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A novel pyrenyl-appended tricalix[4]arene for fluorescence-sensing of Al(III)

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Abstract—In acetonitrile, the *tren-N*-tricalix[4]arene **4** with three appended pyrenyl groups showed an enhanced fluorescence in the presence of Al^{3+} and, to a lesser extent, of In^{3+}. Compound **4** was shown to form a 1:1 complex with Al^{3+}, the metal cation being located in the *tren* part. The association constant (K_a) of **4** for the Al^{3+} cation was calculated to be 8.7×10^3 M^{-1} in acetonitrile.

1. Introduction

The design of photoreactive molecules as specific chemosensors with a fluorescence response to changes in their chemical surroundings, e.g., on complexation of analytes, is a topic of considerable interest.[1] Luminescent sensing is not simply a recognition process. It requires that the binding of the analyte acts as a trigger for signal transduction.[1] *N*-(1-Pyrenylmethyl)amide or 'pyrene-amide' is a useful fluorophore because it displays a well-defined monomer emission at 370–430 nm and an excimer emission near 480 nm.[2] The ratio of excimer to monomer emission intensities (I_E/I_M) is sensitive to the molecular structure of the host and recognition of a cation can be monitored by measuring the I_E/I_M ratio.[2]

The present work is based on developments in our separate laboratories. These concerned the synthesis of pyrene-amide calix[4]arenes as chemosensors for the detection of cations and anions[3] and the synthesis and cation complexing properties of hyperbranched molecules based on *p-tert*-butylcalix[4]arene.[4] In particular, *tren-N*-tricalix **1** (see Chart 1), prepared by reacting the monomethyl ester *p-tert*-butylcalix[4]arene **2** and *tren*, was shown to form a 1:1 complex with zinc, the metal being located in the *tren* cavity.[5] In collaboration, we have now examined the behaviour of tri(pyrene-amide) *tren-N*-tricalix **4**, selectively functionalised at the periphery by three pyrene-amide units, which displays strongly enhanced fluorescence upon interaction with Al^{3+} and, to a lesser extent, with In^{3+}. For comparison, we have also investigated calix **5** and dicalix **6** corresponding to the truncated tricalix **4**.

2. Results and discussion

The synthesis of **4** is depicted in Scheme 1. *tren-N*-Tricalix **1** was refluxed for four days with ~4 equiv of *N*-(1-pyrenylmethyl)chloroacetamide **3**[6] in the presence of 8 equiv of K_2CO_3 and an excess of KI in acetonitrile.[7] Compound **4** was isolated pure by chromatography on SiO_2 (90:10 CH_2Cl_2/acetone).

The ^1H NMR ($CDCl_3$) spectrum of **4** displayed simple patterns showing the effective C_{3v} symmetry of the molecule: two triplets at 9.17 ppm (J=7.1 Hz) and 8.86 ppm (J=7.3 Hz) for the N*H*CO-pyrenyl and N*H*CO, respectively, two singlets at 4.87 ppm and 4.22 ppm for OCH_2CO and NHCH_2–pyrene, respectively, two AB systems at 4.07 ppm and 3.23 ppm (J=13.2 Hz) and 3.21 ppm and 2.77 ppm (J=13.5 Hz) for the ArCH_2Ar. The δ and J values of this last AB system reflect the presence of H-bonding of the type pyrenemethyl–CONH···OHAr as found for related 1,3-dipyrene amide *p-tert*-butylcalix[4]arene.[6] The corresponding Ar*C*H$_2$Ar resonances were detected at 31.501 ppm and 31.033 ppm, consistent with the calix[4]arene units having the cone conformation.[7,8] Three singlets were found at 1.06 ppm, 0.98 ppm and 0.86 ppm in a 2:1:1 ratio for the *tert*-butyl groups. Scheme 2 gives the preparation of **5** and **6**. Methyl ester derivative **2** was refluxed for 14 h with

