Supplementary Material (ESI) for Chemical Communications

Fluoride ion complexation by a cationic borane in aqueous solution

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General Considerations. 1-Dimesitylboryl-4-diphenylphosphinobenzene (Yuan, Z.; Taylor, N. J.; Sun, Y.; Marder, T. B.; Williams, I. D.; Cheng, L.-T. *J. Organomet. Chem.* **1993,** *449*, 27-37.) and *B*-mesityl-*P*-phenylphosphaborin (Agou, T.; Kobayashi, J.; Kawashima, T. *Org. Lett.* **2005,** *7*, 4373-4376.) were synthesized by the published procedures. $[Me_3SiF_2][S(NMe_2)_3]$ (TASF), MeI, Mes_3B, and KF were purchased from Aldrich, n-$Bu_4NF{\cdot}3H_2O$ (TBAF) from Fluka and used as received. Solvents were dried by passing through an alumina column (*n*-hexane) or reflux under N_2 over Na/K (Et_2O and THF). Air-sensitive compounds were handled under a N_2 atmosphere using standard Schlenk and glovebox techniques. UV-vis and emission spectra were recorded on a HP8453 and an Aminco-Bowman 2 Luminescence spectrophotometer, respectively. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). NMR spectra were recorded on Varian Inova 300 FT NMR (121.43 MHz for ^{31}P), Varian Unity Inova 400 FT NMR (399.59 MHz for ^{1}H, 375.99 MHz for ^{19}F), and Varian Unity Inova 500 FT NMR (160.37 MHz for ^{11}B, 125.69 MHz for ^{13}C) spectrometers at ambient temperature unless otherwise stated. Chemical shifts δ are given in ppm, and are referenced against external Me_4Si (^{1}H, ^{13}C), $BF_3{\cdot}Et_2O$ (^{11}B), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P). Melting points were measured on samples in sealed capillaries and are uncorrected.

Crystallography. The crystallographic measurement of **1**-F was performed using a Siemens SMART-CCD area detector diffractometer, with a graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). A specimen of suitable size and quality were selected and mounted onto glass fiber with apiezon grease. The structure was 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 [1]I. MeI (0.15 mL) was added to a solution of 1-dimesitylboryl-4-diphenylphosphinobenzene (400 mg, 0.78 mmol) in Et_2O (20 mL) at room temperature. The mixture was stirred overnight and the solid formed was collected by filtration. After washing with Et_2O (10 mL), drying *in vacuo* afforded [**1**]I as a yellow solid (350 mg, 69% yield). mp. 196 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (s, 12H, Mes-CH_3), 2.26 (s, 6H, Mes-CH_3), 3.22 (d, 3H, $^{2}J_{P\text{-}H}$ = 13.2 Hz, P-CH_3), 6.78 (s, 4H, Mes-C*H*), 7.63-7.78 (m, 14H, P-Ar*H*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.68 (d, $^{1}J_{P\text{-}C}$ = 56.4 Hz, P-CH$_3$), 21.18, 23.51 (Mes-CH$_3$), 118.76 (d, $J_{P\text{-}C}$ = 88.6 Hz), 121.21 (d, $J_{P\text{-}C}$ = 87.0 Hz), 128.51 (Mes-*C*H), 130.45 (d, $J_{P\text{-}C}$ = 12.9 Hz), 132.42 (d, J = 10.7 Hz), 133.30 (d, J = 10.7 Hz), 135.17 (d, J = 3.1 Hz), 136.35 (d, J = 12.9 Hz), 139.88, 140.69 (Mes-*C*Me), 140.84, 153.54 (B-*C*). ^{11}B NMR (160 MHz, $CDCl_3$): δ +78.9. ^{31}P NMR (121 MHz, $CDCl_3$): δ +21.9. UV-vis ($CHCl_3$): λ_{max}/nm (log ε) 347 (3.96). Anal. Calcd for $C_{37}H_{39}BIP$: C, 68.12; H, 6.03. Found: C, 67.54; H, 6.13.

