A Heteronuclear Bidentate Lewis Acid as a Phosphorescent Fluoride Sensor.

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Supplementary information

Experimental part

General Considerations.

Due to the toxicity of the mercury compounds discussed in these studies, great caution should be exercised when synthesizing and handling 2 and its anionic derivatives. Tetrakis(THF)lithium dimesityl-1,8-naphthalenediylborate (Hoefelmeyer, J. D.; Gabbaï, F. P. *Organometallics* **2002**, *21*, 982) and pentafluorophenylmercury chloride (Tschinkl, M. Schier, A. Riede, J. Gabbaï F. P. *Organometallics* **1999**, *18*, 2040) were synthesized by following published procedures. $Me_3SiF_2S(NMe_2)_3$ and trimethylchlorosilane were purchased from Aldrich and used as received. Solvents were dried by reflux under N_2 over the appropriate drying agents, and freshly distilled prior to use. Dichloromethane was dried over CaH_2. Diethylether and THF were dried over Na/K. Air-sensitive compounds were handled under N_2 atmosphere using standard Schlenk and glovebox techniques. UV-vis spectra were recorded on a JASCO V-530 spectrophotometer. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). The luminescence spectra were recorded with a SLM/AMINCO, Model 8100 spectrofluorometer equipped with a xenon lamp. All melting points were measured on samples in sealed capillaries and are uncorrected**.**

NMR spectroscopy

NMR spectra were recorded on a Varian Unity Inova 400 FT NMR spectrometer (399.63 MHz for ^{1}H, 376.03 MHz for ^{19}F, 128.22 MHz for ^{11}B, 100.50 MHz for ^{13}C, 75.52 for ^{199}Hg) by using internal deuterium lock. Chemical shifts δ are given in ppm, and are

referenced against external Me_4Si (^1H, ^{13}C), $BF_3.Et_2O$ (^{11}B), $CFCl_3$ (^{19}F), and $HgMe_2$ (^{199}Hg).

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. Further crystallographic details can be found in table 1.

Synthesis and characterization

1-(dimesitylboron)-8-(pentafluorophenylmercury)naphthalenediyl (2). A solution of pentafluoromecury chloride (360 mg, 0.89 mmol) in THF (3 mL) was added to a solution of tetrakis(THF)lithium dimesityl-1,8-naphthalenediylborate (600 mg, 0.89 mmol) in THF (10 mL) at 0ºC. The mixture was stirred overnight at room temperature. The solvent were removed under reduced pressure and the product was extracted with hexane (3 x 10 mL). Following filtration and evaporation of the solvent, the yellow solid was washed with acetonitrile (4 x 5 mL) and dried under vacuum to yield a pale yellow powder (480 mg : 72%). mp. 235ºC. ^1H NMR ($CDCl_3$): 1.44 (br s, 3H, Mes-CH_3), 1.67 (br s, 3H, Mes-CH_3), 1.89 (br s, 3H, Mes-CH_3), 2.14-2.42 (m, 9H, Mes-CH_3), 6.37 (br s, 1H, Mes-C*H*), 6.83 (br s, 3H, Mes-C*H*), 7.37-7.44 (m, 2H, C*H*), 7.48-7.60 (m, 2H, C*H*), 7.86 (dd, 1H,

