

Supporting Information

For

Bifunctional Fluorescent Calix[4]arene Chemosensor Both for a Cation and for an Anion

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Synthesis

Compounds **3**, **4** and **6** were prepared following procedures reported in literature.¹⁻³

Data S1: Calix[4]amidocrown-5, cone (**5**)

To a solution of **4** (1.00 g, 1.68 mmol)¹ in absolute ethanol (60 mL) and toluene (60 mL) was added 6 mL of diethylenetriamine under N₂ atmosphere. The mixture was refluxed for 48 hours. Solvent was removed *in vacuo* and the residue triturated with MeOH overnight. The precipitated solid was collected, washed with methanol and then dried to afford 0.51 g (50.0 %) of the desired product as crystalline solid. Mp 250 °C (dec.). IR (KBr pellet, cm⁻¹): 3329, 1683. ¹H NMR (CDCl₃): δ 8.26 (br. t, 3 H, NH, *J* = 5.9 & 5.4 Hz), 7.72 (br. s, 2 H, OH), 7.15 (d, 4 H, Ar-*H*, *J* = 7.3 Hz), 6.98 (d, 4 H, Ar-*H*, *J* = 7.3 Hz), 6.76 (t, 2 H, Ar-*H*, *J* = 7.6 & 7.6 Hz), 6.63 (t, 2 H, Ar-*H*, *J* = 7.6 & 7.6 Hz), 4.45 (s, 4 H, OCH₂CO), 4.24 (d, 4 H, Ar-CH₂-Ar, *J* = 13.2 Hz), 3.45 (d, 4 H, Ar-CH₂-Ar, *J* = 13.2 Hz), 3.39 (br. q, 4 H, NCH₂, *J* = 5.9 & 5.4 Hz), 2.82 (br. t, 4 H, NCH₂, *J* = 5.4 Hz). ¹³C NMR (CDCl₃): δ 168.5, 152.9, 152.9, 133.9, 129.8, 129.5, 128.4, 126.2, 120.3, 75.3, 49.1, 40.4, 31.1 ppm. Anal. Calcd. for C₃₆H₃₇O₆N₃: C, 71.15; H, 6.14. Found: C, 71.21; H, 6.08.

Data S2: Fluorogenic calix[4]triazacrown (**1**)

Under nitrogen, calix[4]triazacrown (**5**) (1.00 g, 1.65 mmol), N-(1-pyrene-methyl)chloroacetamide (**3**)² (1.02 g, 3.31 mmol), K₂CO₃ (0.68 g, 4.92 mmol), and catalytic amount of sodium iodide in 100 mL of acetonitrile were heated to reflux temperature. After refluxed for 24 hours, acetonitrile was removed *in vacuo*. To the resulting yellow solid, water (100 mL) and CH₂Cl₂ (50 mL) were added and the organic layer was separated and washed three times with 50 mL of water. The organic layer was dried over anhydrous MgSO₄ and the solvent was evaporated *in vacuo* to give a yellowish solid. Column chromatography on silica gel using THF as an eluent gave 0.97 g (50% yield) of **1** as a yellowish solid. Mp 218-219 °C. IR (KBr pellet, cm⁻¹): 3406, 1769. ¹H NMR (200 MHz, CDCl₃): δ 8.65 (broad t, 2 H, NH in triazacrown), 8.31-7.60 (m, 18 H, Ar-*H*, pyrene; 2 H, NH linked to pyrenes), 7.02 (d, 4 H, Ar-*H*_m, *J* = 7.4 Hz), 6.85-6.70 (m, 4 H, Ar-*H*_p; 4 H, Ar-*H*_m), 5.19 (d, 4 H, NHCH₂pyrene, *J* = 5.6 Hz), 4.16 (s, 4 H, ArOCH₂), 3.77 (d, 4 H, ArCH₂Ar, *J* = 13.4 Hz), 3.41-3.19 (m, 4 H, ArOCH₂; 4 H, ArCH₂Ar; 4 H, NHCH₂CH₂NH; 1 H, CH₂NHCH₂), 2.87 (broad s, 4 H, CH₂CH₂NH). ¹³C NMR (50 MHz, CDCl₃): 168.7, 154.4, 152.4, 150.7, 132.4, 129.5, 128.2, 127.4, 126.6, 125.2, 124.6, 123.0, 120.8, 67.0, 56.3, 31.3 ppm. FAB MS *m/z* (M⁺): Calcd, 1150.3. Found 1150.0. Anal. Calcd. for C₇₄H₆₃O₈N₅: C, 77.26; H, 5.52. Found: C, 77.31;

H, 5.60.