Synthesis of 1-F. [1]I (100 mg, 0.15 mmol) and TASF (42 mg, 0.15 mmol) were mixed in THF (20 mL) at room temperature. An immediate color change from yellow to colorless was observed. After stirring for 30 min, the mixture was filtered. The filtrate was exposed to a vacuum to afford a white solid. This solid was washed with Et_2O and dried under vacuum yielding of **1**-F (78 mg, 96% yield). Colorless single crystals of **1**-F-$CHCl_3$ could be obtained in a 50-60% yield (not optimized) by partial evaporation of a $CHCl_3$ solution of **1**-F. mp. 365 ºC (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (s, 12H, Mes-CH_3), 2.16 (s, 6H, Mes-CH_3), 2.47 (d, 3H, $^{2}J_{P\text{-}H}$ = 12.9 Hz, P-CH_3), 6.58 (s, 4H, Mes-C*H*), 6.94 (br s, 2H, P-Ph*H*-B), 7.44-7.51 (m, 4H, P-Ph*H*), 7.57-7.63 (m, 4H, P-Ph*H*), 7.72-7.77 (m, 2H, P-Ph*H*), 8.32 (br s, 2H, P-Ph*H*-B). ^{1}H

NMR (400 MHz, CD_3CN): δ 1.87 (s, 12H, Mes-C*H*$_3$), 2.13 (s, 6H, Mes-C*H*$_3$), 2.69 (d, 3H, $^2J_{P-H}$ = 13.5 Hz, P-C*H*$_3$), 6.51 (s, 4H, Mes-C*H*), 7.28 (br s, 2H, P-Ph*H*-B), 7.57-7.70 (m, 8H, P-Ph*H*), 7.79-7.83 (m, 2H, P-Ph*H*), 8.08 (br s, 2H, P-Ph*H*-B). ^{13}C NMR (125 MHz, CD_3CN, 333 K): δ 10.05 (d, $^1J_{P-C}$ = 59.5 Hz, P-*C*H$_3$), 21.08, 25.48, 25.51 (Mes-*C*H$_3$), 117.62 (br), 122.39 (d, J_{P-C} = 88.5 Hz), 129.41 (Mes-*C*H), 131.20 (d, J_{P-C} = 12.9 Hz), 133.13, 134.26 (d, *J* = 10.7 Hz), 135.78 (d, J_{P-C} = 2.5 Hz), 136.56 (br), 142.55 (Mes-*C*Me). B-*C* carbon peaks were not observed. ^{11}B NMR (160 MHz, CD_3CN, 333 K): δ +9.8. ^{19}F NMR (376 MHz, CD_3CN): δ -175.5. ^{31}P NMR (121 MHz, CD_3CN): δ +21.2. Anal. Calcd for $C_{38}H_{40}BCl_3FP$: C, 68.75; H, 6.07. Found: C, 68.56; H, 6.07.

Synthesis of [2]I. MeI (1.0 mL, 16 mmol) was added to a solution of *B*-mesityl-*P*-phenylphosphaborin (0.64 g, 1.6 mmol) in benzene (20 mL). The reaction mixture was stirred at 40 °C for 1 h. After cooling of the mixture to room temperature, the solvents were removed under the reduced pressure. The resulting solid was washed with Et_2O and dried at 80 °C *in vacuo* to afford [**2**]I as an orange solid (0.89 g, 100%). mp 173 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.18 (s, 6H), 2.39 (s, 3H), 3.23 (d, *J* = 13.6 Hz, 3H), 6.94 (s, 2H), 7.62-7.66 (m, 2H), 7.69-7.88 (m, 3H), 7.86-7.88 (m, 4H), 8.01 (dd, *J* = 13.6, 7.6 Hz, 2H), 8.33 (dd, *J* = 13.2, 7.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.88 (d, *J* = 55.0 Hz), 21.17 (s), 23.04 (s), 121.50 (d, *J* = 86.6 Hz), 125.69 (d, *J* = 86.9 Hz), 127.75 (s), 128.27 (s), 130.40 (d, *J* = 13.0 Hz), 132.91 (d, *J* = 11.2 Hz), 133.81 (d, *J* = 12.6 Hz), 134.54 (d, *J* = 2.6 Hz), 134.74 (d, *J* = 2.6 Hz), 135.05 (d, *J* = 13.2 Hz), 138.04 (d, *J* = 8.4 Hz), 140.84 (d, *J* = 11.3 Hz), 141.83 (brs) (One signal corresponding to the ipso-carbon atom of the mesityl group could not be observed due to signal broadening.). ^{31}P NMR (162 MHz, $CDCl_3$): δ +3.1. ^{11}B NMR (128 MHz, $CDCl_3$): δ +58.6. UV-vis ($CHCl_3$): λ_{max}/nm (log ε) 369 (3.35), 304 (4.06). Anal Calcd for $C_{28}H_{27}BIP{+}H_2O$: C, 61.12; H, 5.31. Found: C, 61.88; H, 5.44.

