

Fluoride ion capture from water with a cationic borane

Ching-Wen Chiu, François P. Gabbaï*

Department of Chemistry, Texas A&M University, College Station, Texas 77843.

Supplementary Information

General considerations: Tetrakis(THF)lithium dimesityl-1,8-naphthalenediylborate was synthesized by following the published procedure (Hoefelmeyer, J. D.; Gabbaï, F. P. *Organometallics* **2002**, *21*, 982-985). Eschenmoser's salt was purchased from TCI and dried under vacuum at 80 °C before use. Methyl triflate and [(Me₂N)₃S][Me₃SiF₂] were purchased from Aldrich and used without further purification. *n*-Bu₄NF•3H₂O was purchased from Alfa Aesar and used as received. THF and ether were dried by refluxing under N₂ atmosphere over Na/K and freshly distilled prior to use. CH₂Cl₂ was dried over alumina under N₂. All the air sensitive compounds were handled under a N₂ atmosphere utilizing standard Schlenk and glovebox techniques. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). UV-vis spectra were recorded on a HP8430 spectrophotometer. All melting points were measured on samples in sealed capillaries and are uncorrected. NMR spectra were recorded on Varian Unity Inova 400 FT NMR (399.63 MHz for ¹H, 376.03 MHz for ¹⁹F, 128.2 MHz for ¹¹B, and 100.50 MHz for ¹³C) spectrometer. Chemical shifts δ are given in ppm and are referenced against external Me₄Si (¹H, ¹³C), CFCl₃ (¹⁹F), and BF₃•OEt₂ (¹¹B).

Crystallography: The crystallographic measurements were performed using a Siemens SMART-CCD area detector diffractometer, with a graphite-monochromated Mo-K α radiation (λ = 0.71069 Å). Specimens of suitable size and quality were selected and mounted onto glass fiber with apiezon grease. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on *F*² using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms.

Synthesis of borane 2: A THF solution (20 mL) of tetrakis(THF)lithium dimesityl-1,8-naphthalenediylborate (3.00 g, 4.47 mmol) was added to a suspension of Eschenmoser's salt (0.84 g, 4.54 mmol) in THF (10 mL) at room temperature. After stirring for 1 hour, the reaction was quenched with water and extracted with CH₂Cl₂ (2 x 50 mL). The organic phases were combined and washed with water, brine and dried over MgSO₄. The solvents were removed under reduced pressure yielding a light yellow oil. Addition of hexane to the oil resulted in the precipitation of compound 2 which was obtained as a

white powder. Compound **2** was purified by recrystallization from dichloromethane/hexane (1.33 g, yield 69%). Single crystals of compound **2** were obtained by evaporation of a dichloromethane/hexane solution. ^1H NMR (CDCl_3 , 400 MHz): δ 0.77 (s, 3H, Mes- CH_3), 1.88 (s, 3H, Mes- CH_3), 2.08 (s, 6H, Mes- CH_3), 2.14 (s, 3H, Mes- CH_3), 2.17 (s, 3H, Mes- CH_3), 2.33 (s, 3H, $\text{NMe}_2\text{-CH}_3$), 2.42 (s, 3H, $\text{NMe}_2\text{-CH}_3$), 3.04 (d, 1H, $^2J_{\text{H-H}} = 14.4$ Hz, nap- $\text{CH}_2\text{-NMe}_2$), 3.46 (d, 1H, $^2J_{\text{H-H}} = 14.4$ Hz, nap- $\text{CH}_2\text{-NMe}_2$), 6.42 (s, 1H, Mes-CH), 6.75 (s, 1H, Mes-CH), 6.81 (s, 1H, Mes-CH), 6.91 (s, 1H, Mes-CH), 7.35 (dd, 1H, $^3J_{\text{H-H}} = 8.1$ Hz, $^3J_{\text{H-H}} = 6.9$ Hz, nap-CH), 7.48-7.54 (m, 2H, nap-CH), 7.77-7.82 (m, 2H, nap-CH), 7.95 (dd, 1H, $^3J_{\text{H-H}} = 8.1$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, nap-CH). ^{13}C NMR (CDCl_3 , 100.5 MHz): δ 21.1 (Mes-*p*- CH_3), 21.3 (Mes-*p*- CH_3), 22.1 (Mes-*o*- CH_3), 23.2 (Mes-*o*- CH_3), 24.1 (Mes-*o*- CH_3), 25.3 (Mes-*o*- CH_3), 44.9 (NMe_2), 64.7 (nap- $\text{CH}_2\text{-N}$), 124.8, 125.8, 127.3, 128.1, 128.2, 128.7, 128.9, 129.0, 132.9, 133.8, 134.3, 136.0, 136.9, 138.6, 139.2, 140.5, 141.2, 141.3, 141.5, 142.5, 144.3, 147.8. ^{11}B NMR (CDCl_3 , 128.2 MHz): δ 68.7. Anal. Calcd. for $\text{C}_{31}\text{H}_{36}\text{BN}$: C, 85.90; H, 8.37. Found: C, 85.76; H, 8.50

