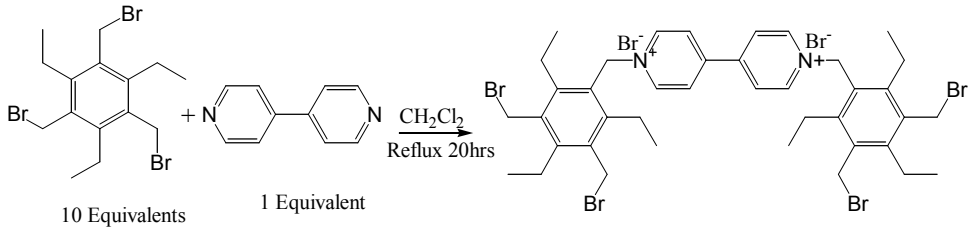
Supplementary Material

Intramolecular binding site competition as a means of tuning the response of a colourimetric anion sensor

Sara Jane Dickson, Emma V. B. Wallace, Adam N. Swinburne, Martin J. Paterson, Gareth O. Lloyd, Andrew Beeby, Warwick J. Belcher and Jonathan W. Steed*

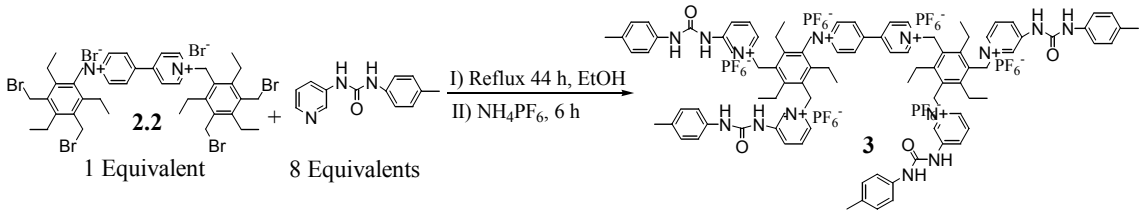
Experimental Details

Synthesis of 1,1'-bis(3,5-bis(bromomethyl)-2,4,6-triethylbenzyl)-4,4'bipyridine-1,1'-diium bromide (1)



1,3,5-tri(bromomethyl)-2,4,6-triethylbenzene (6.00 g, 13.60 mmol) and 4,4'bipyridine (0.21 g, 1.36 mmol) were dissolved in dichloromethane (150 ml) and stirred at reflux for 20 hours. During this time, a pale yellow precipitate of 1,1'-bis(3,5-bis(bromomethyl)-2,4,6-triethylbenzyl-4,4'bipyridine-1,1'-diium bromide was formed. This was filtered and washed with dichloromethane (3 x 50 ml). This yielded the bromide salt as a pale yellow solid (1.32 g, 1.27 mmol, 93%). m.p. – decomposed by 250 ^{o}C. ^{1}H NMR (DMSO-d_6, 500 MHz, δ/ppm, J/Hz) 9.01 (4H, d, J = 7.0, Ho_{bipy}); 8.71 (4H, d, J = 7.0, Hm_{bipy}); 6.05 (4H, s, -C$\underline{H}_2$-py$^+$); 4.78 (8H, s, -C$\underline{H}_2$Br); 2.96 (4H, q, J = 7.3, -C$\underline{H}_2$CH$_3$); 2.76 (8H, q, J = 7.3, -C$\underline{H}_2$CH$_3$); 1.34 (6H, t, J = 7.3, -CH$_2$C$\underline{H}_3$); 1.07 (12H, t, J = 7.3, -CH$_2$C$\underline{H}_3$). ^{13}C–{^{1}H} NMR (DMSO-d$_6$, 100 MHz, δ/ppm): 149.8, 147.6, 147.1, 145.3, 134.3, 127.8, 127.2, 58.3, 31.4, 23.6, 23.2, 16.0. ES$^+$-TOF MS: *m/z* = 878 [M - 2Br]$^{\bullet+}$ (2 x ^{81}Br + 2 x ^{79}Br), 517 [M]$^{2+}$ (1 x ^{81}Br + 5 x ^{79}Br), 494, 439 [$C_{20}H_{25}Br_2N$]$^+$ (1 x ^{81}Br + 1 x ^{79}Br), 361 [$C_{15}H_{19}Br_2$]$^+$ (2 x ^{81}Br), 349, 305, 261 [M]$^{4+}$ (6 x ^{81}Br), 217, 179 [M – 4Br]$^{4+}$ (2 x ^{79}Br). IR (ν/cm^{-1}): 3120 (s, Ar C-H), 3044 (s, Ar C-H), 2967 (s, CH$_2$/CH$_3$), 2923 (s, CH$_2$/CH$_3$), 2879 (s, CH$_3$/CH$_2$), 1636 (s, Ar C=C), 1560 (s, Ar C=C), 1501 (m, Ar C=C), 1444 (s, CH$_2$/CH$_3$ def), 1381 (m, CH$_3$ def) 699 (m, C-Br), 587 (m, C-Br), 509 (m, C-Br). Anal. Calcd for $C_{40}H_{50}N_2Br_6$: C, 44.72; H, 4.85; N, 2.70. Found: C, 44.43; H, 4.80: N, 2.51.