Formation of 2-F. The formation of **2**-F has been observed in situ by NMR spectroscopy of a $CDCl_3$ solution containing [**2**]I and TBAF. ^1H NMR spectra indicated the complete consumption of [**2**]I. The two isomers (A and B) of **2-**F were observed in ca. 3:1 ratio. ^1H NMR (400 MHz): δ 2.09 (A+B, s, 6H, Mes-C*H*$_3$), 2.28 (B) and 2.33(A) (s, 3H, Mes-C*H*$_3$), 2.44 (A, d, *J* = 14.0 Hz) and 2.55 (B, d, *J* = 12.8 Hz) (3H, P-C*H*$_3$), 6.74 (B) and 6.81 (A) (s, 2H, Mes-C*H*), 7.06-7.11, 7.15-7.17, 7.35-7.42, 7.49-7.58, 7.70-7.75, and 7.78-7.83 (A+B, m, 13H, Ar*H*). ^{31}P NMR (162 MHz): δ +3.3 (A), −3.1 (B) (intensity ratio: ca. 3:1). ^{11}B NMR (128 MHz): δ +3.6. ^{19}F NMR (376 MHz): δ −161.30.

UV-vis titration experiments

Titration of [**1**]$^+$ in $CHCl_3$

A solution of [**1**]I (3.0 mL, 5 × 10^{-5} M, $CHCl_3$) was titrated with incremental amounts of fluoride anions by addition of a solution of TBAF in $CHCl_3$ (3.5 × 10^{-3} M). The absorption was monitored at λ_{max} = 347 nm (ε = 9030). In fitting the experimental points, a correction was applied in order to account for the absorbance of **1**-F at 347 nm. The experimental data obtained was fitted by hand to a 1:1 binding isotherm to afford a fluoride binding constant of 6.5(±0.5) × 10^6 M^{-1} (See Table S1, Figures S1 and S2).

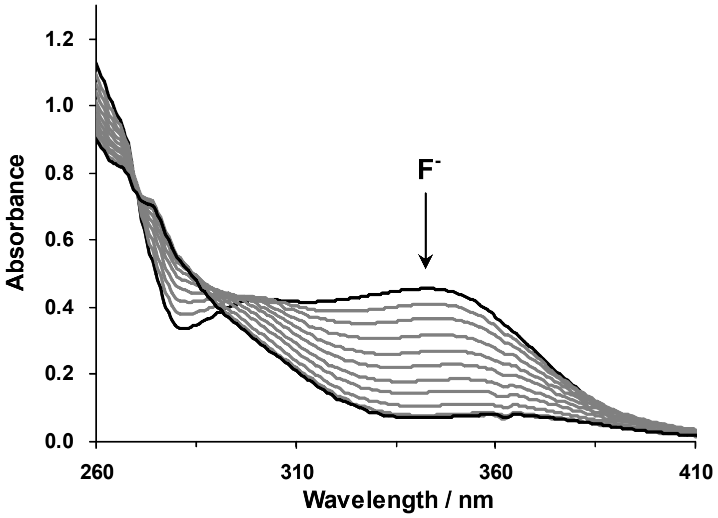

Figure S1. Spectral change accompanying the formation of **1**-F upon addition of *n*-Bu_4NF to a $CHCl_3$ solution of [**1**]I (5 × 10^{-5} M)