Data S3: 25,27-Bis[*N*-(1-pyrenylmethyl)aminocarbonyl]methoxy]-26,28-dipropyl-oxycalix[4]arene, Cone (2).

Under nitrogen, compound **6**³ (0.2 g, 0.21 mmol), *N*-(1-pyrene-methyl)chloroacetamide (**3**)² (0.24 g, 0.78 mmol), and K₂CO₃ (0.09 g, 0.65 mmol) in 100 mL of acetonitrile were heated to reflux temperature. After refluxed for 24 hours, acetonitrile was removed *in vacuo*. To the resulting white solid, 5 % aqueous HCl solution (100 mL) and CH₂Cl₂ (50 mL) were added and the organic layer was separated and washed three times with 50 mL of water. The organic layer was dried over anhydrous MgSO₄ and the solvent was evaporated *in vacuo* to give a white solid. Recrystallization from a mixture of methylene chloride and diethyl ether (1:9) gave 0.15 g (68 % yield) of **2** as a white solid. Mp: 209-210 °C; IR (KBr pellet, cm⁻¹): 3316, 1743; ¹H NMR (400 MHz; CDCl₃): δ 8.14 (m, 18 H, ArH, pyrene), 7.36 (broad t, 2 H, CONHCH₂), 6.90-6.82 (m, 2 H, ArH_p; 4 H, ArH_m), 6.13 (d, 4 H, ArH_m, *J* = 7.2 Hz), 5.96 (t, 2 H, ArH_p, *J* = 6.8 Hz), 5.17 (d, 4 H, NHCH₂pyrene, *J* = 6.0 Hz), 4.21 (s, 4 H, ArOCH₂CO), 3.82 (d, 4 H, ArCH₂Ar, *J* = 13.2 Hz), 3.54 (t, 4 H, ArOCH₂CH₂, *J* = 7.60 Hz), 3.18 (d, 4 H, ArCH₂Ar, *J* = 13.6 Hz), 1.77-1.73 (m, 4 H, CH₂CH₂CH₃), 0.91 (t, 6 H, CH₂CH₂CH₃, *J* = 7.4 & 7.6 Hz); ¹³C NMR (CDCl₃): δ 166.4, 133.8, 130.3, 129.6, 129.2, 129.1, 128.3, 126.8, 126.2, 125.8, 125.4, 123.6, 120.4, 75.6, 32.9, 23.7, 10.7 ppm; FAB MS *m/z* (M⁺): Calcd, 1051.2. Found, 1051.0; Anal. Calcd. for C₇₂H₆₂N₂O₆: C, 82.26; H, 5.94. Found: C, 82.29; H, 5.99.

Data S4: General procedure for fluorescence study

Fluorescence spectra were recorded with a RF-5301PC spectrofluorometer. Stock solutions (1.00 mM) of the metal perchlorate salts were prepared in MeCN. Stock solutions of **1** and **2** (0.06 mM) were prepared in MeCN. For all measurements, excitation was at 343 nm with excitation and emission slit widths at 3 nm. Fluorescence titration experiments were performed using 6 μM solutions of **1** and **2** in MeCN and various concentrations of metal perchlorate in MeCN. After calculating the concentrations of the free ligands and complexed forms of **1** and **2** from the fluorescence titration experiments, the association constants were obtained using the computer program ENZFITTER.⁴

