New Boronic Acid Fluorescent Reporter Compounds II. A Naphthalene-based On-Off Sensor Functional at Physiological pH

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Supporting Information

Experimental:

General Methods. NMR spectra were recorded on either a Mercury-400 (operating at 400 and 100 MHz for ^{1}H and ^{13}C, respectively, using tetramethylsilane as the internal standard) or a GE-300 (operating at 96 MHz for ^{11}B using BF_3 as the external standard). Column chromatography was performed using silica gel (200-400 mesh) from Aldrich. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. ESI-MS spectral analyses were conducted by the Mass Spectrometry Laboratory of the University of Kansas. 1-Bromo-4-(dimethylamino)-naphthalene was purchased from Lancaster. Other commercially available reagents were purchased from Aldrich or ACROS. Tetrahydrofuran (THF) was distilled from Na and benzophenone. All pH values were determined with an Accumet 1003 Handhold pH/mV/Ion Meter (Fisher Scientific). A Shimadzu RF-5301 PC fluorometer was used for the fluorescence studies.

4-(Dimethylamino)-naphthalene boronic acid (**1**) To the solution of 1-bromo-4-(dimethylamino)-naphthalene (0.370 g, 1.48 mmol) in THF (5 mL) at –78 °C was added n-BuLi (0.97 mL, 1.8 M, 1.75 mmol) in hexanes. The solution was stirred at –78 °C for 45 min, and then trimethylborate (0.51 mL, 4.46 mmol) was added. After stirring at –78 °C for an additional 2 h, the solution was gradually warmed to RT, and stirring was continued overnight. After solvent evaporation *in vacuum*, the residue was dissolved in 30 mL 0.1 N HCl and extracted with DCM (2 × 10 mL). The pH of the aqueous phase was then adjusted to 8 with $NaHCO_3$ and the solution was extracted with DCM (3 × 20 mL). The combined organic layers were washed with water and dried over Na_2SO_4. After solvent evaporation, the residue was purified via silica gel column chromatography (DCM/MeOH = 50:1) to give **1** as white solid (0.154 g). Recrystallization from DCM/hexanes afforded **1** as colorless crystals (0.133 g).
Yield: 42%. HRESI-MS: Calcd. for $C_{12}H_{15}BNO_2$ 216.1196 $(M+H)^+$, Found 216.1187; ^{1}H NMR (400 MHz, CD_3OD) δ 2.87 (s, 6H), 7.10 (d, J = 7.2, 1H), 7.45 (m, 3H), 7.76 (m, 1H), 8.21 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 113.2, 124.4, 124.7, 125.7, 128.5, 128.5, 130.5; Anal. Calcd for $C_{12}H_{14}BNO_2$-3/4H_2O: C, 71.51, H, 6.25, N, 6.95; Found: C, 71.80; H, 6.42, N, 6.65.

