Electronic Supplementary Information

Synthesis and Structural Characterisation of the First Bis(bora)calixarene: a Selective, Bidentate, Fluorescent Fluoride Sensor

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1 Synthesis and Preliminary Characterisation

1.1 General Considerations.

All reactions and manipulations were carried out under an atmosphere of dry argon or dinitrogen gas using standard Schlenk and glovebox techniques. Butyllithium and 4-*tert*-butyl-calix[4]arene were purchased from Aldrich and used as received. Phenylboron dichloride was purchased from Aldrich and doubly vacuum distilled prior to use. Solvents for synthesis and NMR spectra were freshly distilled over suitable drying agents and degassed prior to use. NMR spectra were recorded on a Varian 400 MHz or Bruker 300 MHz spectrometer.

1.2 Synthesis of **3**.

To a turbid solution of 3.50g 4-*tert*-butyl-calix[4]arene **H_4L** in 80 ml THF was slowly added 4.08 equivalents of n-BuLi (8.8 ml 2.5M solution in hexanes). Refluxed, THF removed in vacuo at 75 oC for 24 hr, **Li_4L** isolated a white powder and stored under argon in glove box.

To a white suspension of 3.35 g (4.99 mmol) of **Li_4L** in 80 mL of toluene was added dropwise 1.30 mL (9.99 mmol) of $PhBCl_2$. Following complete addition of the $PhBCl_2$ a mildly exothermic reaction occurred and a reduction in the amount of white suspension was noted. The reaction mixture was then held at reflux for 24 h before cooling and isolation of the colourless solution from the nascent LiCl by filtration through Celite. The toluene was then removed *in vacuo* leaving a white solid. Hexane (80 mL) was then added and the resultant solution was again filtered through Celite before having the solvent removed in vacuo, leaving **3** as a white powder (2.69 g, 66% yield).

1.3 Preliminary Characterisation of 3

Yield 2.68 g (66%). M. pt., 219-220 ^{0}C (decomp.) . HRMS (FAB$^+$) 820.484 (calc. for $C_{56}H_{62}O_4B_2$ 820.483). NMR (C_6D_6) ^{1}H δ 0.82 (36H, s, ^{t}Bu), 3.36 (2H, d, J=14.4 Hz, CH_{2exo}), 3.47 (2H, d, J=12.4 Hz, CH_{2exo}), 3.89 (2H, d, J=14.4 Hz, CH_{2endo}), 5.01 (2H, d, J=12.8 Hz, CH_{2endo}), 6.88 (4H, d, J=2.4 Hz, Aryl), 6.93 (4H, t, J=7.2 Hz, BPhenyl), 7.03 (2H, t, J=7.2 Hz, BPhenyl), 7.22 (4H, d, J=2.8 Hz, Aryl), 7.68 (4H, d, J=6.8 Hz, BPhenyl); ^{11}B δ 11.8; ^{13}C δ 31.4 (CH_3), 32.0, 34.0 (CH_2), 36.8 (^{t}Butyl C), 124.6, 126.4, 128.2, 130.9, 131.4, 135.9, 144.9, 148.8 (Aryl C,CH). NMR [$(CD_3)_2SO$] ^{11}B δ 26.9 (s,br).

2 Fluorescence Measurements on 3

All fluorescence measurements were recorded in chloroform solution without special precautions to exclude atmospheric moisture or oxygen. The experimental data of I/I_0 as a function of added tetrabutylammonium fluoride was fitted to the model of **Scheme 1** (below) using the non-linear least-squares solver of Scientist, Ver. 2.01, MicroMath Inc. (input equation file given below).

$$\mathbf{3} + F^{-} \underset{}{\overset{K_1}{\rightleftharpoons}} (\mathbf{3}F)^{-} \underset{}{\overset{K_2}{\rightleftharpoons}} [(\mathbf{3})_2F]^{-}$$

Scheme 1: *Proposed scheme for anion binding of F^- to **3** derived from fluorescence titrations: ($lgK_1 = 6.3 \pm 0.4$; $lgK_2 = 3.8 \pm 0.5$).*

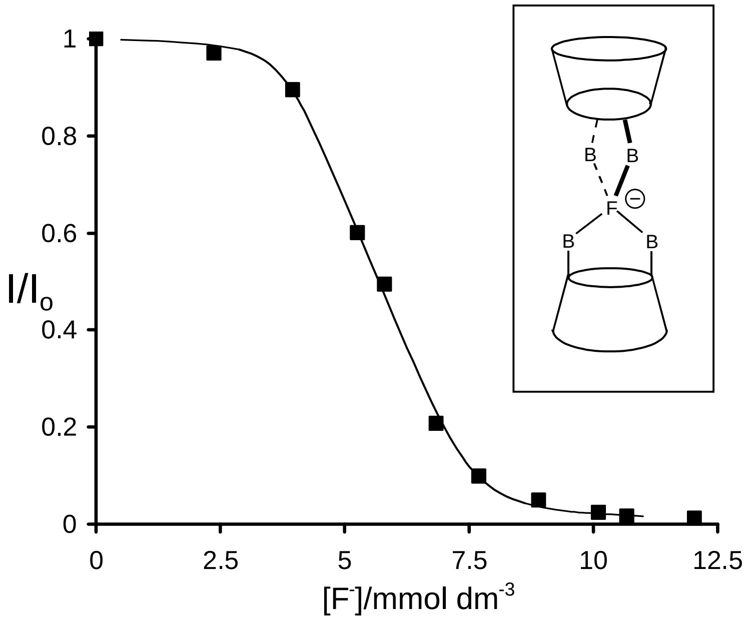

Figure 3: *Fluorescence titration curve for **3**. Experimental (■) and calculated (line) values (based on the model shown in Scheme 1). Insert: proposed structure of $[(\mathbf{3})_2F]^-$ responsible for nonlinear response.*

The total emission is assumed to arise from the free ligand (**3** = L) and the 2:1 complex only, and that the molar emission from the 2:1 complex is twice that of the free ligand. This model gave $r^2 = 0.9996$ for the data of **Figure 3** (above). Uncertainties are the calculated 95% confidence intervals for the constants.

Input equation file for non-linear least-squares solver of Scientist (Ver. 2.01, MicroMath Inc.):

```
IndVars: Ftot
DepVars: Itot
Params: K1, K2
Ltot = 0.0076
Ib = 131.6
A1 = K1 * L
A2 = K2 * L*A1
FF = 1 + A1 + A2
F = Ftot/FF
C1 = A1 * F
C2 = A2 * F
L = Ltot -C1 - 2*C2
Itot = Ib * (L + 2 * C2)
0 < L < 0.02
0 < F < 0.02
```

Ftot = total fluoride concentration
Itot = observed I/I_0
K1, K2 as defined in Scheme 1
Ltot = total concentration of **3**
L = concentration of free **3**
F = concentration of free fluoride
C1 = equilibrium concentration of **3**F
C2 = equilibrium concentration of (**3**)$_2$F
Ib = factor to give emission from **3** at F = 0

3 Notes on the Crystal Structure Refinement of 3

The phenyl ring bound to B2 showed a slight disorder which could not be resolved due to weak reflection data. Three of the four tert-butyl groups of the calixarene molecule also exhibited disorder and were isotropically refined with extensive rigid bond restraints. In addition, the solvent molecule sitting in the cone of the calixarene molecule was disordered and the split positions refined isotropically, as well as the positions of the second solvent molecule, which were assigned 50 % occupation.