Table S1. Absorbance of a solution of [**1**]$^+$ after successive additions of fluoride in $CHCl_3$

$C_{Fluoride}$	Abs_{exp}	Abs_{calc}	$C_{Fluoride}$	Abs_{exp}	Abs_{calc}
0.00E+00	0.45132	4.51E-01	4.61E-05	0.10885	1.06E-01
5.82E-06	0.40785	4.06E-01	5.17E-05	0.08005	8.32E-02
1.16E-05	0.36664	3.62E-01	5.74E-05	0.068705	7.61E-02
1.74E-05	0.31744	3.17E-01	6.30E-05	0.072586	7.37E-02
2.32E-05	0.27013	2.73E-01	6.86E-05	0.072658	7.25E-02
2.89E-05	0.229	2.29E-01	7.42E-05	0.071343	7.18E-02
3.47E-05	0.18462	1.86E-01	7.98E-05	0.071993	7.12E-02
4.04E-05	0.14862	1.44E-01			

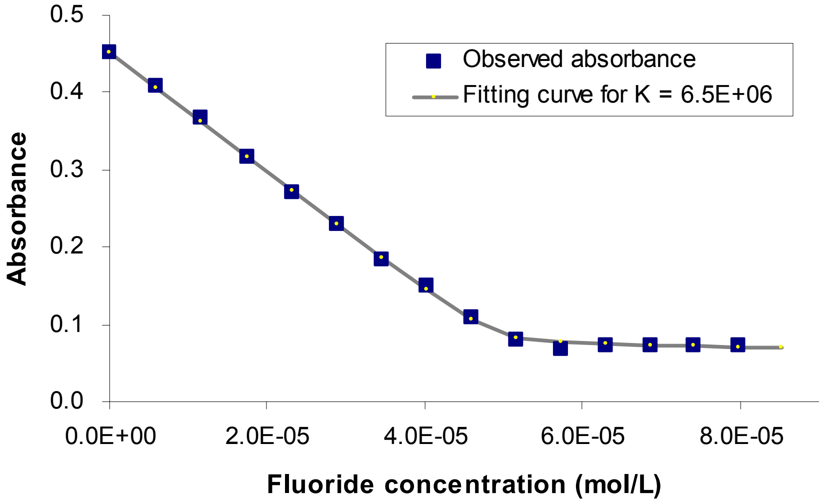

Figure S2. Absorbance change of a solution of **[1]**$^+$ after successive additions of fluoride in $CHCl_3$

Titration of **[1]**$^+$ in aqueous solution

A solution of [**1**]I (3.0 mL, 5×10^{-5} M, H_2O/MeOH 9/1 vol.) was titrated by incremental addition of a solution of KF in water (0.3 M). The absorption was monitored at $\lambda_{max} = 321$ nm ($\varepsilon = 7600$). The experimental data obtained was fitted by hand to a 1:1 binding isotherm to afford a fluoride binding constant of $9.6(\pm 1) \times 10^2$ M^{-1} which, after rounding, can be considered as equal to $1(\pm 0.1) \times 10^3$ M^{-1} (See Table S2, Figure 2 (left), and Figure S3).

Table S2. Absorbance of a solution of **[1]**$^+$ after successive additions of fluoride in H_2O/MeOH 9/1 vol.

