1. Synthetic Procedures

All commercial grade reagents were used as supplied without any further purification. p-tert-butylcalix[4]arene was prepared by an adapted literature procedure\textsuperscript{1}. Where solvents are referred to as dry, they were prepared via the following method\textsuperscript{2, 3}: degassed by sparging with dinitrogen, dried by passing through a column of activated alumina using Grubbs apparatus and used immediately.

**Compound 2**

\[ \text{2-(2-aminoethyl)-ethanol (10.5g, 0.1mol) and phthalic anhydride (14.8g, 0.1mol) were dissolved in toluene (450mL) and the resulting solution placed in a round bottomed flask fitted with a Dean-Stark apparatus. The solution was then heated under reflux for four hours, with the water evolved from reaction periodically removed from the system. The reaction mixture was allowed to cool, dried over MgSO}_4, filtered, then the solvent removed \textit{in vacuo} to give the pure, white phthalamide protected amine in quantitative yield.} \]

\[ \delta_{\text{H}}(\text{CDCl}_3, 300\text{MHz}): 3.61 (2\text{H}, \text{ m, } C\text{H}_2\text{CH}_2\text{OH}), 3.69 (2\text{H}, \text{ m, } C\text{H}_2\text{OH}), 3.75 (2\text{H}, \text{ t, } J = 5.3\text{Hz, } O\text{CH}_2\text{CH}_2\text{N}), 3.91 (2\text{H}, \text{ t, } J = 5.3\text{Hz, } C\text{H}_2\text{N}), 7.73 (2\text{H}, \text{ m, ArH}), 7.85 (2\text{H}, \text{ m, ArH}); m/z (ES+) 236.0933 (M\textsuperscript{+} - H. C_{12}H_{14}NO_4 requires 236.0923), 258.07 (M + Na\textsuperscript{+}), 493.16 (2M + Na\textsuperscript{+}). \]

This material (23.5g, 0.1mol) was then dissolved in dichloromethane (200mL), to which solution triethylamine (21mL, 0.15mol), tosyl chloride (19g, 0.1mol) and a catalytic quantity of DMAP were added. The resulting mixture was stirred under a nitrogen atmosphere at room temperature for 16 hours, then H\textsubscript{2}O (100mL) was added. The vigorously stirred biphasic mixture was neutralised by portionwise addition of a 10% aqueous citric acid solution, then separated. The organic phase was washed with H\textsubscript{2}O (2 x 100mL), dried over MgSO\textsubscript{4}, filtered, and the solvent removed \textit{in vacuo} to give an off-white crude product. Overnight trituration under ether (100mL) gave pure white 2 (31.2g, 80%). \[ \delta_{\text{H}}(\text{CDCl}_3, 300\text{MHz}) 2.47 (3\text{H}, \text{ s, } C\text{H}_3), 3.70 (4\text{H}, \text{ m, } C\text{H}_2\text{OCH}_2), 3.87 (2\text{H}, \text{ m, } C\text{H}_2\text{N}), 4.14 (2\text{H}, \text{ m, } C\text{H}_2\text{OSO}_2), 7.35 (2\text{H}, \text{ m, TosH}), 7.77 (4\text{H}, \text{ m, ArH}), 7.88 (2\text{H}, \text{ m, PhthH}); m/z (ES+) 380.0995 (M\textsuperscript{+} - H. C_{19}H_{20}NO_6S requires 390.1011), 412.08 (M + Na\textsuperscript{+}), 801.19 (2M + Na\textsuperscript{+}). \]

**Compounds 3 and 4**

p-Tert-butylcalix[4]arene (3.82g, 5.89mmol) and K\textsubscript{2}CO\textsubscript{3} (1.63g, 12mmol) were suspended in dry CH\textsubscript{3}CN (120mL). To this stirred suspension compound 2 (5.74g, 14.7mmol) was added, and the resulting mixture was heated under reflux under a nitrogen atmosphere for 4 days. After this time, the suspension was allowed to cool,
then the solvent carefully removed in vacuo to give an solid mass which was triturated with 1M HCl(aq). The resulting suspension was extracted with CH₂Cl₂ (3 x 100mL), then the were extracts combined and washed with H₂O (2 x 100mL). The solution was dried over MgSO₄, filtered, and the solvent removed in vacuo to give a crude material which could be further purified by trituration under ethanol (75mL) to give the pure pale green product 3 (4.32g, 68%).

δH(CDCl₃, 300MHz): 1.03 (s, 18H, C(CH₃)₃), 1.25 (s, 18H, C(CH₃)₃), 3.07 (4H, d, J = 12.75 Hz, ArCH₂Ar (a)), 4.05 (m, 20H, 3 x OCH₂, NC₂H₂ & ArCH₂Ar (b)), 6.81 (4H, s, calixArH), 6.84 (4H, s, calixArH), 7.50 (4H, m, PhthH), 7.60 (4H, m, PhthH); δC(CDCl₃, 75.47MHz): 31.07, 31.49, 31.67, 33.70, 33.95, 38.09, 68.41, 69.96, 74.92, 122.67, 124.73, 125.38, 125.92, 127.80, 131.86, 133.35, 141.04, 146.90, 149.48, 149.87, 168.57; m/z (ES+) 1105.5552 (M + Na+).