$^{3}J_{H\text{-}H}$ = 8.0 Hz, $^{4}J_{H\text{-}H}$ = 1.1 Hz, C*H*), 7.98 (dd, 1H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, $^{4}J_{H\text{-}H}$ = 1.2 Hz, C*H*). ^{13}C NMR ($CDCl_3$): 21.34, 22.54, 23.83, 25.23 (*C*H_3-Mes), 125.53, 125.75, 130.48 133.74, 135.18, 137.29 (*C*H-Np), 127.63 (br s), 128.64 (br s), 130.36 (br s), 130.72 (br s) (*C*H-Mes), 134.76, 142.42, 151.50, (*C*F). 136.89 (br s), 138.65 (br s), 138.89 (br s), 139.34 (br s), 139.81 (br s), 143.50 (br s), 143.88 (br s), 146.22, 146.43, 146.96, 148.51, 148.70, 163.54 (quaternary C, *C*B and *C*Hg). ^{19}F NMR ($CDCl_3$): -116.8 (m, 2F, $^{3}J_{F\text{-}Hg}$ = 499 Hz, F_{ortho}), -152.5 (t, 1F, $^{3}J_{F\text{-}F}$ = 19.7 Hz, F_{para}), -159.09 (m, 2F, F_{meta}). ^{199}Hg NMR ($CDCl_3$): -741.9 (tt, $^{3}J_{Hg\text{-}F}$ = 499 Hz, $^{4}J_{Hg\text{-}F}$ = 165 Hz). ^{11}B NMR ($CDCl_3$): +72. Anal. Calcd for $C_{34}H_{28}BF_5Hg$: C, 54.96; H, 3.80. Found: C 54.92; H 3.75.

[2•μ_2-F]$^-$[S(NMe$_2$)$_3$]$^+$: To a solution of **2** (100 mg, 0.13 mmol) in $CHCl_3$ (2 mL) was added one equivalent of TASF (37 mg, 0.13 mmol) at room temperature. The mixture is stirred at room temperature for 10 minutes and stored at -18°C overnight to induce the crystallization of [**2**•μ_2-F]$^-$[S(NMe$_2$)$_3$]$^+$. After filtration and washing with hexane (2 mL) and ether (2 mL), the product was obtained as colorless crystals (m= 110 mg, 89 %). mp. 215 ºC (dec). ^{1}H NMR (CD_3CN): 1.67 (br s, 6H, Mes-CH_3), 1.83 (br s, 3H, Mes-CH_3), 2.00 (br s, 3H, Mes-CH_3), 2.16 (m, 6H, Mes-CH_3), 2.84 (s, 18H, N-CH_3), 6.32-6.64 (br s, 4H, Mes-C*H*), 7.08 (t, 1H, $^{3}J_{H\text{-}H}$ = 7.5 Hz), 7.19 (dd, 1H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}H}$ = 1.4 Hz), 7.30 (d, 2H, $^{3}J_{H\text{-}H}$ = 5.1 Hz), 7.54 (dd, 1H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}H}$ = 1.4 Hz), 7.69 (t, 1H, $^{3}J_{H\text{-}H}$ = 5.1 Hz).^{13}C NMR (CD_3CN): 20.04 (Br s), 23.65 (Br s), 24.44 (Br s) (*C*H_3-Mes), 37.99 (N-*C*H_3), 123.10, 124.78, 126.35, 129.40, 132.81, 135.88 (*C*H-Np), 127.91 (Br s), 128.33 (Br s), 128.92 (Br s) (*C*H-Mes), 131.90 (br s), 134.29 (br s), 135.53, 136.46, 138.24, 138.68, 138.94, 140.59 (br s), 142.50 (br s), 145.54, 145.92, 146.32, 148.51,

149.11, 150.12 (br s), 156.26 (br s), 161.18 (br s), 165.87 (*C*F, quaternary C, *C*B and *C*Hg). ^{19}F NMR (CD_3CN): -117.1 (m, 2F, $^{2}J_{F\text{-}Hg}$ = 384.8 Hz, F_{ortho}), -159.0 (t, 1F, $^{3}J_{F\text{-}F}$ = 19.2 Hz, F_{para}), -163.5 (m, 2F, F_{meta}), -164.3 (m, 1F, μ^2-F). ^{199}Hg NMR (CD_3CN): -811.8 (dtt, $^{1}J_{Hg\text{-}F}$ = 135.2 Hz, $^{3}J_{Hg\text{-}F}$ = 387.1 Hz, $^{4}J_{Hg\text{-}F}$ = 65.8 Hz). ^{11}B NMR (CD_3CN): +8.5 Anal. Calcd for $C_{40}H_{46}BF_6HgN_3S$: C, 51.87; H, 5.01. Found: C 51.48; H 4.91. MS (ESI) *m*/*z*= 763.135 [**2**-F]$^-$. CV (DMSO): reversible wave at 1.965 eV relatice to Fc/Fc^+.