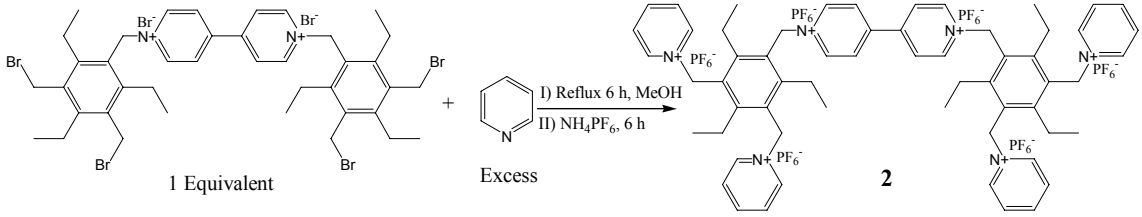
Synthesis of 1,1'-bis(2,4,6-triethyl-3,5-bis((3-(3-p-tolylureido)pyridinium-1-yl)benzyl)-4,4'-bipyridine-1,1'-diium hexafluorophosphate(V) (3)



1,1'-bis(3,5-bis(bromomethyl)-2,4,6-triethylbenzyl)-4,4'bipyridine-1,1'-diium bromide (0.75 g, 0.72 mmol) and 1-pyridin-3-yl-3-*p*-tolyl-urea (1.31 g, 5.77 mmol) were dissolved in ethanol (340 ml) and stirred at reflux for 44 h. During this time, a brown precipitate was formed, stuck to the round-bottomed flask. The reaction mixture was filtered to remove any of the brown solid. The solution was concentrated by removing ethanol (290 ml) under reduced pressure. The observed precipitate

