Probing the influence of steric bulk on anion binding by triarylboranes: comparative studies of $FcB(o\text{-}Tol)_2$, $FcB(o\text{-}Xyl)_2$ and $FcBMes_2$

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Supporting Information

(1) Determination of binding constants for FcB(*o*-Tol)$_2$, 1

(a) Fluoride: 3.5 mg of FcB(*o*-Tol)$_2$, **1**, (9.25 µmol) were dissolved in 20 mL of dichloromethane. Subsequently, portions of 10 or 20 µL of a solution made up from 11.9 mg of [^{n}Bu$_4$N]F·4H$_2$O (35.7 µmol),[S1] in 4 mL dichloromethane were added sequentially to 3 mL of the stock solution of **1** placed in the UV-vis cell. After adding each aliquot of the fluoride solution, the mixture was stirred for 1 min before the UV-vis measurement was carried out.

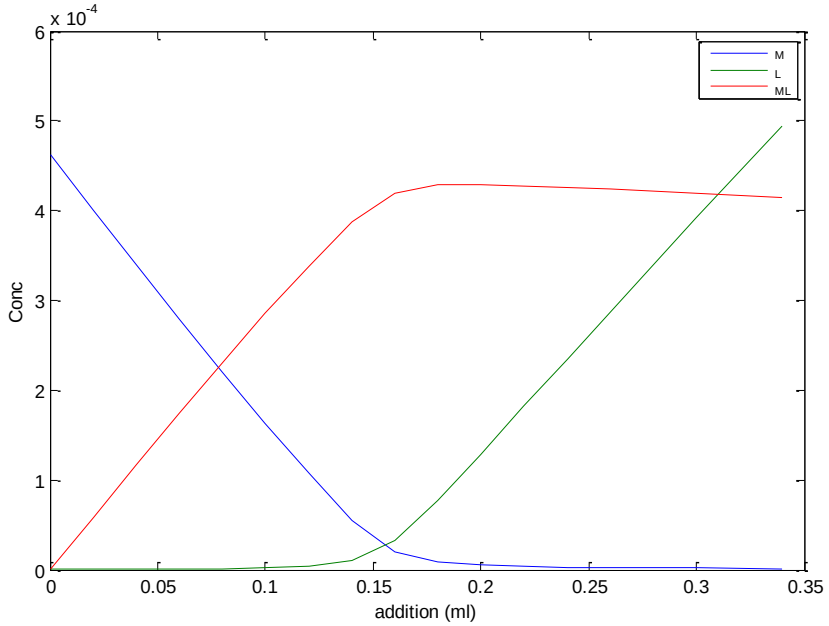

Figure S1: Calculated concentration profile, M = **1**, L = [^{n}Bu$_4$N]F·4H$_2$O, ML = [^{n}Bu$_4$N][**1**·F].

(b) Cyanide: 4.3 mg of **1** (11.4 µmol) were dissolved in 20 mL of dichloromethane. Subsequently, portions of 10 or 20 µL of a solution made up from 12.5 mg of [^{n}Bu$_4$N]CN·2H$_2$O (41.0 µmol),[S1] in 2.8 mL dichloromethane were added sequuentially to 3 mL of the stock solution of **1** placed in the UV-vis cell. After adding each aliquot of the cyanide solution the mixture was stirred for 1 min before the UV-vis measurement was carried out.