UV-Vis spectrum of 2 and [2-μ^2-F]$^-$[nBu$_4$N]$^+$ - Titration of 2 with F$^-$

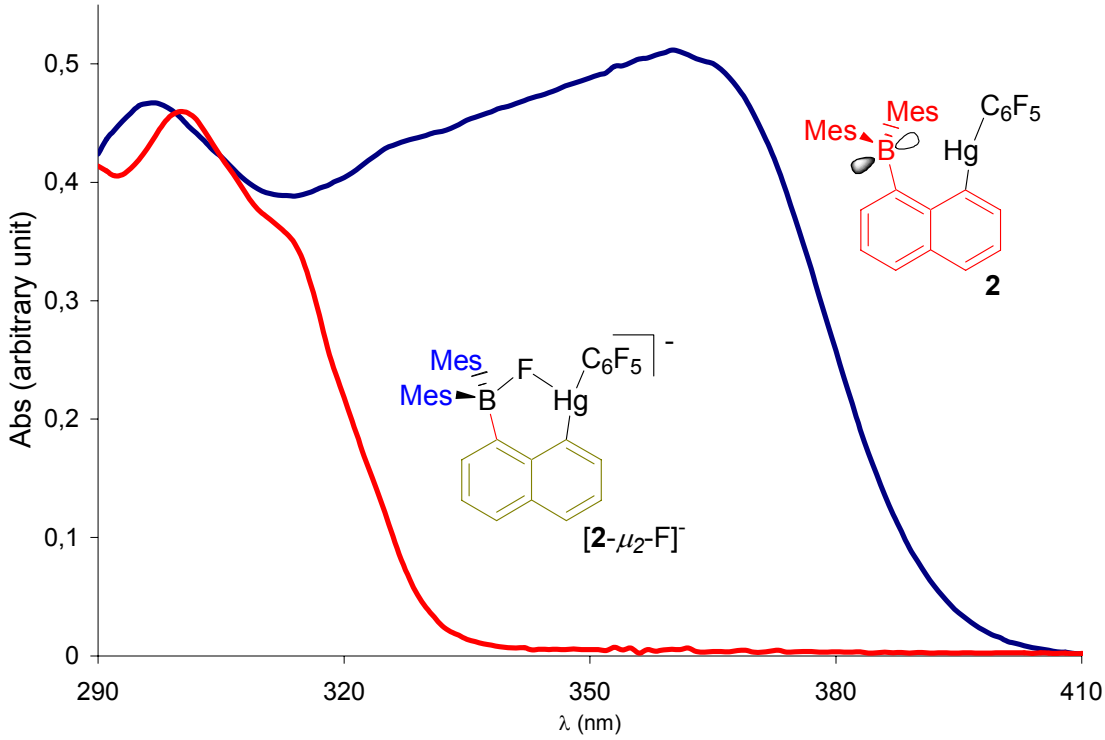

Figure SI- 1: UV-Visible spectrum of **2** and [**2**-μ^2-F]$^-$.[nBu$_4$N]$^+$.

<u>Derivation of the fluoride titration isotherm</u>

In the following equations pFBHg = **2** and pFBHgF = [**2**•μ^2-F]$^-$..

$$\begin{array}{ccccc} \text{pFBHg} & + & \text{F}^- & \xrightarrow{K_{pFBHg}} & [\text{pFBHgF}]^- \\ C_{pFBHg\,0} - x & & F_0 - x & & x \end{array}$$

Equation SI- 1: Chemical distribution after addition of fluoride to a solution of **2.**

$$K_{pFBHg} = \frac{[pFBHg]}{[pFBHgF]*[F^-]} = \frac{x}{(C_{pFBHg0} - x)*(F_0^- - x)}$$

$$\Rightarrow x^2 - x\left(C_{pFBHg0} + F_0^- + \frac{1}{K_{pFBHg}}\right) + C_{pFBHg0} * F_0^- = 0$$

$$\Rightarrow x = \frac{A - \sqrt{A^2 - 4 * C_{pFBHg0} * F_0^-}}{2} \qquad \text{with } A = C_{pFBHg0} + F_0^- + \frac{1}{K_{pFBHg}}$$

Equation SI- 2: Relationship between the observed absorption with respect to the amount of fluoride added and to the binding constant K_{pFBHg}.