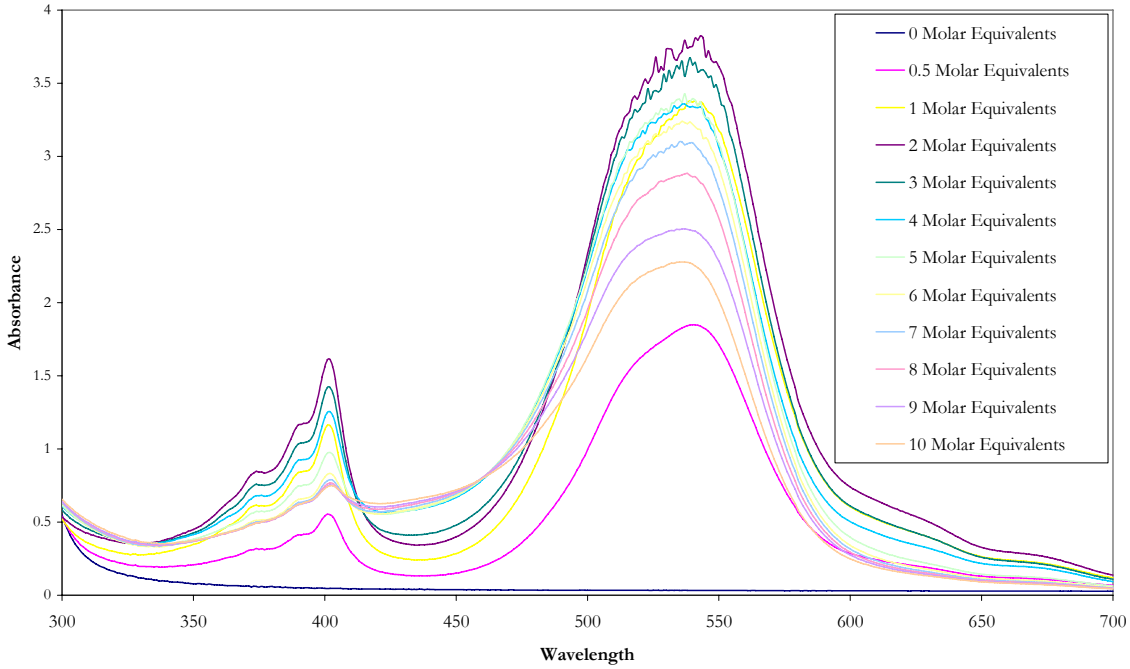
was filtered and a ^{1}H NMR spectrum was taken of the bromide salt. The resultant precipitate was sticky and was not fully characterised. The precipitate was dissolved in methanol (50 ml) with 10 equiv of NH_4PF_6 (1.17 g, 7.22 mmol) and stirred at ambient temperature for 6 h. A pale orange precipitate of 1,1'-bis(2,4,6-triethyl-3,5-bis((3-(3-p-tolylureido)pyridinium-1-yl)benzyl)-4,4'-bipyridine-1,1'-diium hexafluorophosphate was observed which was recovered by filtration and dried under ambient conditions (0.44 g, 0.19 mmol, 31%). m.p. – 206-213 ^{o}C decomposes in this region. ^{1}H NMR (CD_3CN-d_3, 400 MHz, δ/ppm, J/Hz): 8.97 (4H, s, PyH); 8.95 (4H, br s, NH); 8.62 (4H, d, J = 6.6, Ho_{bipy}), 8.51 (4H, d, J = 6.8, PyH); 8.26 (4H, s, NH); 7.97 (4H, d, J = 8.4, PyH); 7.92 (4H, dd, J_d = 9.0, J_{dd} = 5.9, PyH); 7.65 (4H, d, J = 6.6, Hm_{bipy}); 7.04 (8H, d, J = 8.1, ArH), 6.79 (8H, d, J = 8.1, ArH); 5.96 (4H, s, -C$\underline{H_2}$-py$^+$); 5.92 (8H, s, -C$\underline{H_2}$-py$^+$); 2.79 (4H, q, J = 7.4, -C$\underline{H_2}$CH$_3$); 2.53 (8H, br s, -C$\underline{H_2}$CH$_3$), 2.08 (12H, br s, -C$\underline{H_3}$), 1.29 (6H, t, J = 7.4, -CH$_2$C$\underline{H_3}$); 1.22 (12H, t, J = 7.5, -CH$_2$C$\underline{H_3}$). ^{13}C–{^{1}H} NMR (CD_3CN-d_3, 100 MHz, δ/ppm): 206.5, 152.4, 152.0, 151.4, 149.6, 144.8. 141.4, 137.5, 135.6, 133.8, 133.4, 132.0, 129.6, 128.6, 128.4, 127.3, 120.0, 58.4, 58.1, 24.5, 24.3, 20.0, 15.1, 14.8. ES$^+$ - TOF MS: *m/z* = 1024 $[M - 2(PF_6)]^{2+}$, 748, 732, 634 $[M - 3(PF_6)]^{3+}$, 569, 478, 337, 227 $[TUP]^+$, 183 $[C_{12}H_{11}N_2]^+$, 174, 129. IR (ν/cm^{-1}): 3413 (s, N-H), 3120 (m, Ar C-H), 2983 (m, CH_2/CH_3), 1714, 1636 (s, Ar C=C), 1593 (s, urea C=O), 1551 (s, Ar C=C), 1503 (s, Ar C=C), 1460, 1443, 1408 (m, CH_2/CH_3 def), 1390 (w, CH_3 def) 1315, 1295, 1243. 840. Anal. Calcd for $C_{92}H_{102}N_{14}P_6F_{36}$: C, 47.27; H, 4.40; N, 8.39. Found: C, 47.36; H, 4.56: N, 8.23.

