Supplemental Information

The titration curves of **3** with potassium fluoride (Figure) was analysed using a 1:1 binding model in OPIUM[1] with two variable parameters: the fluorescence enhancement of the fluoride complex relative to free **3**, and the stepwise binding constant. This gave a model for the binding of KF by **1** and **2** that involved only two complexes: the 1:1 cation (M) and sensor (S) complex (MS) and the ternary complex (MSF) with the cation and fluoride (F). This model defined two cumulative formation constants:

$$M + S \rightleftharpoons MS \qquad \beta(110) = \frac{[MS]}{[M][S]}$$

$$M + S + F \rightleftharpoons MSF \qquad \beta(111) = \frac{[MSF]}{[M][S][F]}$$

The model assumed that all fluorescence arose from three species; S, MS and MSF. The initial observed intensity and the analytical concentration of the sensor S defined an 'emissive constant' a(S). The magnitude of the 'emissive constant' for MS (a(MS)) was determined from the limiting value of the fluorescence enhancement factor (EF) observed on addition of MCl and MBr to the sensor S under conditions where MSF cannot be formed. Thus, a(MS) = a(S) × EF. The unknown constant a(KSF) was refined during the fitting process, together with the two cumulative constants defined above.

Two independent curve fitting procedures were performed. A single wavelength analysis was performed using the DOS version of the program OPIUM[1] based on a linear response function for the total fluorescence intensity (OPIUM type 7 calibration function). The input data file was structured according to the sample file INPANS. Alternative models with additional complexes, such as SF complexes did not give refined values. Refining a(MS) and/or a(S) recovered values similar to the fixed input values and moreover did not alter the values of formation constants, but increased their uncertainties considerably.

The second fitting used the program HYPERQUAD[2] to analyse a dataset consisting of emission intensities at eleven wavelengths between 367 and 417 nm for the twenty one different KF concentrations. This model made no assumptions about "emissive coefficients". The values of the two cumulative formation constants and their uncertainties were identical with th single wavelength fitting procedure.

Values are reported as $\pm 3\sigma$ to give the 95% confidence limit as calculated by the program. The model fits exceeded $r^2 = 0.997$ in all cases. The output file was imported to Excel for subsequent plotting. The graphs obtained for the potassium fluoride titrations are illustrated in the figures below for single wavelength fits at 397nm.

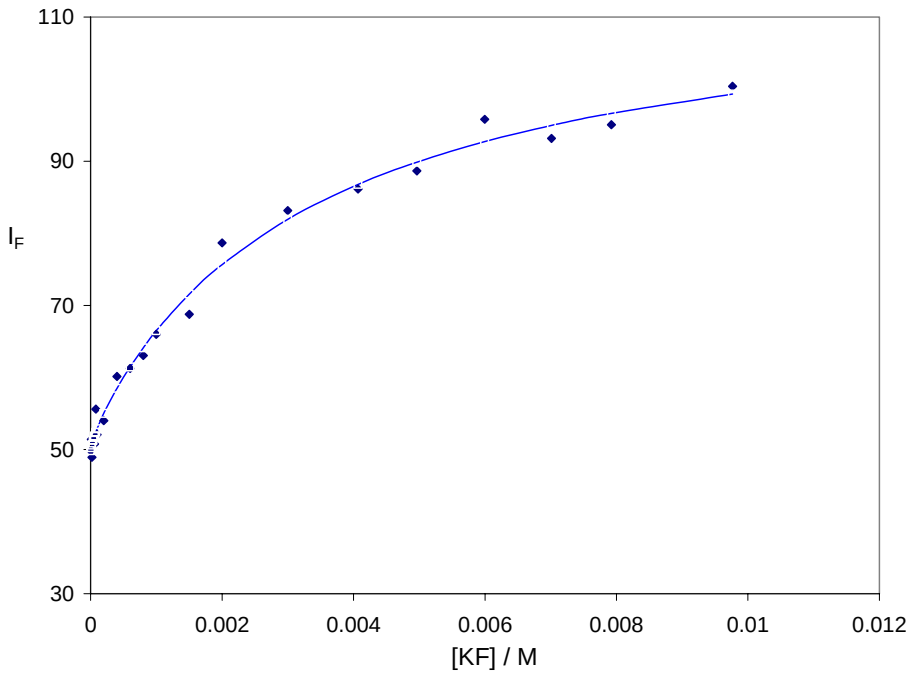

Figure 1. Fluorescence Intensity (I_F) of sensor **1** (5×10^{-7} M) *versus* KF (♦) at 25 °C in methanol; λ_{ex} = 345 nm, λ_{em} = 397 nm.