Titration in THF

A solution of **2** (3 mL, 5 10^{-5} M, THF) was placed in the cell and was titrated with incremental amounts of fluoride by addition of a solution of nBu_4NF in THF (5.82 10^{-3} M). The absorption was monitored at λ_{max} = 361 nm (ε = 10200).

$C_{Fluoride}$	$Abs_{(361\ nm)}$	$C_{Fluoride}$	$Abs_{(361\ nm)}$
0.00E+00	0.51022	3.61E-05	0.13821
2.42E-06	0.48784	3.85E-05	0.11064
4.84E-06	0.45853	4.09E-05	0.08489
7.26E-06	0.43579	4.33E-05	0.05932
9.68E-06	0.41097	4.57E-05	0.03284
1.21E-05	0.38955	4.81E-05	0.01376
1.45E-05	0.36446	5.04E-05	0.00443
1.69E-05	0.34091	5.28E-05	0.00377
1.93E-05	0.31701	5.52E-05	0.00579
2.17E-05	0.29065	5.76E-05	0.0055
2.41E-05	0.26501	6.00E-05	0.00513
2.65E-05	0.23971	6.23E-05	0.00585
2.89E-05	0.2119	6.47E-05	0.00732
3.13E-05	0.18763	6.71E-05	0.00599
3.37E-05	0.16385		

Table SI- 1: Absorbance of a solution of **2** (THF) after successive additions of fluoride.

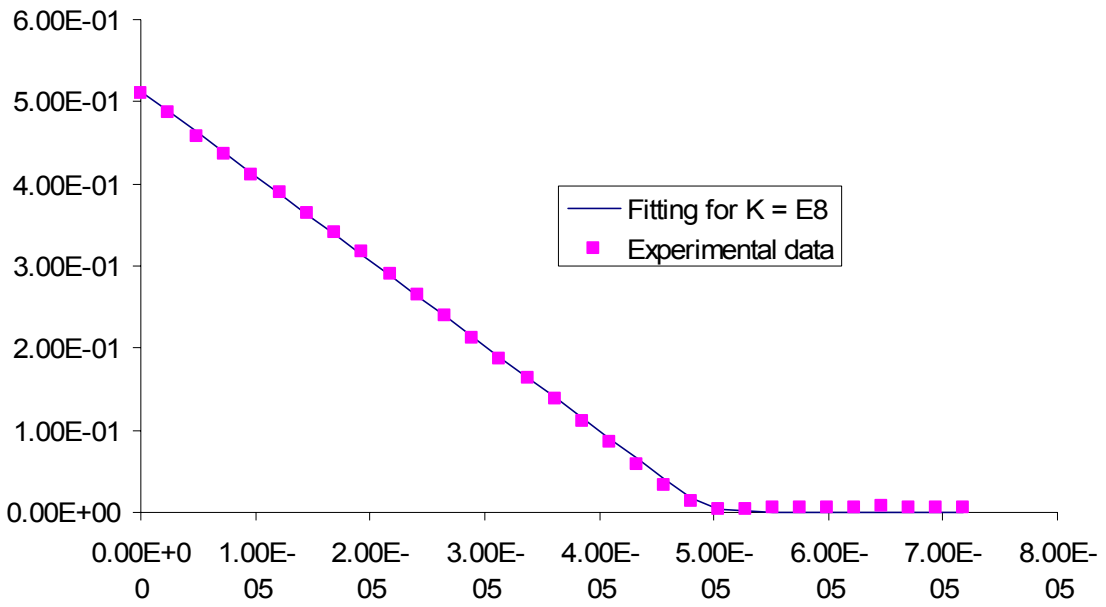

Figure SI- 2: Absorbance of a solution of **2** (THF) vs. fluoride concentration (M)

The experimental data obtained indicated that the binding constant is higher than 10^8 M^{-1} in THF.