Synthesis of 1,1'-bis(2,4,6-triethyl-3,5-bis(pyridinium-1-ylmethyl)benzyl)-4,4'-bipyridine-1,1'-diium hexaflorophosphate(V) (2)

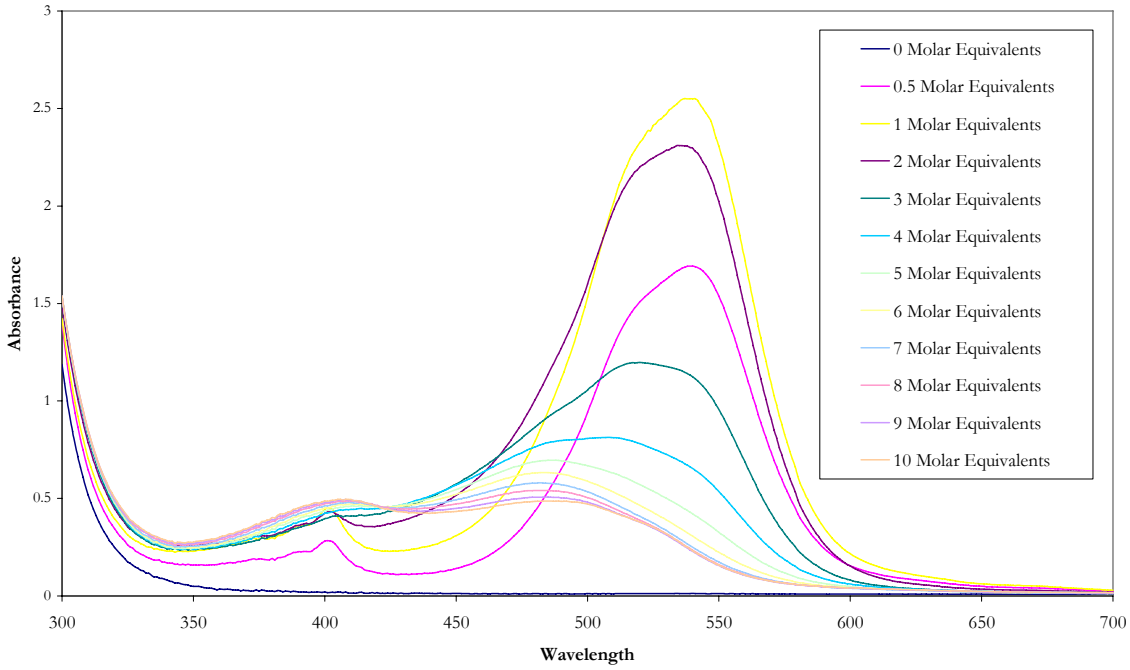


1,1'-bis(3,5-bis(bromomethyl)-2,4,6-triethylbenzyl)-4,4'bipyridine-1,1'-diium bromide (0.25 g, 0.24 mmol) and pyridine (2.85 g, 36 mmol) were dissolved in methanol (125 ml) and stirred at reflux for 6 h. The reaction mixture was then cooled and the solvent (105 ml) removed under reduced pressure. Diethyl ether (30 ml) was added to the solution and a yellow precipitate was observed. This was filtered and a ^{1}H NMR spectrum was taken of the bromide salt. The resultant precipitate was sticky and was not fully characterised. The solid was dissolved in methanol (30 ml) with 10 equiv of NH_4PF_6 (0.39 g, 2.41 mmol) and stirred at ambient temperature for 6 h. A very pale yellow precipitate of 1,1'-bis(2,4,6-triethyl-3,5-bis(pyridinium-1-ylmethyl)benzyl)-4,4'-bipyridine-1,1'-diium hexafluorophosphate was observed which was recovered by filtration and dried under ambient conditions. The solid was recrystallised in acetonitrile and diethyl ether, producing a sticky, pale yellow solid. This was filtered, re-dissolved in acetonitrile (10ml) and then the solvent was removed under reduced pressure to producing a pale yellow solid powder (0.23 g, 0.13 mmol, 55%). m.p. – decomposed by 230 ^{o}C. ^{1}H NMR (DMSO-d_6, 500 MHz, δ/ppm, J/Hz) 9.17 (4H, d, J = 6.7, Ho_{bipy}); 8.93 (8H, d, J = 6.2, PyH); 8.65 (8H, m, - Hm_{bipy}, and PyH); 8.18 (8H, t, J = 7.1, PyH); 6.14 (4H, s, -C$\underline{H_2}$Py); 6.08 (8H, s, -C$\underline{H_2}$Py) 2.69 (12H, q, J = 7.5, -C$\underline{H_2}$CH$_3$); 0.82 (18H, m, -CH$_2$C$\underline{H_3}$). ^{13}C–{^{1}H} NMR (DMSO-d_6, 100 MHz, δ/ppm): 151.1, 151.0, 150.0, 146.9, 145.7, 144.7, 129.2, 129.0, 128.4, 127.6, 58.4, 58.1, 24.2, 15.5, 15.4. ESI$^+$-MS: *m/z* = 805 $[C_{35}H_{39}N_4P_2F_{12}]^+$, 728 $[M - 2(PF_6)]^{2+}$, 519, 437 $[M - 6(PF_6)]^{\bullet 2+}$, 437 $[M - 3(PF_6)]^{3+}$, 330, 291 $[M - 4(PF_6)]^{4+}$, 275, 259, 227, 212, 204 $[M - 5(PF_6)]^{5+}$. IR (ν/cm^{-1}): 3143 (m, Ar C-H), 3104 (m, Ar C-H), 2978 (m, CH_2/CH_3), 2940 (m, CH_2/CH_3), 1637 (s, Ar C=C), 1567 (s, Ar C=C), 1503 (s, Ar C=C), 1485, 1448 (m, CH_2/CH_3 def), 1391 (m, CH_3 def) 1219, 1149, 1043, 838, 558. Anal. Calcd for $C_{60}H_{70}N_6P_6F_{36}$: C, 41.30; H, 4.04; N, 4.82. Found: C, 41.77; H, 4.14; N, 4.75.

