Supporting Information

For

A fluoride-selective PCT chemosensor based on formation of a static
pyrene excimer

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Experimental

Synthesis

Compound **2** was prepared by the literature procedure.¹

Data S1: 25,27-Bis[(N-(1-pyrenyl)aminocarbonyl)methoxy]-26,28-dipropoxy-calix[4]arene in the 1,3-alternate conformation (1**)**

A solution of **2** (0.30 g, 0.45 mmol), 1-aminopyrene (0.14 g, 0.91 mmol) and triethylamine (1.5 ml, 2.07 mmol) in dry THF (20 mL) was refluxed with stirring for 2 days and then evaporated *in vacuo*. The resulting solid was dissolved in CH₂Cl₂ (100 ml) and the organic layer was washed three times with water, dried over MgSO₄, and evaporated *in vacuo*. The crude product was chromatographed on silica gel with EtOAc as eluent to give 0.25 g (54 %) of **1** as a brownish solid. Mp: 320-324 °C. IR (KBr pellet): 3288, 1678 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 9.21 (br s, 2 H, NH) 8.19-7.69 (m, 16 H, ArH, pyrene), 7.34 (d, 2 H, ArH, pyrene, *J* = 8.4 Hz), 7.20 (d, 8 H, ArH_m, *J* = 7.40 Hz), 6.91 (t, 2 H, ArH_p, *J* = 7.4 Hz), 6.67 (t, 2 H, ArH_p, *J* = 7.0 Hz), 3.87 (s, 8 H, ArCH₂Ar), 3.72 (t, 4 H, ArOCH₂CH₂CH₃, *J* = 7.6 Hz), 3.51 (s, 4 H, ArOCH₂CO), 1.78-1.68 (sextet, 4 H, CH₂CH₂CH₃, *J* = 7.6 Hz), 0.96 (t, 6 H, CH₂CH₂CH₃, *J* = 7.6 Hz). ¹³C NMR (50 MHz, CDCl₃): 168.3, 157.8, 154.4, 154.3, 135.0, 133.3, 131.8, 131.2, 130.8, 130.4, 130.1, 129.2, 127.5, 127.2, 126.7, 126.0, 125.2, 124.9, 124.7, 124.4, 123.0, 122.3, 121.3, 73.6, 71.2, 37.6, 23.2, 10.2 ppm. FAB MS *m/z* (M⁺) calcd 1023.2, found 1023.0. Anal. Calcd. for C₇₀H₅₈N₂O₆: C, 82.17; H, 5.71. Found: C, 82.38; H, 5.75.

Data S2: General Procedure for Fluorescence Studies

Fluorescence spectra were recorded with a RF-5301PC spectrofluorimeter. Stock solutions (1.00 mM) of the tetrabutylammonium salts and stock solutions of **1** and **2** (0.060 mM) were prepared in MeCN. For all measurements, excitation was at 346 and 400 nm, respectively, with excitation and emission slit widths of 3 nm. Fluorescence titration experiments were performed with 6.0 μM solutions of **1** and **2** in MeCN and varying concentrations of Bu₄N⁺F⁻ in MeCN. The association constants were determined by a published method.²

Scheme S1. Synthetic route for fluorescence chemosensor **1**

Figure S1. UV/Vis spectra of **1** (0.10 mM) upon titration with $\text{Bu}_4\text{N}^+\text{F}^-$ in MeCN.

Figure S2. Partial ^1H NMR spectra (200 MHz) of **1** (0.030 mM) in CDCl_3 : (a) **1** only; (b) **1** + 2.0 equivalents of $\text{Bu}_4\text{N}^+\text{F}^-$. The peaks for the NMR solvent (CDCl_3) are removed for clarity.

Figure S3. Partial ¹H NMR spectra (200 MHz) of **3** (0.030 mM) in CDCl₃: (a) **3** only; (b) **3** + 1.0 equivalents of Bu₄N⁺F⁻.

Figure S4. Excitation spectra (normalized) of free **1** monitored at 385 nm (solid line) and 482 nm (dashed line).

Figure S5. Competitive titration profile of fluorescence spectra for **1** ($10\ \mu\text{M}$) with $\text{Bu}_4\text{N}^+\text{F}^-$ in MeCN containing six different anions (Cl^- , Br^- , I^- , CH_3CO_2^- , HSO_4^- and H_2PO_4^- , 100 equivalents of each anion). The excitation wavelength was 346 nm.

References

1. Kim, S. K.; Lee, S. H.; Lee, J. Y.; Lee, J. Y.; Bartsch, R. A.; Kim, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 16499.
2. (a) Association constants were calculated using the computer program ENZFITTER, available from Elsevier-BIOSOFT, 68 Hills Road, Cambridge CB2 1LA, United Kingdom. (b) Connors, K. A. *Binding Constants*; Wiley: New York, 1987.