Compound 3 (1.13g, 1.04mmol) was suspended in ethanol (25mL), and hydrazine monohydrate (0.5mL, excess) added carefully. This suspension was then heated under reflux for 15 hours, during which time the solid was seen to dissolve. The reaction mixture was allowed to cool, then poured into H₂O (50mL) to give a milky white suspension which was extracted with CH₂Cl₂ (4 x 40mL). The organic extracts were combined, dried over MgSO₄, filtered, and the solvent removed in vacuo to give the pure white diamine intermediate (0.86g, 100%).

δH(CDCl₃, 300MHz): 0.98 (s, 18H, C(CH₃)₃), 1.29 (s, 18H, C(CH₃)₃), 2.88 (4H, br, NH₂), 2.97 (4H, m, C₂H₂NH₂), 3.31 (4H, d, J = 13.05 Hz, ArCH₂Ar (a)), 3.71 (4H, m, OCH₂C₂H₂O), 3.71 (4H, m, OCH₂C₂H₂O), 3.96 (4H, m, OCH₂C₂H₂O), 4.05 (d, 4H, ArCH₂Ar (b)), 6.82 (4H, s, ArH), 7.06 (4H, s, ArH); δC(CDCl₃, 75.47MHz): 31.07, 31.59, 31.73, 33.85, 33.98, 42.09, 69.74, 73.43, 75.24, 125.11, 125.57, 127.80, 132.77, 141.45, 146.94, 149.78, 150.45; m/z (ES+) 412.28 (M + 2H+), 432.79 (M + 2Na+), 823.5590 (M + H). C₅₂H₇₅N₂O₆ requires 823.5625.

Separate solutions of this amine intermediate (0.86g, 1.04mmol) in CH₂Cl₂ (100mL) and isophthaloyl chloride (0.21g, 1.04mmol) in CH₂Cl₂ (100mL) were added dropwise, simultaneously, to a stirred solution of triethylamine (0.56mL, 4mmol) in CH₂Cl₂ (250mL) over 2 hours, the whole system being kept under a nitrogen atmosphere. Once addition was complete, the reaction mixture was concentrated in vacuo to a volume of ca 100mL, then washed with 1M HCl(aq) (2 x 100mL), H₂O (100mL), 1M NaOH (100mL) and brine (100mL). The organic layer was dried over MgSO₄, filtered, then concentrated in vacuo to give a crude product which could be purified by silica gel chromatography (ethyl acetate/acetone 70:30) followed by trituration under hexane to give pure white compound 4 (0.52g, 52%). Found: C, 75.47; H, 7.91; N, 2.86. C₆₀H₇₆N₂O₈ requires C, 75.60; H, 8.04; N, 2.94%. δH(CDCl₃, 300MHz): 0.84 (s, 18H, C(CH₃)₃), 1.28 (s, 18H, C(CH₃)₃), 3.21 (4H, d, J = 13.48 Hz, ArCH₂Ar (a)), 3.71 (12H, m, AlCH₂), 4.21 (8H, m, AlCH₂ & ArCH₂Ar (b)), 6.64 (4H, s, calixArH), 6.79 (2H, s, OHH), 6.94 (4H, s, calixArH), 7.32 (1H, m, isophthalyl CH), 7.67 (2H, bm, NH), 7.91 (2H, m, isophthalyl CH), 8.18 (1H, m, isophthalyl CH); m/z (ES+) 975.52 (M + Na+).

Synthesis of Receptor 1

Note that caution should be exercised when handling thallium derivatives due to their high toxicity. Tl(O₂CF₃)₃.TFA solution was prepared using a previously described method; briefly, a suspension of Tl₂O₃ (5g) in TFA (25mL) was heated under reflux
in the absence of light for 92 hours. The resulting solution was cooled, then filtered and stored in a light protected vessel until required.

Compound 4 (0.3g, 0.32mmol) was added to a portion of Tl(O2CF3)3.TFA solution (4mL) and stirred at room temperature in the absence of light for 2 hours. The resulting orange solution was concentrated to approximately one third of its original volume, then added to ice-water (50mL). This orange suspension was extracted with CHCl3 (3 x 50mL), then the organic extracts were combined, dried over MgSO4, filtered and concentrated \textit{in vacuo} to give an orange solid. This was purified by recrystallisation from CH2Cl2/Et2O to give the orange receptor 1 (116mg, 42%).