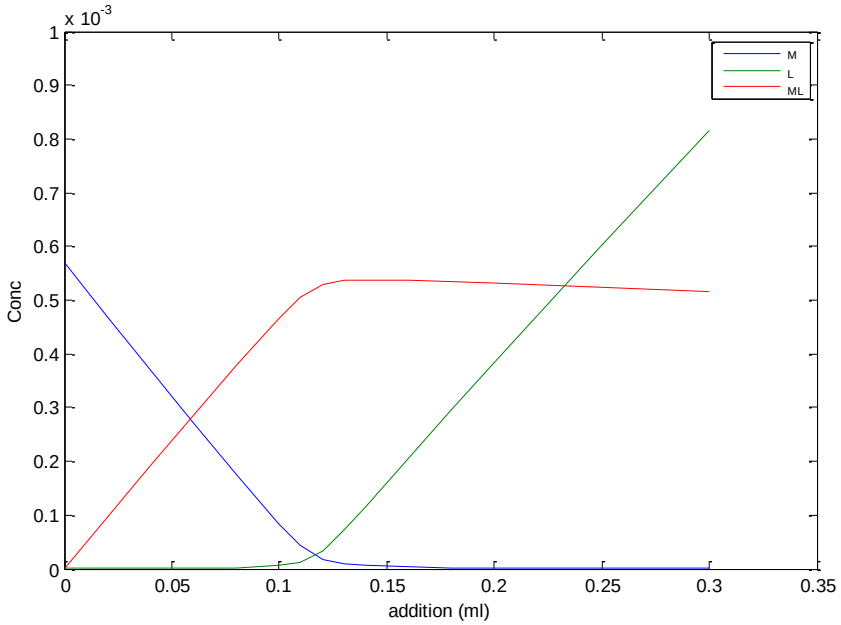

Figure S2: Calculated concentration profile, M = **1**, L = [^{n}Bu$_4$N]CN·2H$_2$O, ML = [^{n}Bu$_4$N][**1**·CN].

(2) Determination of CN^- binding constants for FcB(*o*-Xyl)$_2$, 2, and FcBMes$_2$, 3

(a) Synthetic details for **2** can be found in ref S2. The binding constant was calculated within the wavelength range of 460 nm to 560 nm using the program ReactLab^{TM} equilibria.[S3]

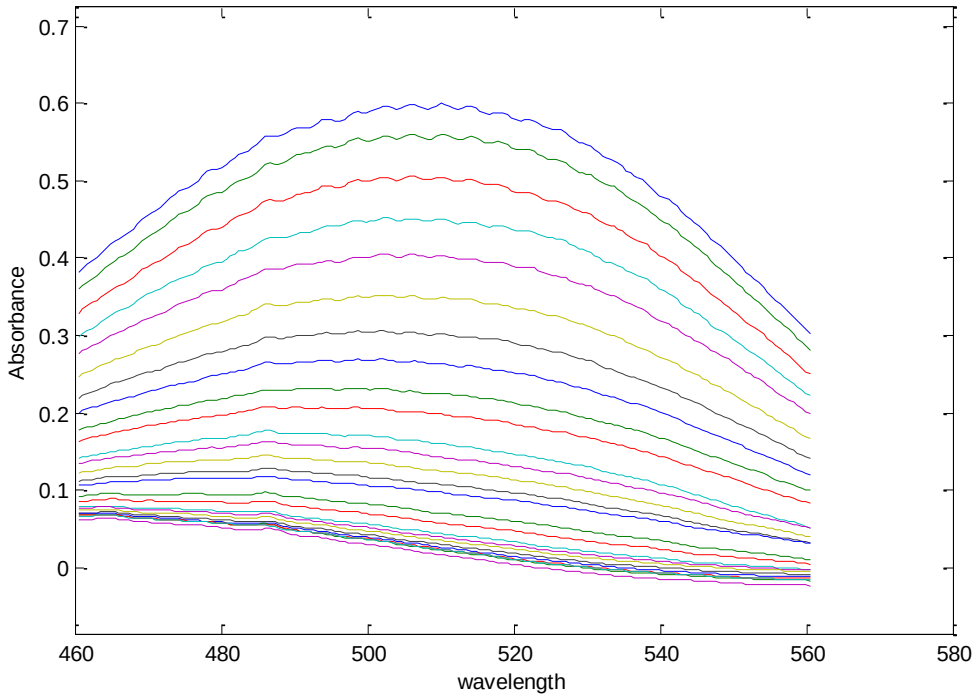

Figure S3: The response of **2** to exposure to [^{n}Bu$_4$N]CN·2H$_2$O in CH_2Cl_2 as monitored by UV-vis spectroscopy.