$C_{Fluoride}$	Abs_{exp}	Abs_{calc}
0.00E+00	0.38022	3.80E-01
4.99E-04	0.27235	2.59E-01
9.97E-04	0.19248	1.96E-01
1.49E-03	0.15237	1.57E-01
1.99E-03	0.12838	1.31E-01
2.48E-03	0.10900	1.13E-01
2.97E-03	0.098060	9.86E-02
3.46E-03	0.092130	8.77E-02
3.95E-03	0.085299	7.90E-02

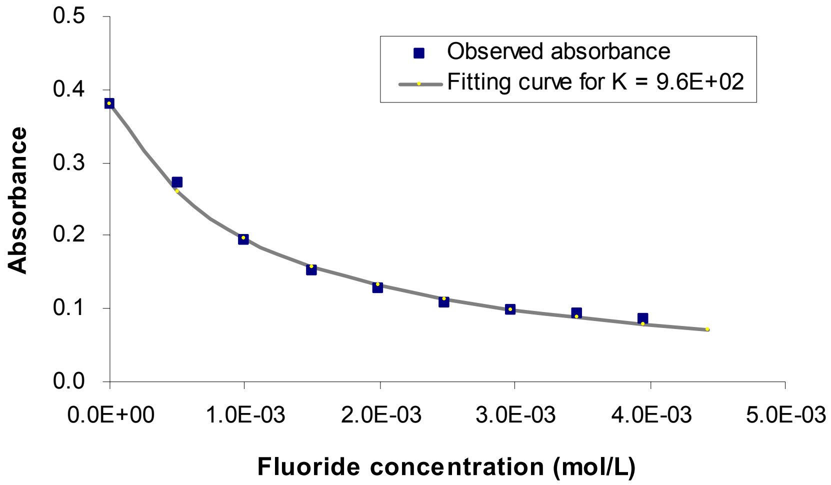

Figure S3. Absorbance change of a solution of **[1]**$^+$ after successive additions of fluoride in H_2O/MeOH 9/1 vol.

Titration of **I** with F^- in $CHCl_3$

A solution of **I** (3.0 mL, 5 × 10^{-5} M, $CHCl_3$) was titrated by incremental addition of a solution of TBAF in $CHCl_3$ (5.7 × 10^{-3} M). The absorption was monitored at λ_{max} = 361 nm (ε = 10600). The experimental data obtained was fitted by hand to a 1:1 binding isotherm to afford a fluoride binding constant of 2.1(±0.2) × 10^4 M^{-1} (See Table S3 and Figure S4).

Table S3. Absorbance of a solution of **I** after successive additions of fluoride in $CHCl_3$

$C_{Fluoride}$	Abs_{exp}	Abs_{calc}	$C_{Fluoride}$	Abs_{exp}	Abs_{calc}
0.00E+00	0.53113	5.31E-01	1.48E-04	0.15118	1.53E-01
9.45E-06	0.50202	4.81E-01	1.56E-04	0.14200	1.45E-01
1.89E-05	0.46678	4.37E-01	1.65E-04	0.13511	1.38E-01
2.83E-05	0.42924	3.97E-01	1.74E-04	0.12836	1.32E-01
3.76E-05	0.39010	3.61E-01	1.83E-04	0.12302	1.26E-01
4.69E-05	0.36071	3.30E-01	1.92E-04	0.11650	1.21E-01
5.62E-05	0.32755	3.02E-01	2.01E-04	0.11121	1.16E-01
6.55E-05	0.30056	2.78E-01	2.10E-04	0.10631	1.11E-01
7.47E-05	0.27309	2.57E-01	2.18E-04	0.10169	1.07E-01
8.39E-05	0.25288	2.38E-01	2.27E-04	0.097779	1.03E-01
9.31E-05	0.23146	2.21E-01	2.36E-04	0.093973	9.90E-02
1.02E-04	0.21589	2.07E-01	2.45E-04	0.090184	9.55E-02
1.11E-04	0.20050	1.93E-01	2.53E-04	0.087212	9.23E-02
1.20E-04	0.18716	1.82E-01	2.62E-04	0.083414	8.93E-02
1.30E-04	0.17386	1.71E-01	2.70E-04	0.080685	8.65E-02
1.39E-04	0.16135	1.62E-01			