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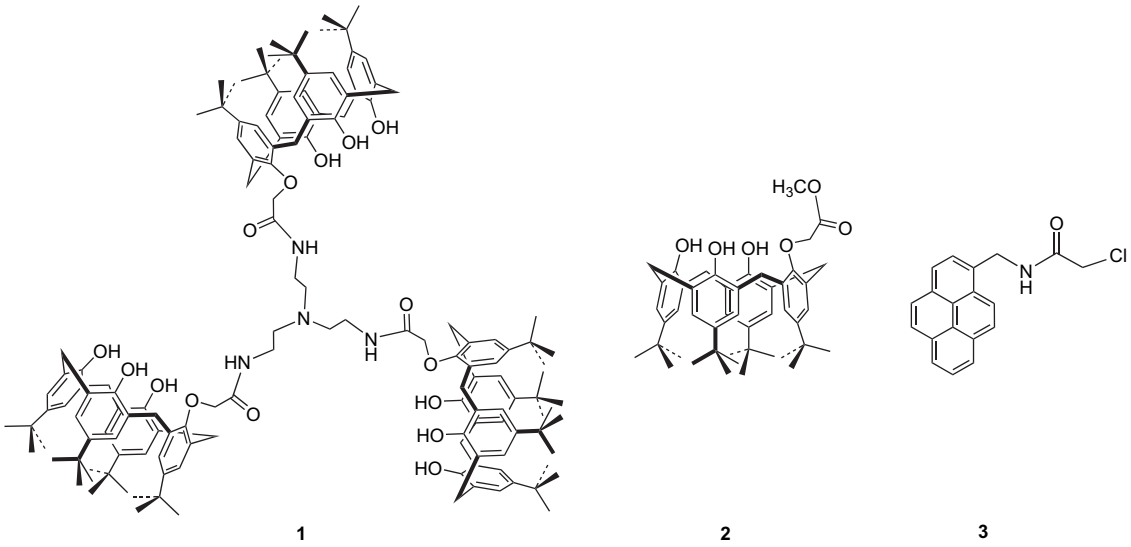
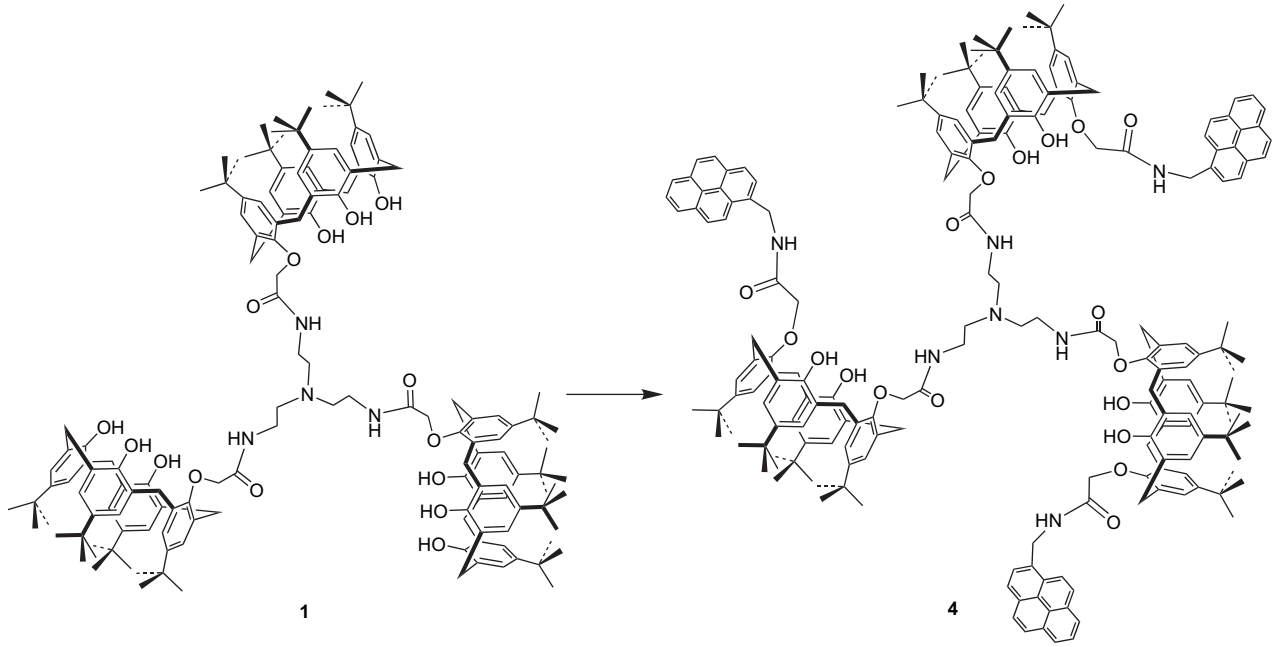