Synthesis of cationic borane [3][OTf]: An excess methyl triflate was added to a dichloromethane solution (2 mL) of **2** (0.50 g, 1.16 mmol) under an inert atmosphere. After stirring for 1 hour, ether was added to the reaction mixture which resulted in the precipitation of [3][OTf] (0.61 g, yield 88%). Single crystals of [3][OTf] were obtained by vapor diffusion of diethyl ether into a solution of dichloromethane. ^1H NMR (CDCl_3 , 400 MHz): δ 0.34 (s, 3H, Mes- CH_3), 1.70 (s, 3H, Mes- CH_3), 2.13 (s, 3H, Mes- CH_3), 2.19 (s, 3H, Mes- CH_3), 2.33 (s, 3H, Mes- CH_3), 2.60 (s, 3H, Mes- CH_3), 2.84 (s, 9H, $\text{NMe}_3^+\text{-CH}_3$), 3.69 (d, 1H, $^2J_{\text{H-H}} = 13.4$ Hz, nap- $\text{CH}_2\text{-NMe}_3^+$), 4.81 (d, 1H, $^2J_{\text{H-H}} = 13.4$ Hz, nap- $\text{CH}_2\text{-NMe}_3^+$), 6.35 (s, 1H, Mes-CH), 6.79 (s, 2H, Mes-CH), 6.98 (s, 1H, Mes-CH), 7.48 (dd, 1H, $^3J_{\text{H-H}} = 8.1$ Hz, $^3J_{\text{H-H}} = 7.2$ Hz, nap-CH), 7.52-7.60 (m, 2H, nap-CH), 7.84 (dd, 1H, $^3J_{\text{H-H}} = 6.9$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, nap-CH), 8.00 (dd, 2H, $^3J_{\text{H-H}} = 8.1$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, nap-CH). ^{13}C NMR (CDCl_3 , 100.5 MHz): δ 21.0 (Mes-*p*- CH_3), 21.2 (Mes-*p*- CH_3), 21.3 (Mes-*o*- CH_3), 22.5 (Mes-*o*- CH_3), 23.3 (Mes-*o*- CH_3), 25.7 (Mes-*o*- CH_3), 52.5 (NMe_3), 69.1 (nap- $\text{CH}_2\text{-N}$), 118.9, 122.1, 125.1, 125.3, 126.6, 128.7, 128.9, 129.2, 130.8, 132.7, 134.3, 134.5, 138.4, 139.1, 139.3, 139.6, 140.0, 140.3, 140.6, 141.4, 142.5, 144.6. ^{11}B

NMR (CDCl₃, 128.2 MHz): δ 67.8. ¹⁹F NMR (CDCl₃, 375.95 MHz): δ -79. Anal. Calcd. for C₃₃H₃₉BF₃NO₃S: C, 66.33; H, 6.58. Found: C, 65.83; H, 6.56