Determination of the fluoride binding constant of trimesitylborane in THF-H_2O (90/10)

$$\underset{C_0 - x}{Mes_3B} + \underset{C_0 - x}{F^-} \xrightarrow{K_{Mes_3B}} \underset{x}{[Mes_3BF]^-}$$

with $C_0 = C_{Mes_3B0} = F_0^- = 0.163$ M.

$$K_{Mes_3B} = \frac{[Mes_3BF]^-}{[Mes_3B]*[F^-]} = \frac{x}{(C_0 - x)^2}$$

Equation SI- 3: Chemical distribution after addition of fluoride to a solution of Mes_3B and TBAF**.**

60 mg of trimesitylborane (1.63 mmol) and 51 mg of TBAF-3H_2O (1.63 mmol, 1 eq) were dissolved in 1 mL of a THF-H_2O (90/10) solution. The ^{19}F NMR (400 MHz) was recorded, showing two signals at -119.3 ppm and -151.7 ppm for free fluoride anion and trimesitylborane fluoride adduct respectively.

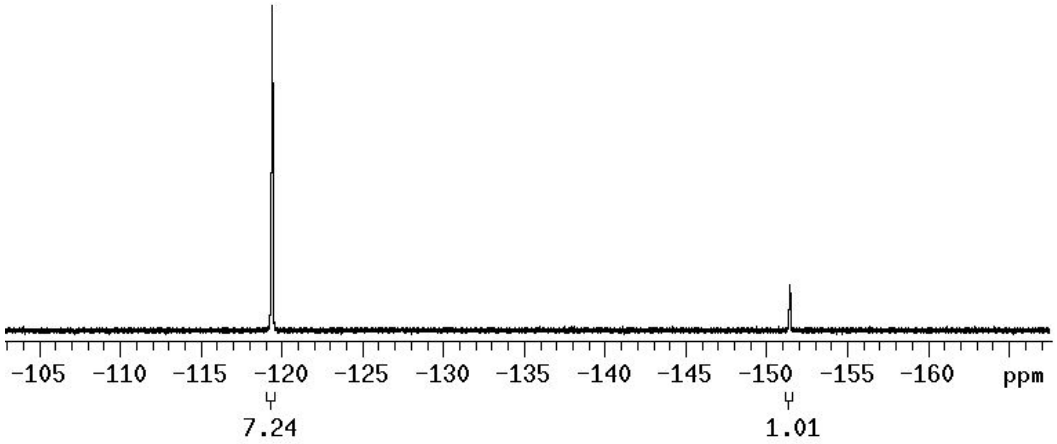

Figure SI- 3: ^{19}F NMR of a 0.163 M solution of $BMes_3$ and TBAF in THF-H_2O (90/10).

The relative integration gives x = 1.99 10^{-2} M, and C_0-x = 0.143 M. Therefore the binding constant of trimesitylborane is K_{Mes3B}= 1 (±0.3) M^{-1}.

Titration in a THF-H_2O (90/10)

A solution of **2** (3 mL, 4.5 10^{-5} M, THF-H_2O 90/10 (vol.)) was placed in the cell and was titrated with incremental amounts of fluoride by addition of a solution of nBu_4NF in THF (5.7 10^{-3} M). The absorption was monitored at λ_{max} = 361 nm (ε = 9850).