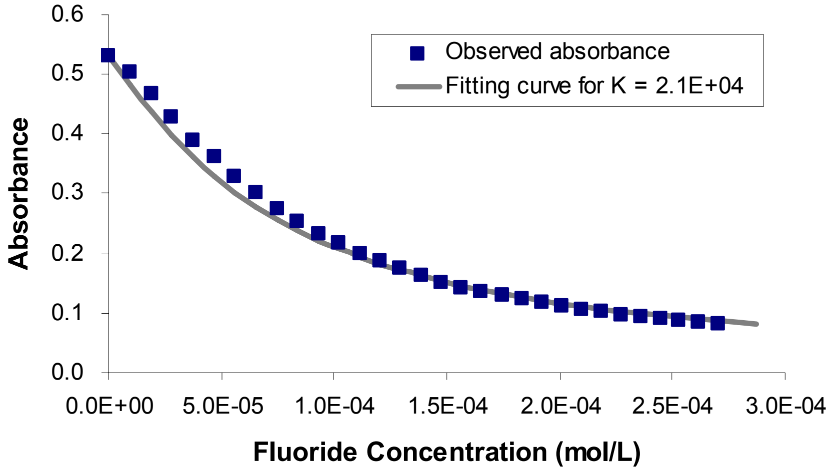

Figure S4. Absorbance change of a solution of **[1]**$^+$ after successive additions of fluoride in $CHCl_3$

Titration of Mes_3B with F^- in $CHCl_3$

A solution of Mes_3B (3.0 mL, 5 × 10^{-5} M, $CHCl_3$) was titrated by incremental addition of a solution of TBAF in $CHCl_3$ (5.8 × 10^{-3} M). No changes in the absorption spectra were observed indicating that fluoride binding does not occur (The small decrease in absorbance results from dilution effect) (See Table S4 and Figure S5). Similar conclusions were derived from the ^1H NMR spectrum of a 1:1 reaction of Mes_3B and TBAF in $CDCl_3$.

Table S4. Absorbance of a solution of Mes_3B after successive additions of fluoride in $CHCl_3$

$C_{Fluoride}$	Abs_{exp}	Abs_{calc}(dilutn)	$C_{Fluoride}$	Abs_{exp}	Abs_{calc}(dilutn)
0.00E+00	0.71237	7.12E-01	7.62E-05	0.70171	7.03E-01
9.63E-06	0.70950	7.11E-01	8.56E-05	0.70048	7.02E-01
1.92E-05	0.70865	7.10E-01	9.49E-05	0.69941	7.01E-01
2.88E-05	0.70684	7.09E-01	1.04E-04	0.69839	7.00E-01
3.83E-05	0.70596	7.08E-01	1.14E-04	0.69732	6.98E-01
4.79E-05	0.70387	7.06E-01	1.23E-04	0.69704	6.97E-01
5.73E-05	0.70386	7.05E-01	1.32E-04	0.69590	6.96E-01
6.68E-05	0.70320	7.04E-01			

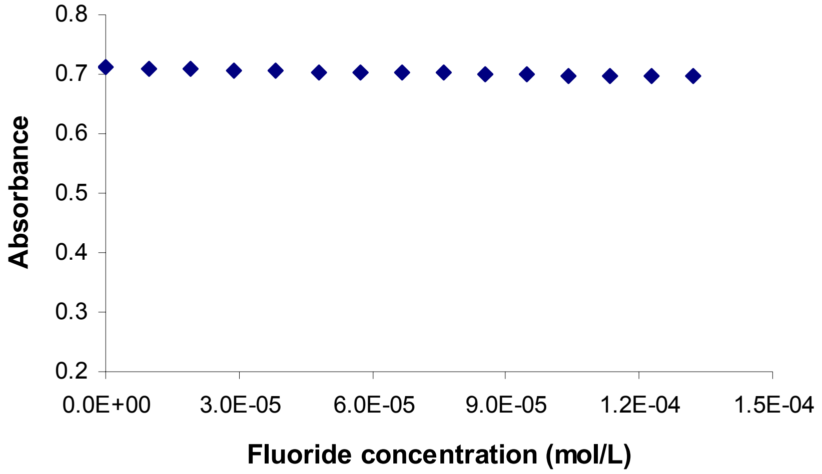

Figure S5. Absorbance change of a solution of Mes_3B after successive additions of fluoride in $CHCl_3$