Synthesis of 3-F: TSAF (20 mg, 0.07 mmol) was added to a solution of [3][OTf] (44 mg, 0.07 mmol) in CH₂Cl₂ (1 mL). After stirring at room temperature for 10 minutes, the solvents were removed under reduced pressure and the residual white solid was extracted with ether. The combined ether solution was dried to afford 3-F as a white powder (22 mg, yield 64%). Single crystals of 3-F were obtained by evaporation of an ether solution. ¹H NMR (acetone-d₆, 233K): δ 0.82 (s, 3H, Mes-CH₃), 1.53 (s, 3H, Mes-CH₃), 2.14 (s, 6H, Mes-CH₃), 2.33 (d, 3H, ¹*J*_{H-F} = 6.9 Hz, NMe₃⁺-CH₃), 2.97 (s, 6H, Mes-CH₃), 3.35 (s, 6H, NMe₃⁺-CH₃), 3.82 (dd, 1H, ²*J*_{H-H} = 12.9 Hz, nap-CH₂-NMe₃⁺), 6.17 (s, 1H, Mes-CH), 6.43 (s, 1H, Mes-CH), 6.50 (dd, 1H, ²*J*_{H-H} = 12.9 Hz, ¹*J*_{H-F} = 9.2 Hz, nap-CH₂-NMe₃⁺), 6.56 (s, 1H, Mes-CH), 6.67 (s, 1H, Mes-CH), 7.16 (t, 1H, ³*J*_{H-H} = 7.5 Hz, nap-CH), 7.37 (dd, 1H, ³*J*_{H-H} = 7.8 Hz, ³*J*_{H-H} = 7.1 Hz, nap-CH), 7.45 (dd, 1H, ³*J*_{H-H} = 7.1 Hz, ⁴*J*_{H-H} = 1.6 Hz, nap-CH), 7.68 (d, 2H, ³*J*_{H-H} = 7.5 Hz, nap-CH), 7.98 (dd, 1H, ³*J*_{H-H} = 7.9 Hz, ⁴*J*_{H-H} = 1.4 Hz, nap-CH). ¹³C NMR (acetone-d₆, 233K): δ 20.8 (Mes-*p*-CH₃), 24.5 (Mes-*o*-CH₃), 24.8 (Mes-*o*-CH₃), 25.3 (d, *J*_{C-F} = 10.3 Hz, Mes-*o*-CH₃), 26.4 (d, *J*_{C-F} = 13.0 Hz, Mes-*o*-CH₃), 51.9 (NMe₃), 68.9 (d, d, *J*_{C-F} = 17.6 Hz, nap-CH₂-N), 122.7, 126.4, 127.7, 128.7, 129.0, 129.4, 129.8, 132.2, 132.3, 132.5, 133.7, 136.4, 136.5, 141.1, 141.2, 141.3, 143.3, 143.7. ¹¹B NMR (acetone-d₆, 233K): δ 12.2. ¹⁹F NMR (acetone-d₆, 233K): δ -152. Anal. Calcd. for C₃₂H₃₉BFN: C, 82.22; H, 8.41. Found: C, 81.05; H, 8.27.

UV-Vis spectrum of [3][OTf] and 3-F:

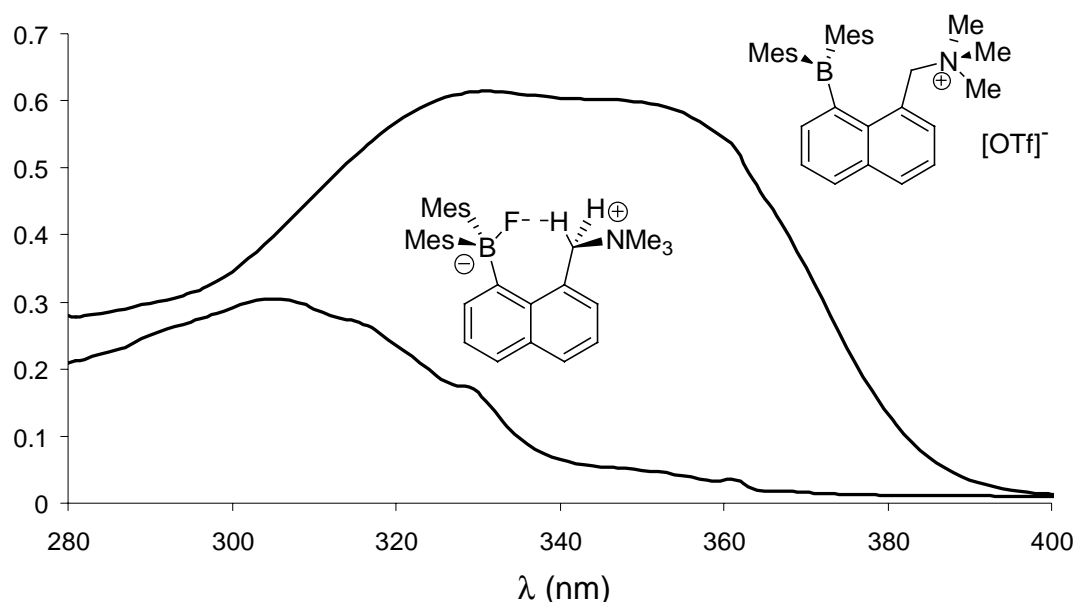


Figure SI-1: UV-Visible spectrum of [3][OTf] and 3-F in THF.

Titration in THF-MeOH (75/25)

A solution of [3][OTf] (3 mL, 3.72×10^{-5} M, THF-MeOH (75/25)) was placed in the cuvette and titrated with incremental amounts of fluoride anions by addition of a solution of $n\text{Bu}_4\text{NF}$ in THF (4.92×10^{-3} M). The absorption was monitored at $\lambda = 352$ nm ($\epsilon = 11850$ for 3^+ , $\epsilon = 773$ for 3-F). The experimental data obtained was fitted to a 1:1 binding isotherm which indicated that the fluoride binding constant of 3^+ is about $5.0 \times 10^6 \text{ M}^{-1}$ in THF-MeOH (75/25).