δH(CD3CN, 300MHz): 1.06 (s, 18H, C(CH3)3), 3.11 (4H, b, ArCH2Qu (a)), 3.67 (12H, m, AlCH2), 3.89 (8H, bm, AlCH2 & ArCH2Ar (b)), 6.62 (4H, bs, calixQuH), 6.81 (4H, s, calixArH), 7.37 (1H, m, isophthalyl CH), 7.59 (2H, bm, NH), 7.96 (2H, m, isophthalyl CH), 8.25 (1H, m, isophthalyl CH); δc(CDCl3, 75.47MHz): 31.37, 32.43, 34.05, 41.05, 70.04, 74.14, 124.06, 126.57, 129.01, 129.26, 131.96, 133.19, 133.85, 146.50, 147.35, 167.42, 185.48, 191.51; m/z (ES+) 891.3850 (M + Na+). C52H56N2O10Na requires 891.3833.

2. Titration Protocols

\textit{1H} NMR Titrations

All titrations were conducted on a Varian Unity Plus 500MHz spectrometer, at 298K in CD3CN solution. Sample volumes used were 500µL, and all titrations were conducted at 1.5 x 10^{-3} moldm^{-3} concentrations (7.5 x 10^{-7} moles/sample). Where necessary, 1:1 mixtures of metal salt and receptor were pre-prepared. All salts were thoroughly dried before use; all anions were added as TBA salts, all metals as PF6 salts except for Na and Li which were added as the ClO4- salts for solubility reasons. Aliquots of the anion solution (0.075 moldm^{-3}) were then added (10 x 2µL, 2 x 5µL, 2 x 10µL, 1 x 20µL & 1 x 30µL) so that ten equivalents of anion in total were used. Spectra were recorded after each addition, and the sample shaken thoroughly before measurement.

The resulting titration data were analysed by the WINEQNMIR computer program\textsuperscript{7} to attempt binding constant determination.

\textit{UV-visible} Titrations

UV-visible experiments were conducted on a Perkin-Elmer Lamda 6 spectrophotometer, at 298K, in dry CH3CN. The sample volume was 3mL, of 1 x 10^{-4} moldm^{-3} concentration. Where necessary, 1:1 mixtures of receptor and co-analyte were pre-prepared. All salts were thoroughly dried before use; all anions were added as TBA salts, all metals as PF6 salts except for Li and Na which was added as the ClO4- salt for solubility reasons. Aliquots of the anion solution (0.03 moldm^{-3}) were then added (10 x 2µL, 2 x 5µL, 2 x 10µL, 1 x 20µL & 1 x 30µL) so that ten equivalents of analyte in total were used. Spectra were recorded after each addition, and the sample mixed thoroughly before each measurement.
The resulting titration data were analysed by the SPECFIT computer program\textsuperscript{8} to attempt binding constant determination. Where only dilution effects were seen, it was inferred that the quinone units were not involved in cation binding.

3. Single X-Ray Crystal Data

\textit{Inorganic Chemistry Crystallography Service}

Single-crystal X-ray diffraction report for C\textsubscript{52}H\textsubscript{56}N\textsubscript{2}O\textsubscript{10}\cdot MeCN (ARC1262) (see attached .cif file).

Crystals of 1 were grown by slow diffusion of diethyl ether into an acetonitrile solution of 1. A single crystal having dimensions approximately 0.18 x 0.24 x 0.32 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150K in a stream of cold N\textsubscript{2} using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Oxford Diffraction Gemini CCD diffractometer (graphite-monochromated MoK\textsubscript{α} radiation, \( \lambda = 0.71073 \) Å). Intensity data were processed using the Crysalis software package\textsuperscript{9}.

The structure was solved in the space group \( P \bar{1} \) using the direct-methods program SIR92\textsuperscript{10}, which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite\textsuperscript{11}. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. The NH hydrogen atoms were located in a difference Fourier map and their coordinates and isotropic thermal parameters subsequently refined. Other hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give R = 0.0447, wR = 0.0514.
Attached is a thermal ellipsoid plot (ORTEP-3\textsuperscript{12}) at 40\% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning geometrically-positioned H atoms.

Comments:

The molecule does not adopt the typical conformation of a calixarene. The two \textit{t}-butylphenyl rings are approximately parallel (the angle between the best planes of the C\textsubscript{6} rings is 1.0°). However, the two quinone rings are not parallel (interplanar angle 30.5°). The ‘pendant’ polyether loop adopts an extended conformation such that the two amide NH groups can form relatively long intramolecular hydrogen bonds to one of the quinone O atoms (N(1)···O(4) 3.171(3), N(2)···O(4) 3.237(3) Å).

The molecule of solvent resides within a small pocket bounded by the polyether loop and hydrogen-bonded quinone. It does not participate in hydrogen bonding or any other apparent supramolecular interaction.

Acknowledgement

Oxford Diffraction Ltd are thanked for the loan of the Gemini diffractometer.

4. References

8. SPECFIT, v. 2.02, \textit{Spectrum Software Associates, Chapel Hill, NC}.
9. Crysallis, Oxford Diffraction, 2005