Absorbance change of **[1]**$^+$ with other anions in aqueous solution

To a solution of [**1**]I (3.0 mL, 5 × 10^{-5} M, H_2O/MeOH 9/1 vol.) was added 40 µL of a 0.3 M solution of X^- (X = Cl, Br, NO_3 in water; I in MeOH; 80 equiv). The absorption was monitored at λ_{max} = 321 nm and the background absorption correction from a free anion was applied, especially to the iodide and nitrate. The absorbance changes are compared to that from fluoride and depicted in Figure S6. The results show no significant response of **[1]**$^+$ toward other anions.

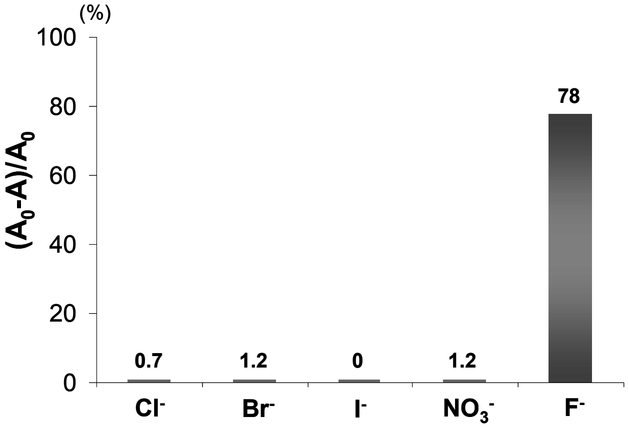

Figure S6. Comparison of absorbance change (%) of a solution of **[1]**$^+$ after addition of 80 equiv of anions in H_2O/MeOH 9/1 vol.