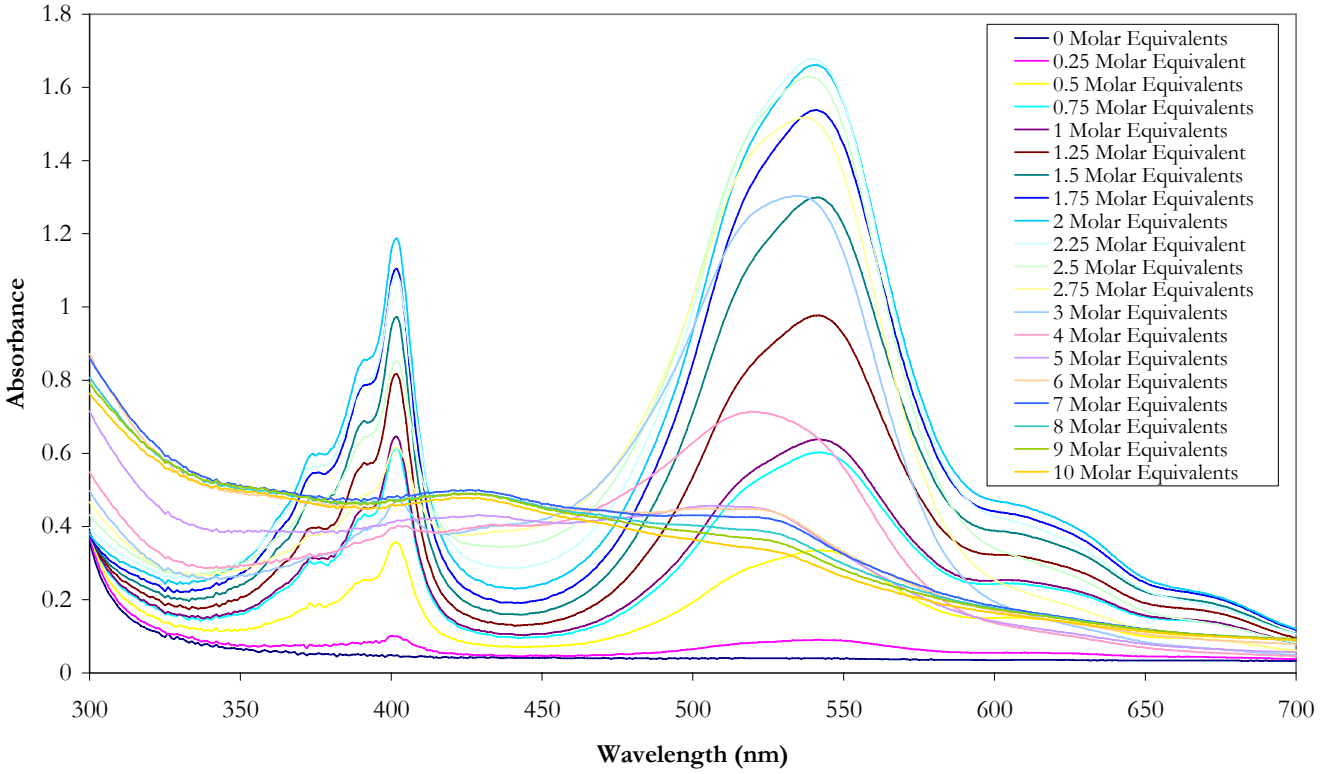
Anaerobic UV-Vis titration data for compound 2 with TBA acetate