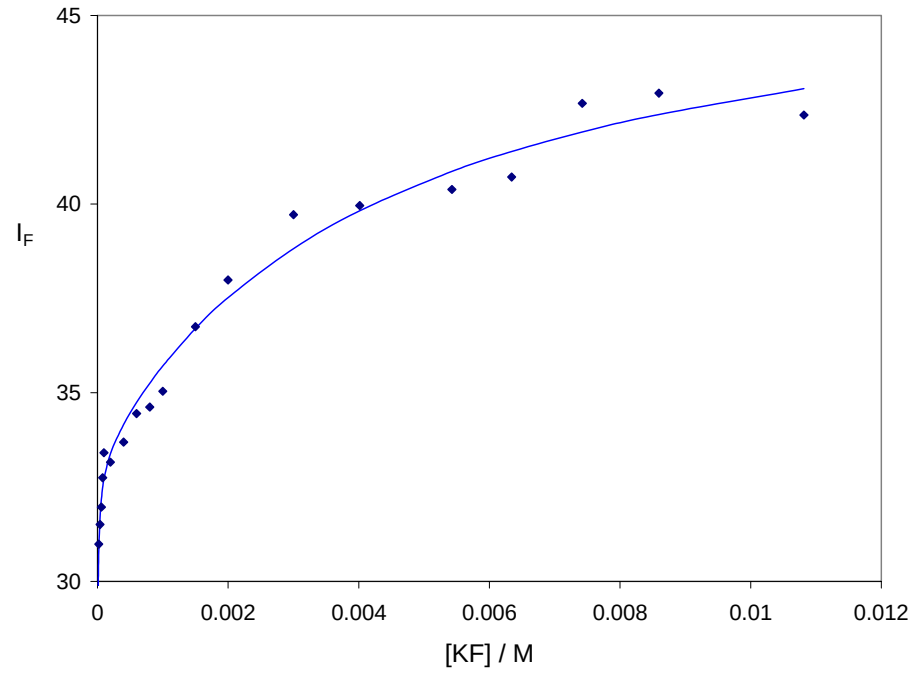

Figure 2. Fluorescence Intensity (I_F) of sensor **2** (5×10^{-7} M) *versus* KF (♦) at 25 °C in methanol; λ_{ex} = 347 nm, λ_{em} = 397 nm.

