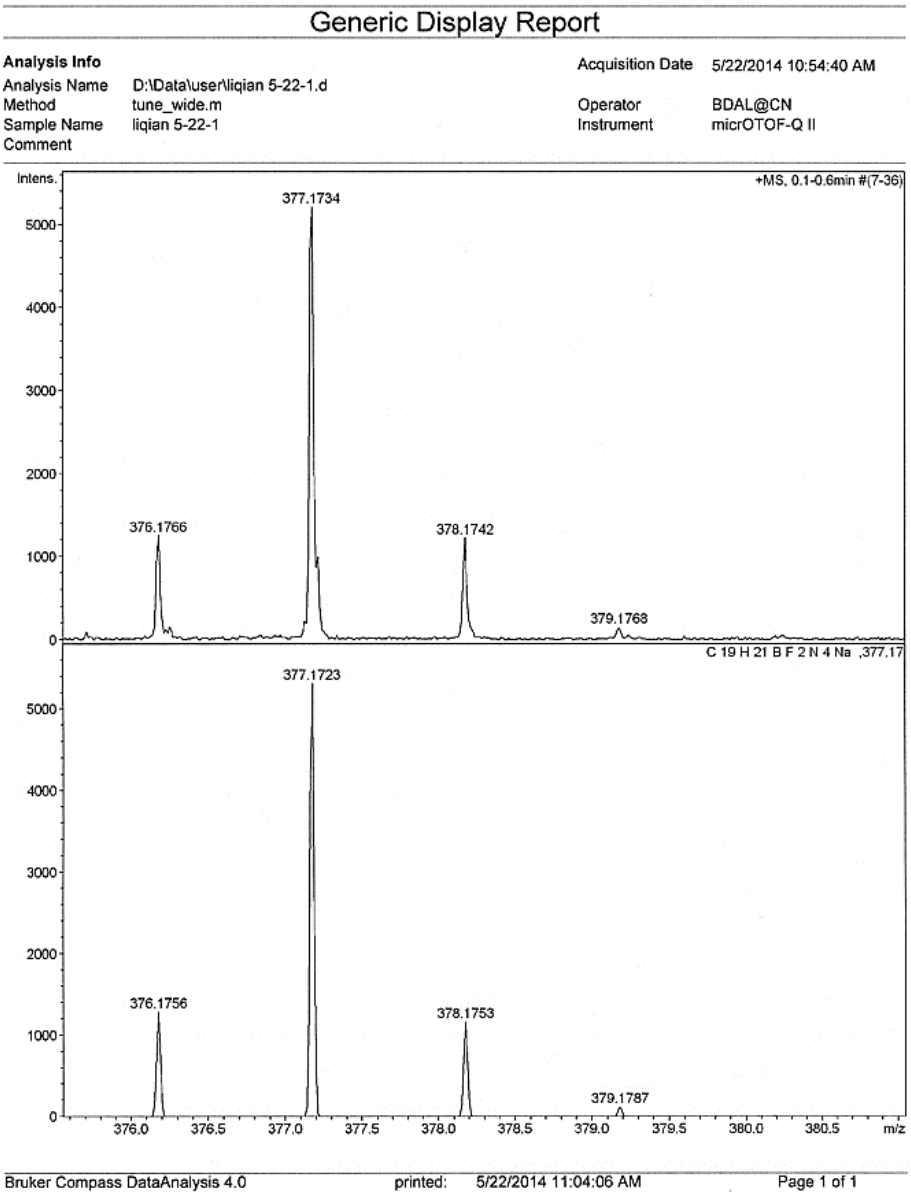

Fig. S2 HR-MS Spectra of probe 1.