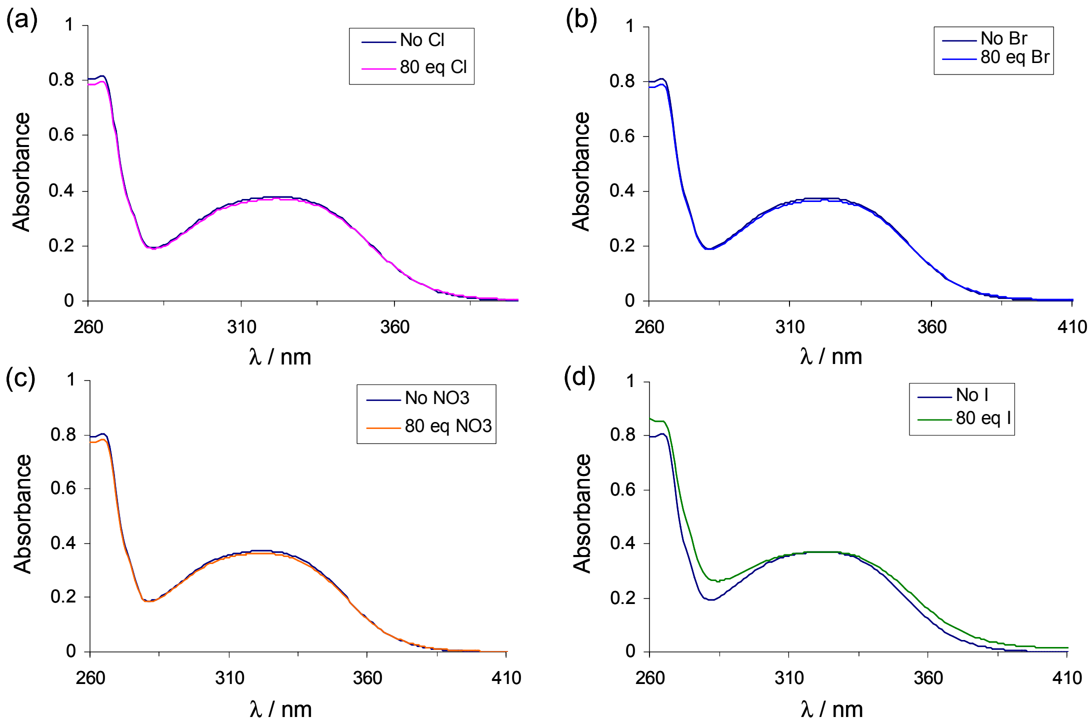

Figure S7. UV-vis spectral change of a solution of **[1]**$^+$ (5 × 10^{-5} M) after addition of 80 equiv of anions (a) Cl^- (b) Br^- (c) NO_3^- and (d) I^- in H_2O/MeOH 9/1 vol. (Note: Addition of an excess of [*n*Bu$_4$N]I does not initially affect the absorption spectrum of [**1**]$^+$ but leads, over time, to the formation of a precipitate presumed to be the salt [**1**]I).

Reversibility of fluoride binding by **[1]**$^+$ in aqueous solution

To a solution of [**1**]I (3.0 mL, 6 × 10^{-5} M, H_2O/MeOH 9/1 vol.) was added 5 µL of a 0.3 M solution of fluoride (KF solution in water) leading to partial formation of **1**-F as indicated partial quenching of the absorbance at 321 nm (Figure S8-A). Addition of aliquots of an $AlCl_3$ solution (0.1 M) to the solution containing **1**-F results in an increase of the absorbance at 321 nm (Figure S8-B). After addition of > 10.0 µL of the $AlCl_3$ solution, the absorbance was restored to its original value, indicating that the fluoride binding to **[1]**$^+$ is reversible.

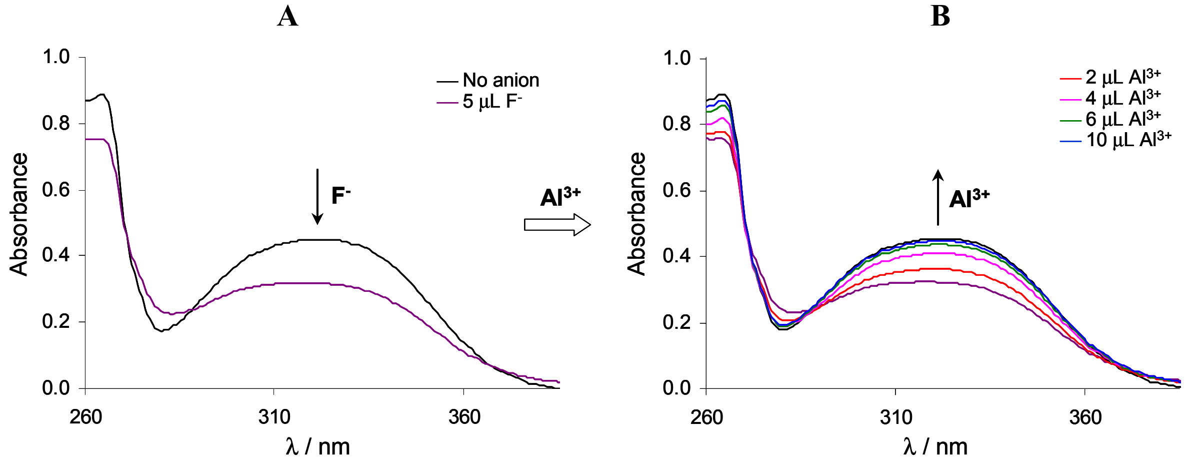

Figure S8. UV-vis spectral changes observed for a solution of **[1]**$^+$ (6 × 10^{-5} M) upon addition of fluoride (Figure S8-A) and aq $AlCl_3$ (Figure S8-B) in H_2O/MeOH 9/1 vol.