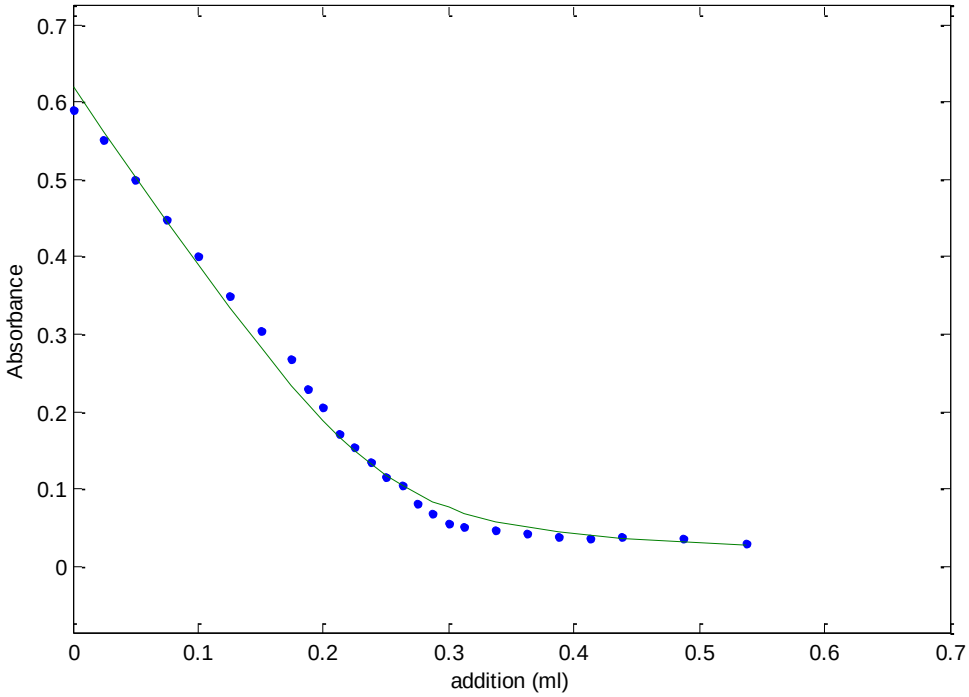

Figure S4: Experimental data (points) obtained at λ = 500 nm as a function of added cyanide, and the best-fit line obtained using ReactLab^{TM} equlibria.[S3]

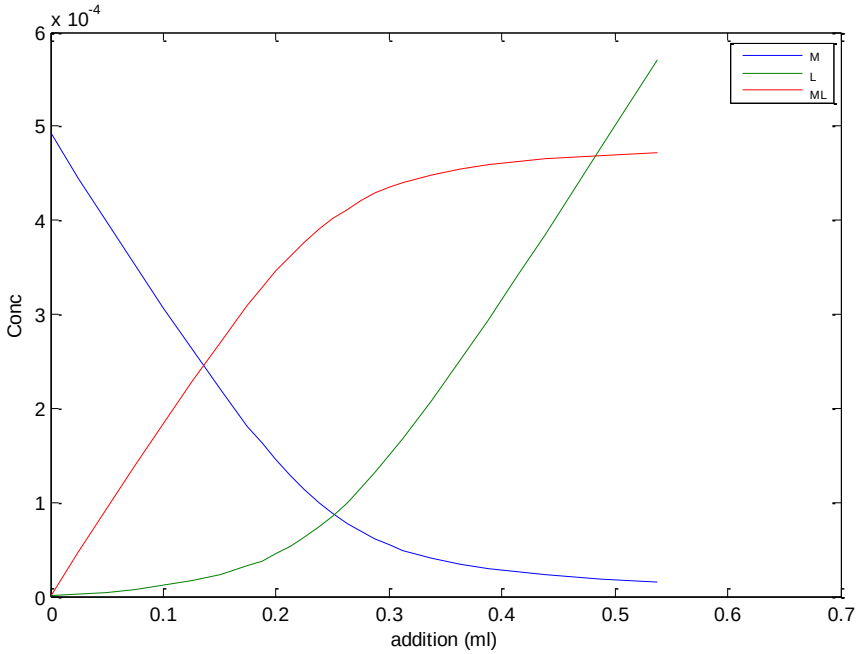

Figure S5: Concentration profile, M = **2**, L = [^{n}Bu$_4$N]CN·2H$_2$O, ML = [^{n}Bu$_4$N][**2**·CN].