$C_{Fluoride}$	$Abs_{(361\ nm)}$	$C_{Fluoride}$	$Abs_{(361\ nm)}$
0.00E+00	0.45047	5.18E-05	0.24579
4.75E-06	0.43114	5.64E-05	0.21995
9.48E-06	0.40972	7.50E-05	0.1829
1.42E-05	0.38949	9.34E-05	0.15881
1.89E-05	0.3701	1.12E-04	0.13525
2.37E-05	0.34852	1.30E-04	0.11735
2.84E-05	0.31669	1.48E-04	0.10578
3.31E-05	0.30459	1.66E-04	0.09523
3.77E-05	0.28971	1.84E-04	0.08509
4.24E-05	0.26564	2.02E-04	0.07974
4.71E-05	0.25625		

Table SI- 2: Absorbance of a solution of **2** (THF-H_2O: 90/10) after successive addition of fluoride.

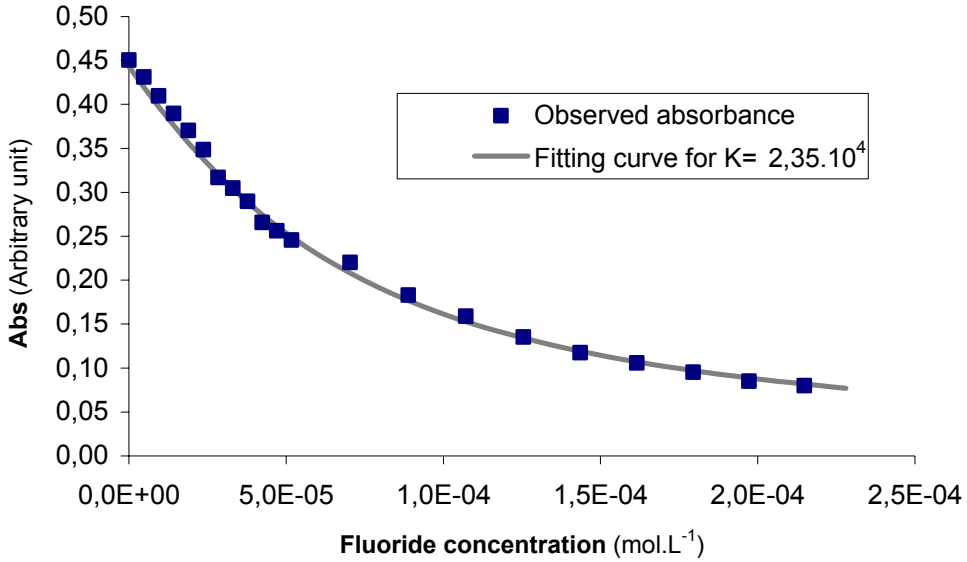

Figure SI- 4: Absorbance of a solution of **2** (THF-H_2O: 90/10) vs. fluoride concentration.

The experimental data was fitted by hand to the above equation (C_{pFBHg0} = 4.5 10^{-5} M). This fit yielded K_{pFBHg} = 2.35 (±0.2) 10^4 M^{-1}.

Binding selectivity studies

Fluoride binding by **2** also occurs in the presence of other anions. This has been confirmed by monitoring the absorption, ^{1}H NMR, or ^{19}F NMR spectra of **2** upon successive additions of different anions. For example, the successive addition of chloride, bromide, and iodide to a solution of **2** in THF does not lead to any noticeable changes of the spectroscopic features of **2**. Addition of fluoride to the same solution results in the formation of [**2**-F]$^-$. Similar experiments have been carried out with the other anions.

Solid state luminescence spectrum of 2 and $[2\text{-}\mu^2\text{-F}]^-.[S(NMe_2)_3]^+$