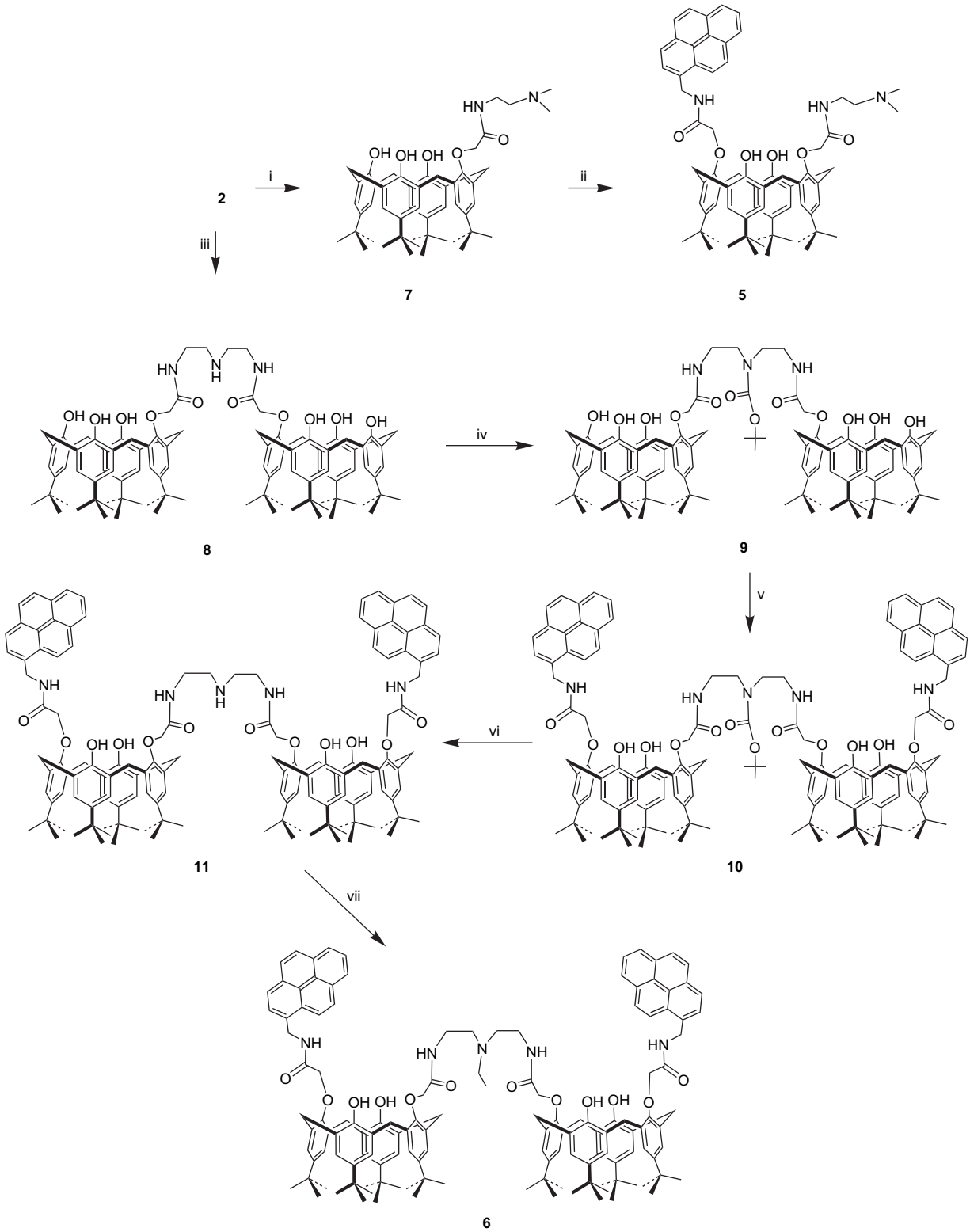
Chart 1.

~2 equiv of $(CH_3)_2NCH_2CH_2NH_2$, in 1:1 methanol/toluene to give pure *N*,*N*-dimethylene amido calix **7** after chromatography on silica (CH_2Cl_2 as eluent). Then, **7** was refluxed for three days with ~1.5 equiv of **3**, in the presence of 1 equiv of K_2CO_3 and excess of KI in acetonitrile to give **5**, purified by chromatography on silica (95:5 CH_2Cl_2/acetone as eluent). The 1,3-alkylation and the cone conformation of **5** were deduced from the simplicity of its ^{1}H NMR spectrum. Three singlets (in a 1:2:1 integration ratio) were observed at 1.17 ppm, 1.21 ppm and 1.23 ppm for the *tert*-butyl groups. Two AB systems were found at 3.38 ppm and 4.03 ppm (J=15.0 Hz) and 3.45 ppm and 4.23 ppm (J=15.0 Hz) for the ArCH_2Ar protons. Two singlets appeared at 4.50 ppm and 4.78 ppm for the OCH_2CONH while a doublet appeared at 5.15 ppm (J=6.0 Hz) for the CONHCH_2–pyrene protons.