(b) 5.5 mg of **3** (12.7 µmol) were dissolved in 20 mL of dichloromethane. Subsequently, 10, 20 or 50 µL of a solution made up from 15.5 mg of [^{n}Bu$_4$N]CN·2H$_2$O (50.9 µmol),[S1] in 3 mL dichloromethane were added sequentially to 3 mL of the stock solution of **3** placed in the UV-viscell. After adding each aliquot of the cyanide solution the mixture was stirred for 1 min before the UV-vis measurement was carried out. The binding constant was calculated within the wavelength range of 476 nm to 536 nm using the program ReactLab^{TM} equilibria.[S3]

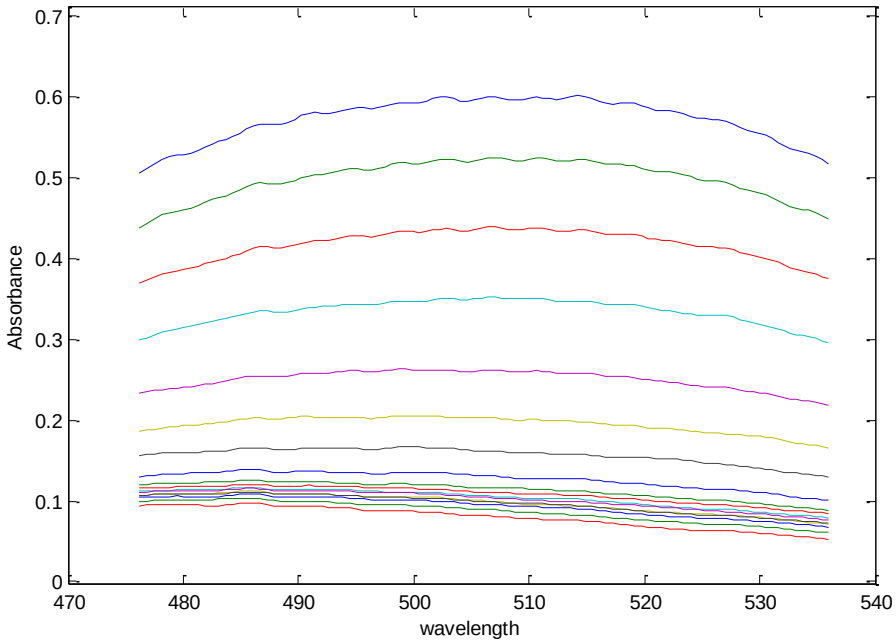

Figure S6: Response of **3** to exposure to [^{n}Bu$_4$N]CN·2H$_2$O in CH$_2$Cl$_2$ as monitored by UV-vis spectroscopy.