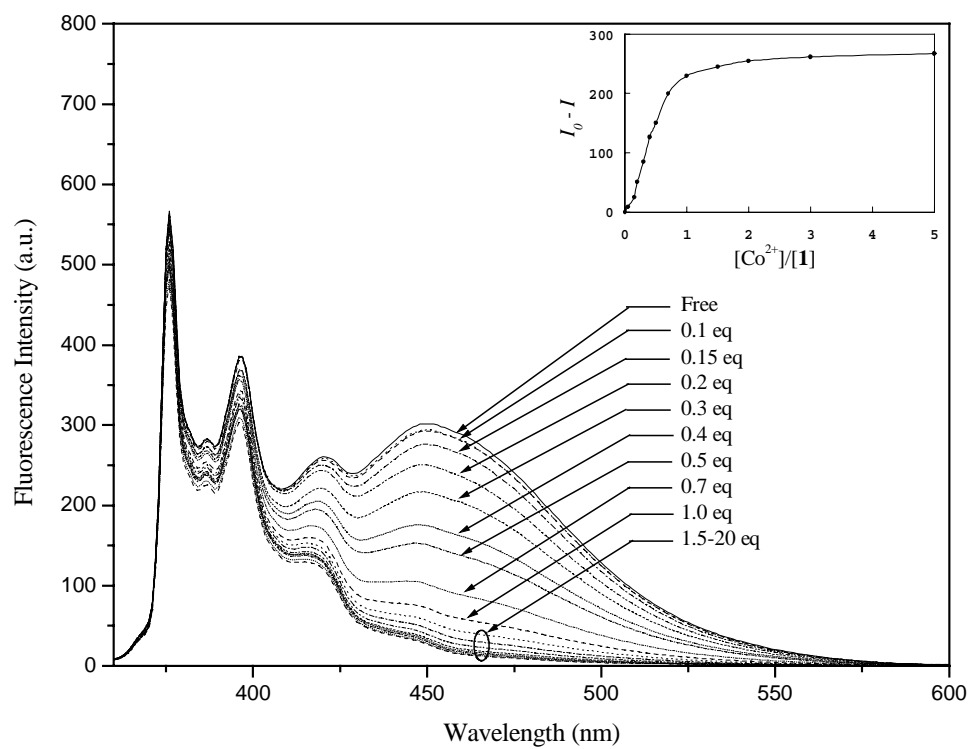


Figure S1. Fluorescence emission spectra of **1** (6.0 μM) upon additions of various amounts of Co(ClO₄)₂ in CH₃CN. The excitation wavelength was 343 nm.