C_{Fluoride}	Abs(352 nm)	Abs(352 nm)
0	0.44032	0.44506
8.08E-06	0.34028	0.35061
1.61E-05	0.24296	0.25743
2.42E-05	0.15728	0.17175
3.22E-05	0.088276	0.10115
4.01E-05	0.050787	0.061166
4.81E-05	0.03589	0.03825
5.6E-05	0.02838	0.029698

Table SI-1: Absorbance of a solution of **3⁺OTf** (THF-MeOH 75/25) after successive additions of fluoride

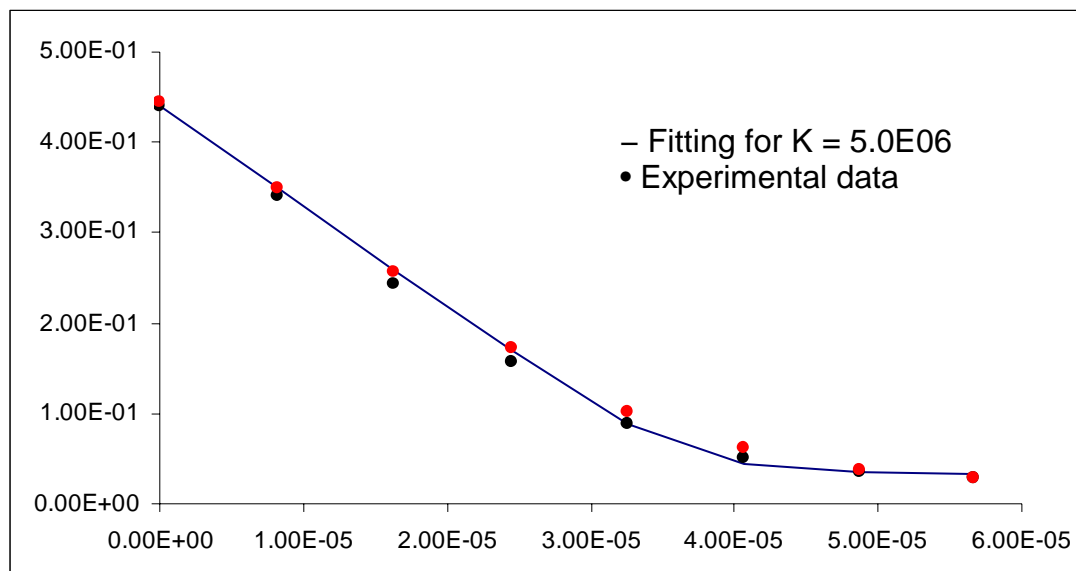


Figure SI-2: Absorbance of a solution of **3⁺OTf** (THF-MeOH 75/25) vs. fluoride concentration (M)

Biphasic fluoride capture:

A solution of **[3][OTf]** in CDCl_3 (1 mL, 6.9×10^{-2} M) and a solution of $n\text{-Bu}_4\text{NF}$ in D_2O (1 mL, 2.7×10^{-1} M) were mixed and shaken for a few minutes. The ^1H NMR spectrum of the CDCl_3 layer showed a 82% conversion of **[3]⁺** into **3-F**.

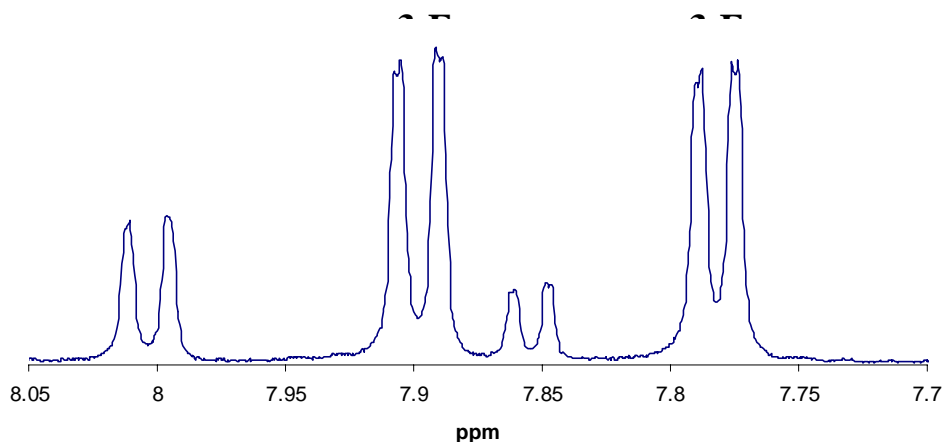


Figure SI-3: portion of the ^1H NMR spectra of the CDCl_3 layer after shaking.