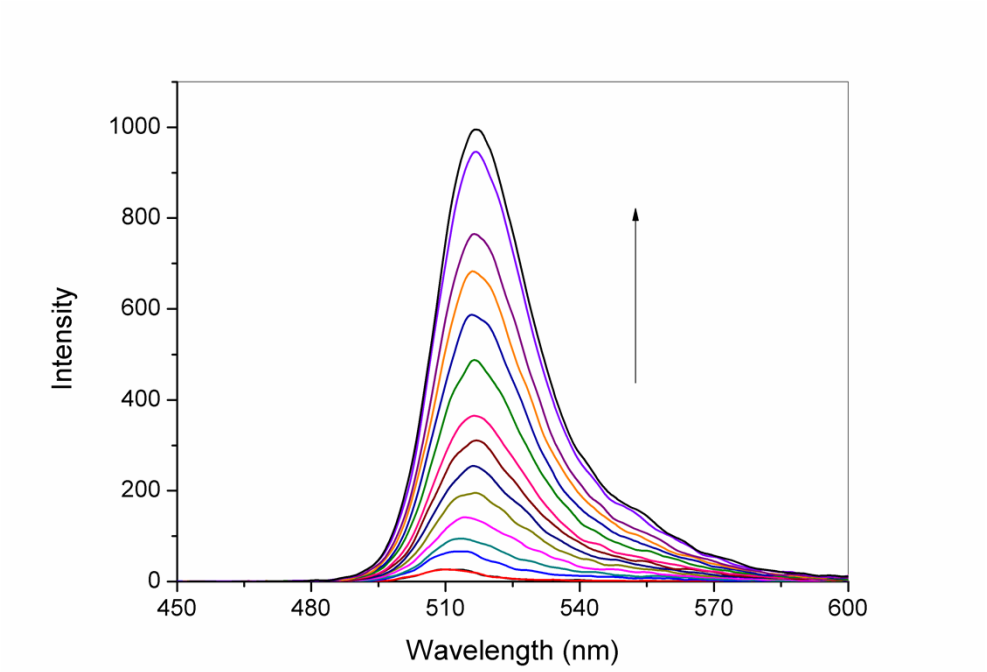

Fig. S3 Fluorescence emission spectra of Probe **1** (5 μM) in EtOH-H_2O solution in the prescence of salicyladehyde (0-15 mM). The inset shows the titration curve of salicyladehyde with Probe **1** by fluorescence emission intensity at 522 nm.