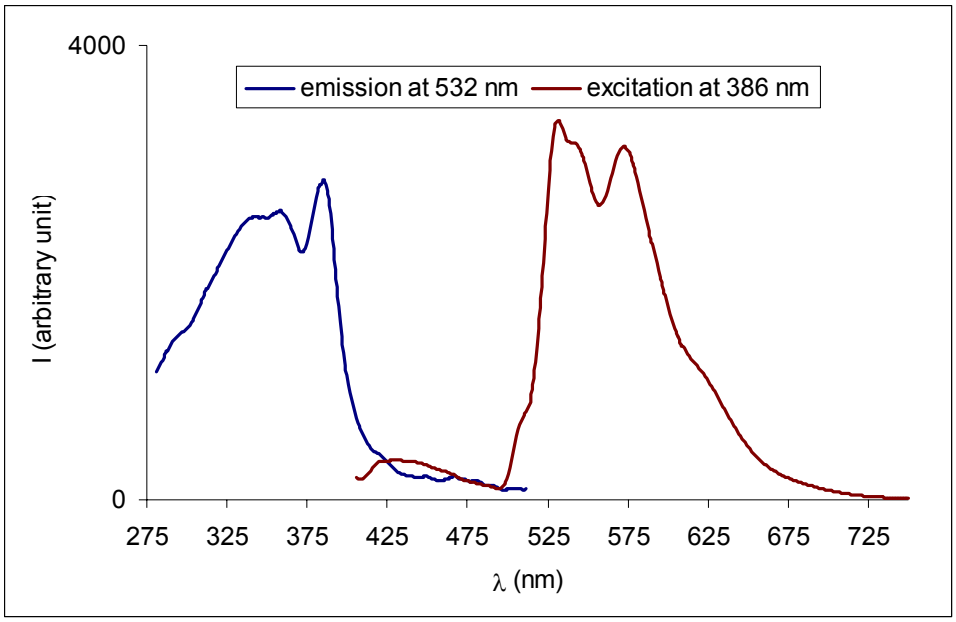

Figure SI- 5: Emission and excitation spectrum of **2** at 77 K.

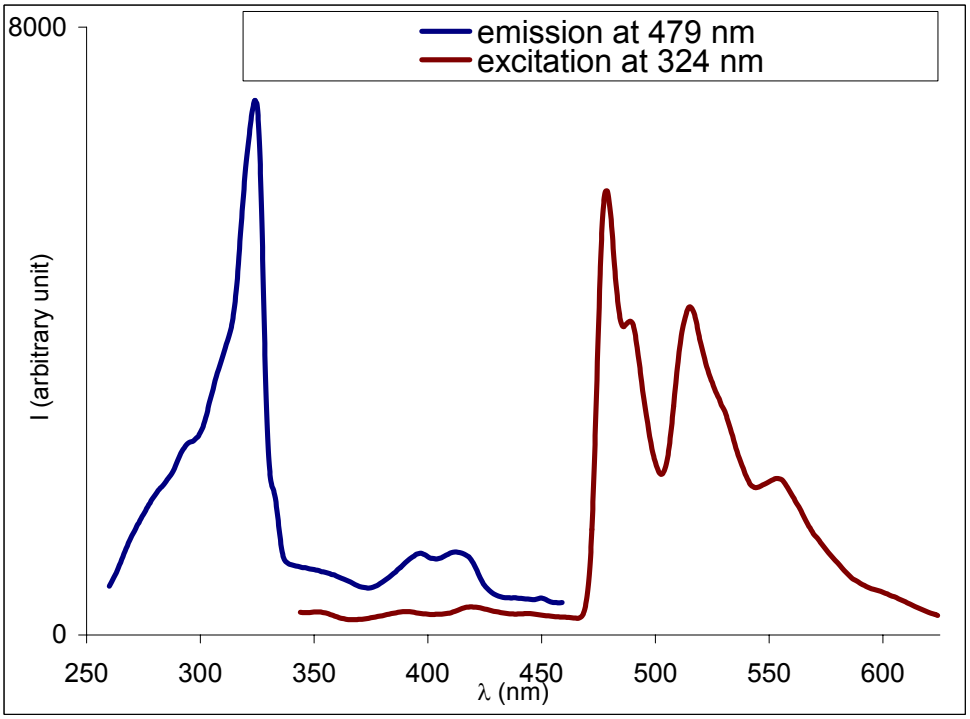

Figure SI- 6: Emission and excitation spectrum of $[\mathbf{2}\text{-}\mu^2\text{-F}]^-.[S(NMe_2)_3]^+$ at 77 K.