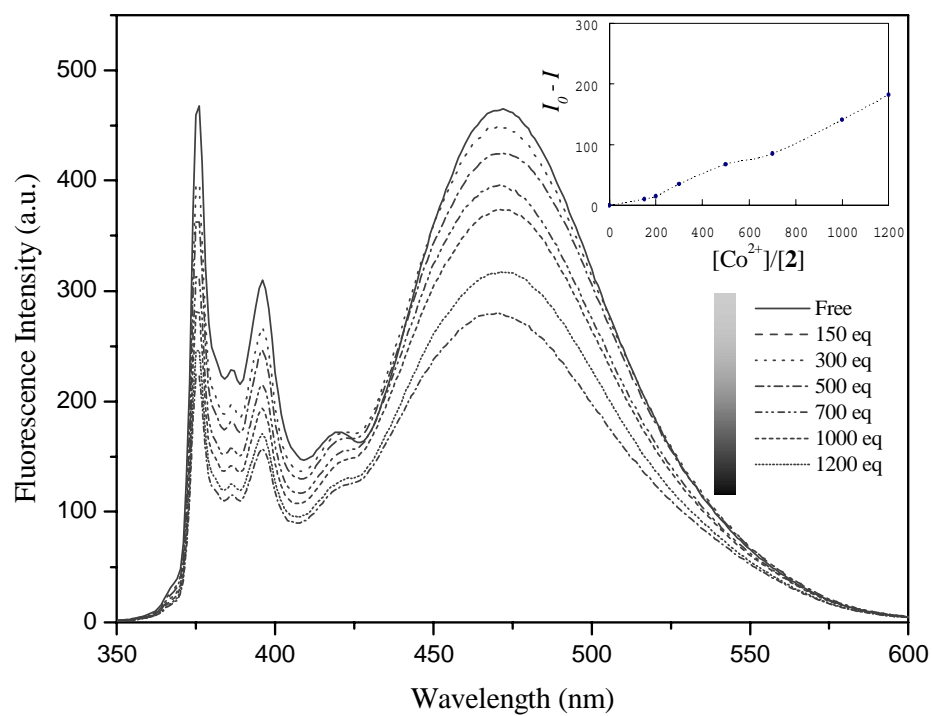


Figure S2. Fluorescence spectra of **2** (6.0 μM) upon the addition of various concentrations of $\text{Co}(\text{ClO}_4)_2$ in CH_3CN . The excitation wavelength is 343 nm.

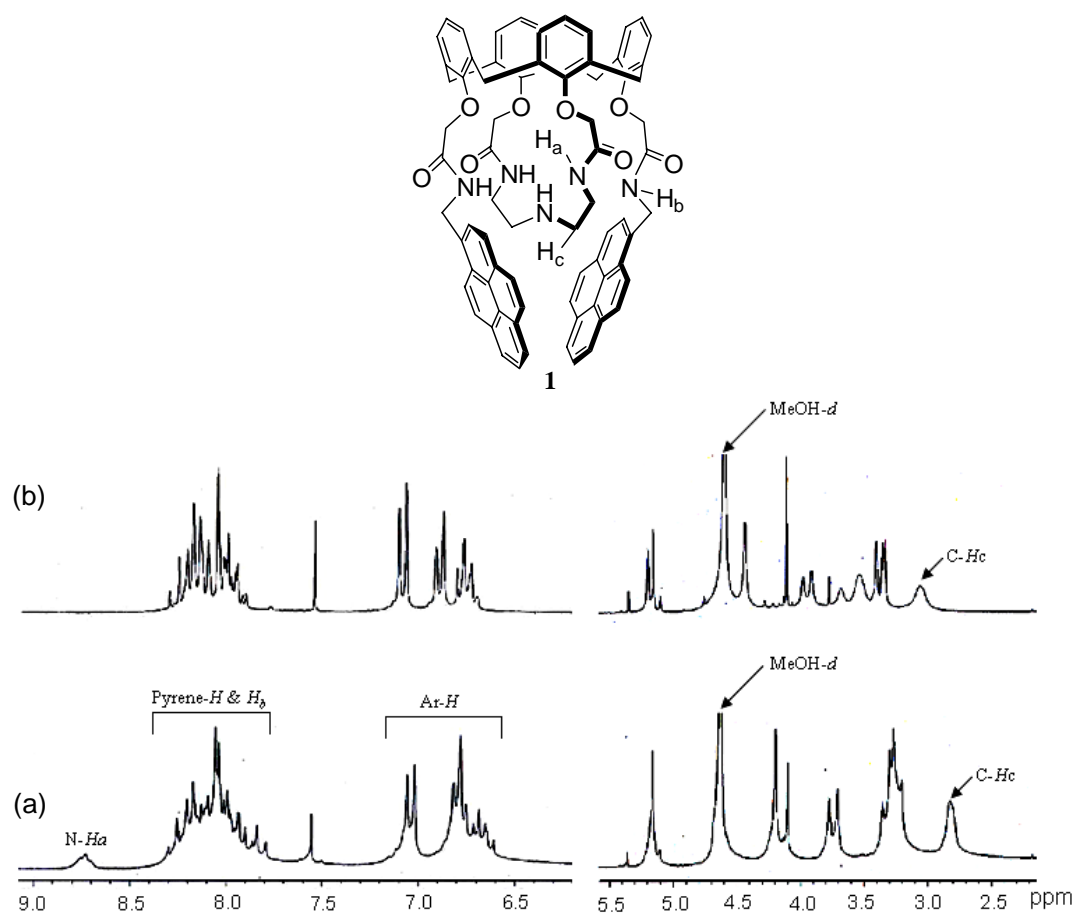


Figure S3. Partial ¹H NMR (200 MHz) of **1** (0.03 mM) in CDCl₃/MeOH-*d*₄ (3:1): (a) **1** only; (b) **1** + 5.0 equiv. of Pb²⁺.