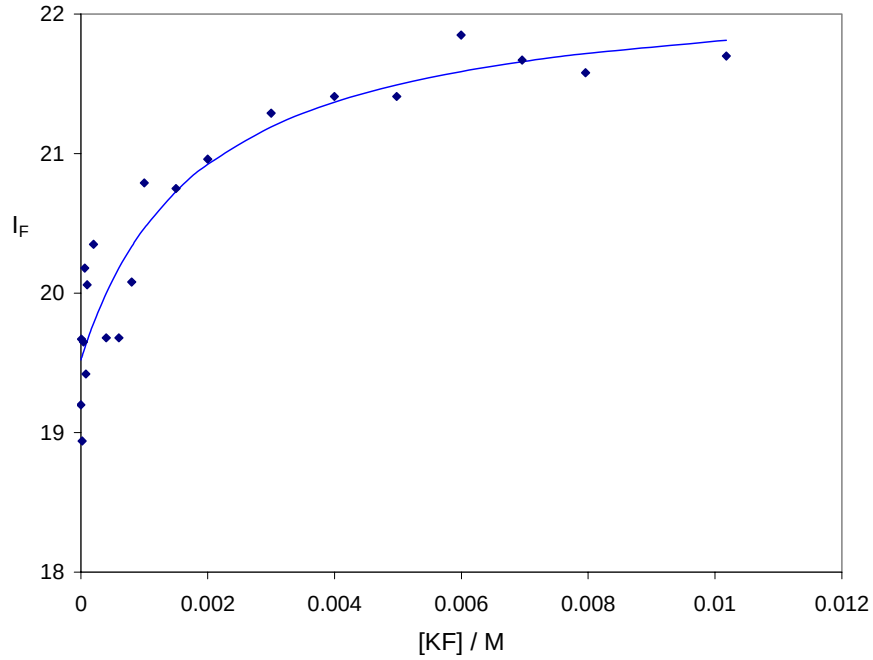

Figure 3. Fluorescence Intensity (I_F) of model compound **3** (5×10^{-7} M) *versus* KF (♦) at 25 °C in methanol; λ_{ex} = 343 nm, λ_{em} = 397 nm.

Selected data for **2**: mp 133 °C (dec.); $\nu_{max}(CHCl_3)/cm^{-1}$ 1370s (B–O), 1130s (B–C); δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.54 (2H, s, NCH_2-$C_6H_4B(OH)_2$), 3.68-3.75 (16H, m, 8×CH_2), 3.86-3.89 (4H, m, 2×CH_2), 3.99-4.07 (2H, m, NCH_2-Benzocrown), 4.23 (2H, s, Pyrene-CH_2N), 6.69-6.71 (3H, m, 3×BenzocrownC*H*), 7.30-7.42 (4H, m, 4×$C_6H_4B(OH)_2$), 7.91-8.17 (9H, m, 9×PyreneC*H*); δ_C(75 MHz; $CHCl_3$; Me_4Si) 55.7 (NCH_2-$C_6H_4B(OH)_2$), 58.5 (Pyrene-CH_2N), 62.5 (NCH_2-Benzocrown), 69.0, 69.3, 69.8, 70.0, 71.0, 70.1, 71.2 (CH_2), 113.7, 123.6, 125.0, 125.1, 125.3, 125.5, 125.6, 126.3, 127.8, 127.9, 128.1, 129.4, 130.4, 130.7, 131.1, 131.4, 131.6, 131.9, 137.0 (Ar); *m/z* (ES^+) 690 (100%, $[M+H]^+$); (HRMS: Found 690.3235, $[M+H]^+$. $C_{41}H_{45}BNO_8$ requires 690.3238).

Selected data for **3**: mp 142 °C (dec.); $\nu_{max}(CHCl_3)/cm^{-1}$ 1373s (B–O), 1028s (B–C); δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.47 (2H, s, NC*H*$_2$-$C_6H_4B(OH)_2$), 3.65 (2H, s, NC*H*$_2$-$C_6H_3(OMe)_2$), 3.69-3.75 (6H, m, 2×OC*H*$_3$), 4.11 (2H, s, Pyrene-C*H*$_2$N), 6.64-6.76 (3H, m, 3×$C_6H_3(OMe)_2$), 7.14-7.34 (4H, m, 4×$C_6H_4(OH)_2$), 7.68-8.07 (9H, m, 9×PyreneC*H*); δ_C(75 MHz; $CDCl_3$) 53.6 (N*C*H$_2$-$C_6H_4B(OH)_2$), 54.08 (O*C*H$_3$), 54.14 (O*C*H$_3$), 56.6 (N*C*H$_2$-$C_6H_4B(OH)_2$), 60.5 (Pyrene-*C*H$_2$N), 109.0, 111.0, 120.6, 121.4, 122.9, 123.0, 123.45, 123.53, 124.2, 125.7, 125.78, 125.83, 126.06, 126.09, 127.1, 127.4, 128.4, 128.7, 129.0, 129.4, 129.5, 129.7, 135.1, 140.0, 146.8, 147.3 (Ar); m/z (ES^+) 516 (100%, $[M+H]^+$); (HRMS: Found 516.2340, $[M+H]^+$. $C_{33}H_{31}BNO_4$ requires 516.2346).

1 Opium, 2000, http://www.natur.cuni.cz/~kyvala/opium.html
2 P. Gans, A. Sabatini, and A. Vacca, *Talanta*, 1996, **43**, 1739.