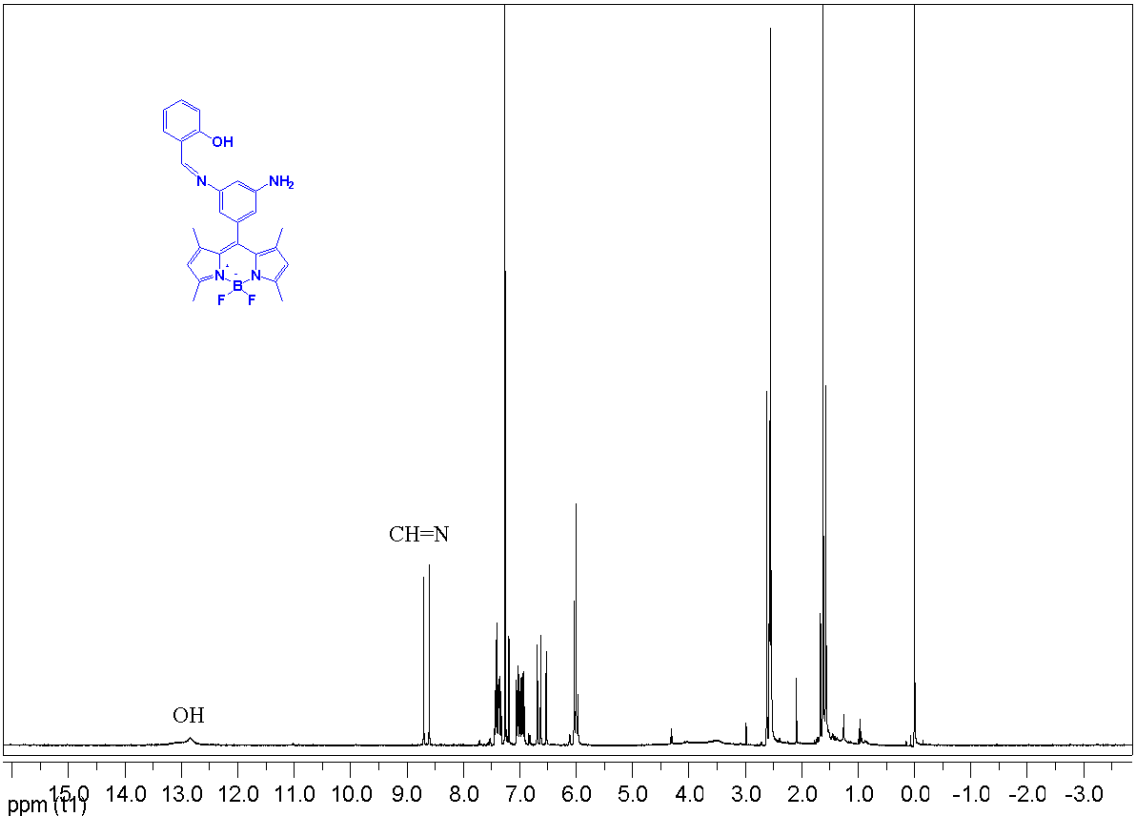

Fig. S4 ^{1}HN MR Spectra of reaction product P1 of probe 1 with salicylaldehyde

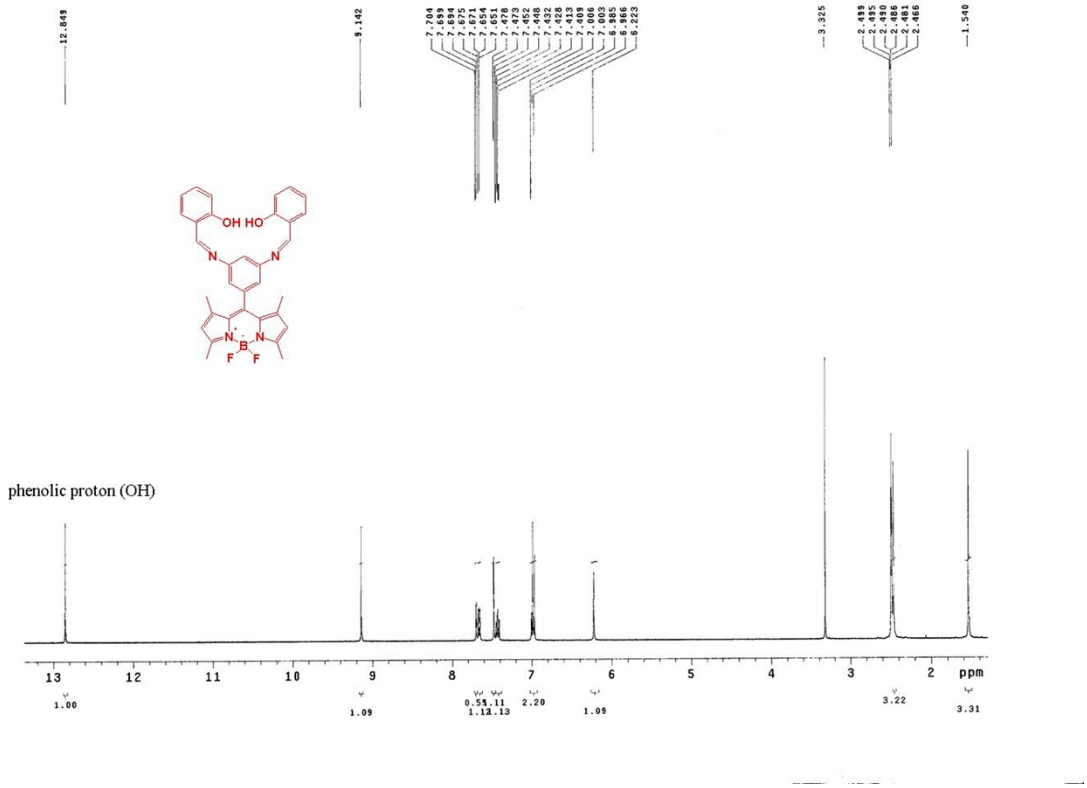

Fig. S5 [1]HN MR Spectra of reaction product P2 of probe 1 with salicylaldehyde