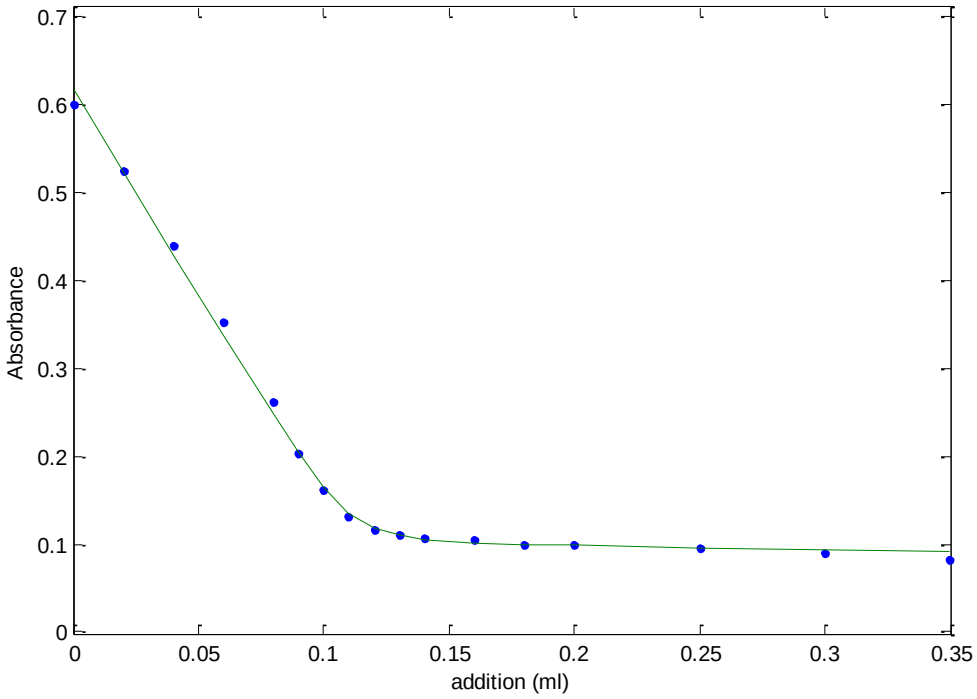

Figure S7: Experimental data (points) obtained at λ = 506 nm as a function of added cyanide, and the best-fit line obtained using ReactLab^{TM} equlibria.

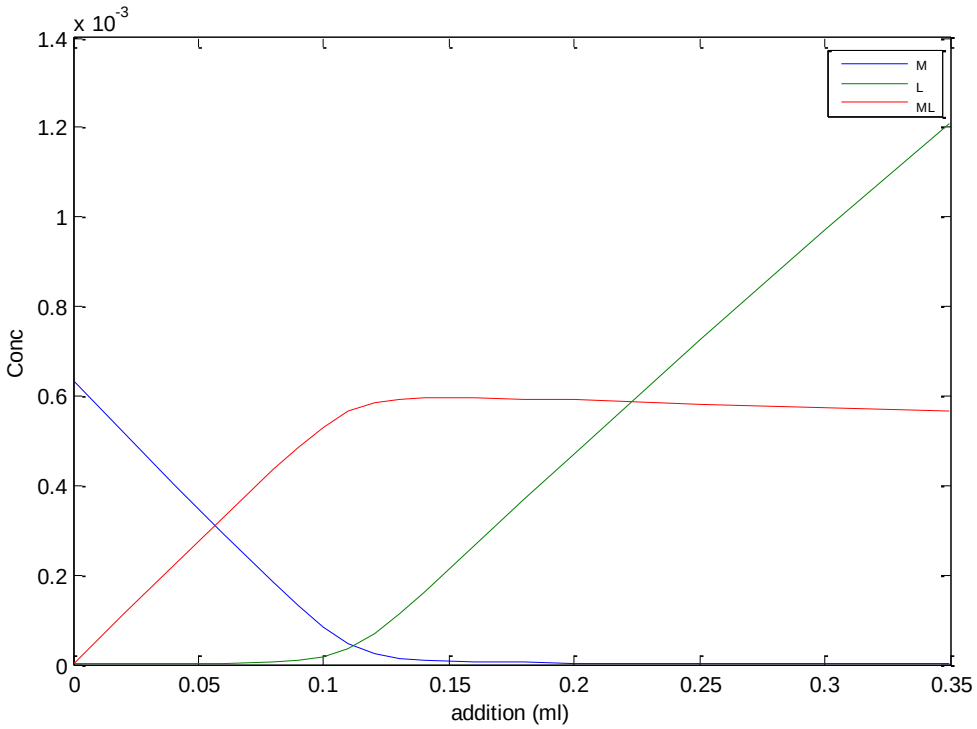

Figure S7: Concentration profile, M = **3**, L = [^{n}Bu$_4$N]CN * 2H$_2$O, ML = [^{n}Bu$_4$N][**3**·CN].

(3) References supporting information

[S1] The compositions of the tetra^{n}butylammonium fluoride and cyanide hydrates used in anion binding studies (and prepared by prolonged drying *in vacuo*) were determined to be [^{n}Bu$_4$N]F·4H$_2$O and [^{n}Bu$_4$N]CN·2H$_2$O by elemental microanalysis.

[S2] A. E. J. Broomsgrove, D. A. Addy, A. Di Paolo, I. R. Morgan, C. Bresner, V. Chislett, I. A. Fallis, A. L. Thompson, D. Vidovic and S. Aldridge, *Inorg. Chem.*, 2010, ***49***, 157.

[S3] ReactLab^{TM} equlibria, Version 1.0, JPlus Consulting Pty Ltd., 2010.