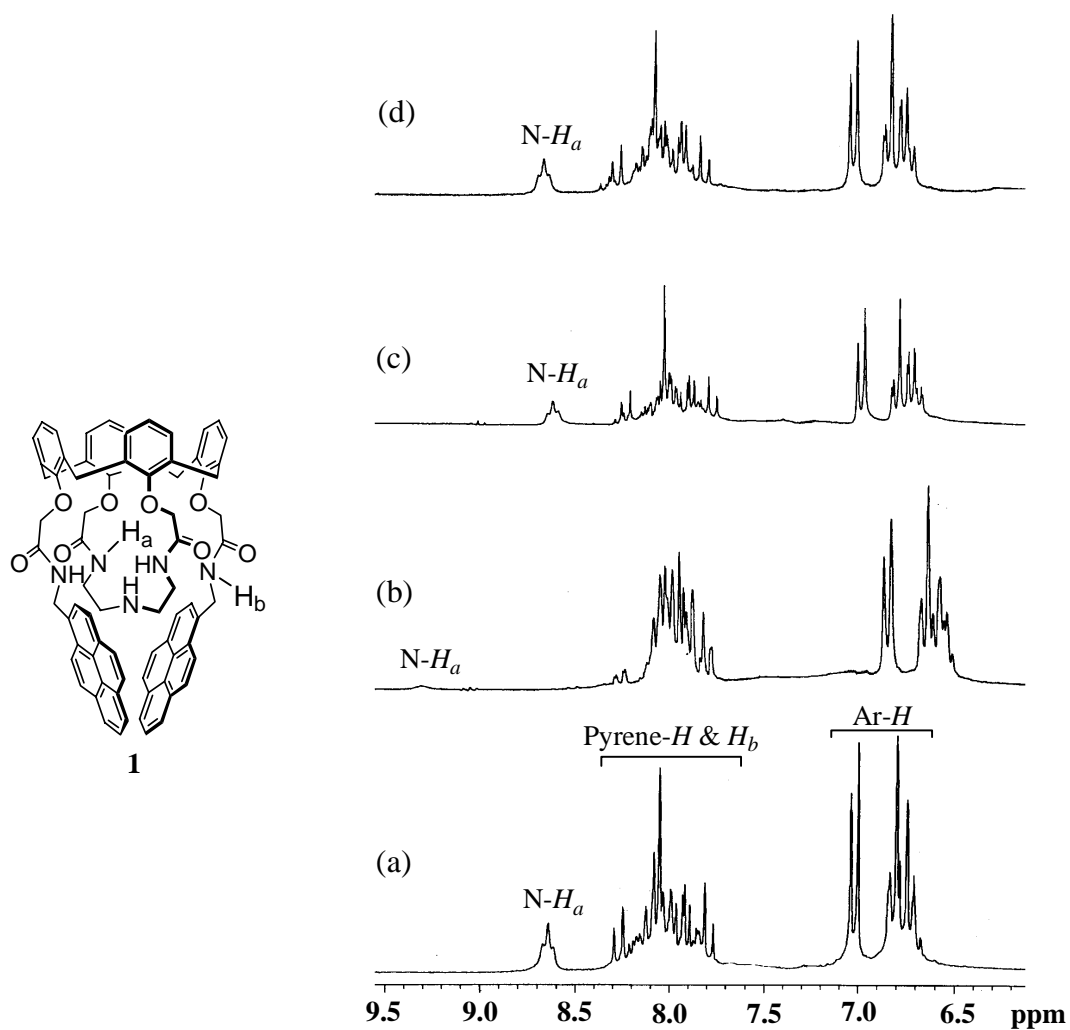


Figure S4. Partial ¹H NMR (200 MHz) of **1** (0.03 mM) in CDCl₃: (a) **1** only; (b) **1** + 1.0 equiv. of tetrabutylammonium fluoride; (c) **1** + 10.0 equiv. of tetrabutylammonium iodide; (d) **1** + 10.0 equiv. of tetrabutylammonium hydrogensulfate. The peaks of NMR solvents (CDCl₃) are removed for clarity.

References

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