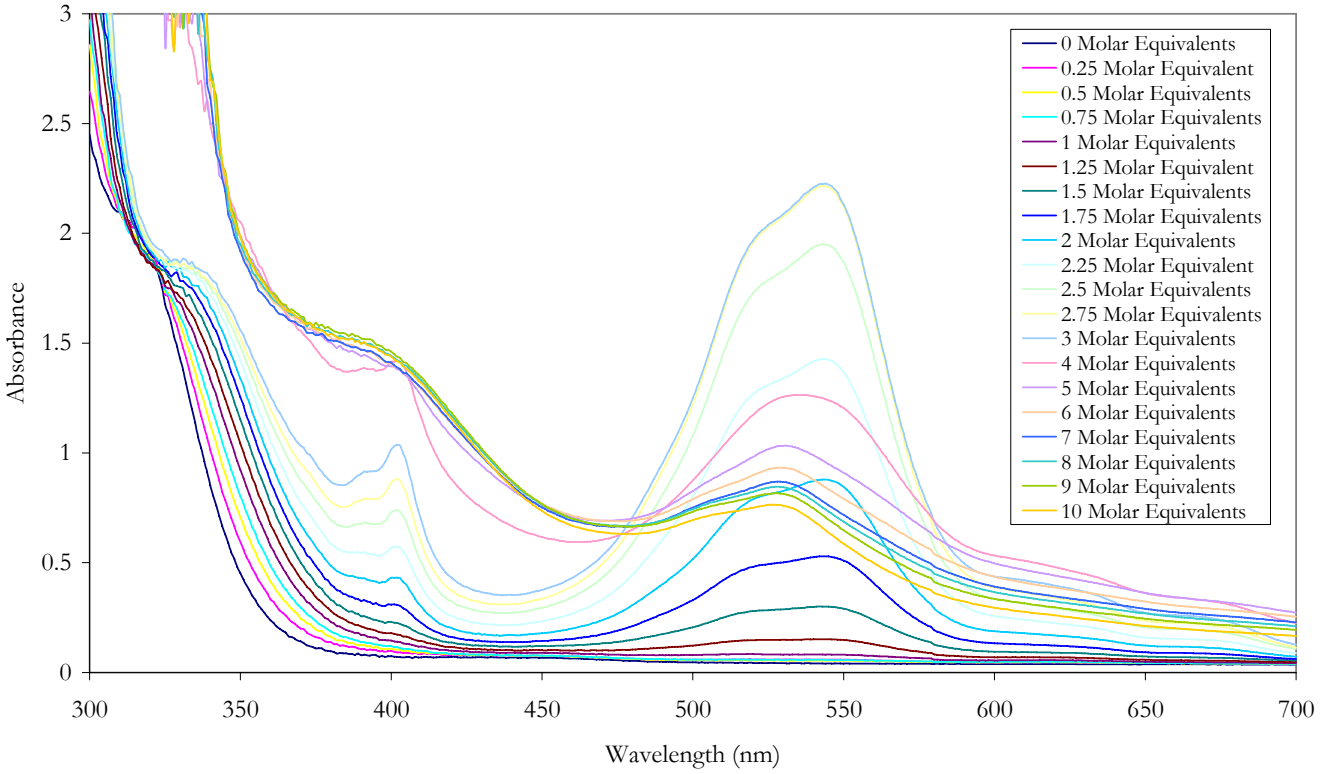
UV-Vis titration data for compound 2 with TBA acetate without removal of oxygen



Anaerobic UV-Vis titration data for compound 2 with TBA succinate



Anaerobic UV-Vis titration data for compound 3 with TBA succinate



Determination of binding constants by ^{1}H NMR spectroscopy.

^{1}H NMR titration experiments were carried out at room temperature using Varian Inova-500 spectrometer operating at 500 MHz (Durham University). All chemical shifts are reported in ppm relative to TMS as an internal reference. A solution of the host species of known concentration typically 0.5-1.5mM, was made up in an NMR tube using the appropriate deuterated solvent (0.5 ml). Solutions of the anions, as tba salts, were made up in volumetric flasks (2 ml) with a concentration five times greater than that of the host. The guest solution was typically added in 10 μl aliquots, representing 0.1 equivalents of the guest with respect to the host. Larger aliquots were used in some cases where no inflection of the trace was evident. Spectra were recorded after each addition and the trace was followed simultaneously. Results were analysed using the curve-fitting program HypNMR 2006.