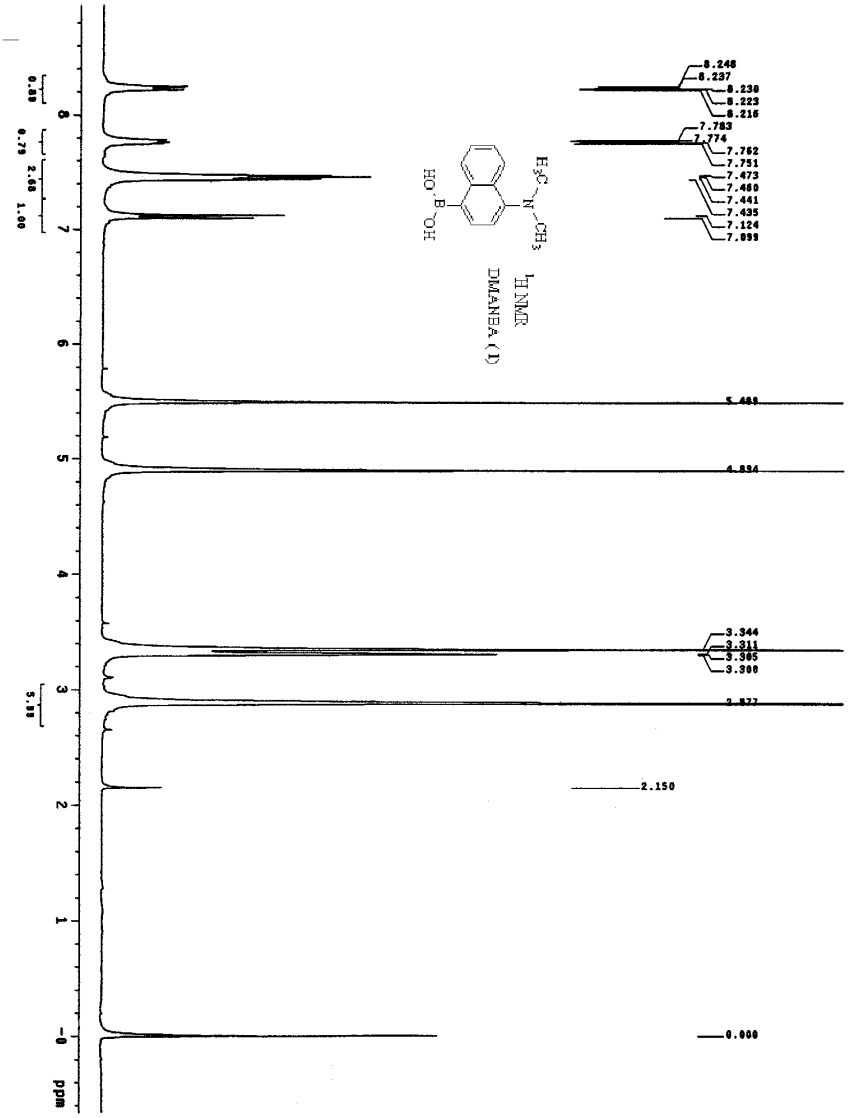

Figure S-1. ^{11}H NMR of DMANBA (**1**) (400 MHz, CD_3OD).

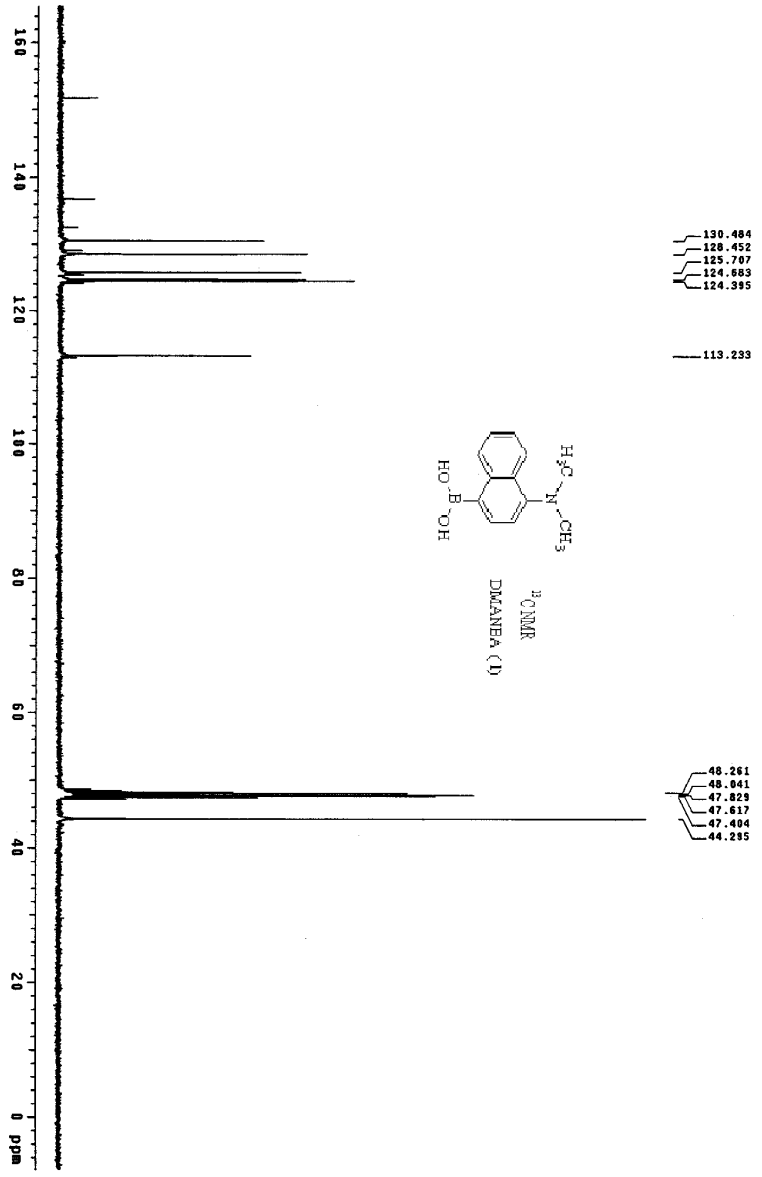

Figure S-2. ^{13}C NMR of DMANBA (**1**) (100 MHz, CD_3OD).