The synthesis of **6** began by amidation of **2** with $NH(CH_2CH_2NH_2)_2$ (six days reflux) to give NH-dicalix **8**. To introduce the pyrenylmethyl amido groups on the calix[4] units, the NH function was protected as NBoc by reacting **8** with ~2.0 equiv of di-*tert*-butyl dicarbonate or $(Boc)_2O$ in CH_2Cl_2 at rt for 12 h. NBoc-dicalix **9** was reacted with ~2.5 equiv of **3** in the presence of ~5 equiv of K_2CO_3 and excess of KI in acetonitrile to give **10**. Deprotection by CF_3CO_2H in CH_2Cl_2 gave pure **11**. Compound **11** was reacted with K_2CO_3 and C_2H_5I in refluxing acetonitrile for three days to produce **6**, which was purified on silica with 85:15 CH_2Cl_2/acetone as eluent. The ^{1}H NMR spectrum of **6** displayed three singlets (in a 1:1:2 integration ratio) at 0.85 ppm, 0.91 ppm and 1.12 ppm for the *tert*-butyl groups. Two AB systems appeared at 2.71 ppm and 3.05 ppm with J=13.2 Hz (corresponding to the AB system of ArCH_2Ar



Scheme 1. Synthesis of **4**. Reagents and conditions: **3**, K_2CO_3, KI, acetonitrile, reflux four days.



Scheme 2. Synthesis of **5** and **6**. Reagents and conditions: (i) $(CH_3)_2NCH_2CH_2NH_2$, methanol/toluene, reflux 14 h; (ii) **3**, K_2CO_3, KI, acetonitrile, reflux three days; (iii) $NH(CH_2CH_2NH_2)_2$, methanol/toluene, reflux six days; (iv) $(Boc)_2O$, CH_2Cl_2, room temperature, 12 h; (v) **3**, K_2CO_3, KI, acetonitrile, reflux 24 h; (vi) CF_3CO_2H, CH_2Cl_2, room temperature, 4 h; (vii) C_2H_5I, K_2CO_3, acetonitrile, reflux three days.

with H-bonding of the type pyrenemethyl–CONH···OHAr) and 3.24 ppm and 4.02 ppm (J=13.5 Hz) for the remaining ArCH_2Ar. Two singlets were observed at 4.14 ppm and 4.73 ppm for the –OCH_2CONH– and a doublet at 5.30 ppm (J=3.3 Hz) for the CONHCH_2–pyrene protons. Two triplets were detected at 8.62 ppm (J=3.6 Hz) and 9.12 ppm (J=5.4 Hz) for the –CONH–. The presence of the NC_2H_5 group was indicated by a triplet at 2.70 ppm (J=6.2 Hz) for the NCH_2CH_3 and a quartet at 3.67 ppm (J=6.2 Hz) for the NCH_2CH_3. In addition to the NMR

results, all the analytical data were in agreement with the given structures **5**–**11**. Compounds **5** and **6** showed resonances at about 32 ppm in their ^{13}C NMR spectra and were assumed to adopt the cone conformation.

The fluorescence behaviour of **4**, **5** and **6** was investigated in CH_3CN in the presence of various metal perchlorates (Fig. 1) in large excess. Only **4** showed a marked response to any metal ions, with a strong increase in fluorescence for Al(III) and a slightly weaker increase for In(III).[9,10] This enhanced fluorescence is attributed to the formation of a complex in which the geometry favours intramolecular excimer formation by pairs of pyrene residues, indicated by the stronger emission enhancement being near 480 nm. Such excimer formation is not possible with monofunctionalised **5**, and we assume that the weaker ligating ability of **6** causes the pyrene units not to be brought into proximity.

Quantitative titration of an acetonitrile solution of **4** with Al^{3+} caused significant fluorescence changes depending upon the amount of metal added. Upon the addition of up to 60 equiv of Al^{3+} to **4**, the excimer emission at 480 nm gradually decreased while the monomer emission at 394 nm concomitantly increased, with an isoemissive point at 424 nm (Fig. 2a). This is presumably because Al^{3+} complexation to the *tren* part causes less efficient π–π^* interaction of two pyrenes, and thus excimer emission to decline. Addition of more than 60 equiv of the Al^{3+} ion provided the increasing emission in both monomer and excimer bands responsible for the effects defined in Figure 1. It is possibly an example of CHEF (CHelation-Enhanced Fluorescence)[1d,1p,11] due to the metal ion coordinating to an atom otherwise engaged in PET, as well as being due to the proximity of pyrene units in an M_2L species. An approximate value for the association constant defining the initial interaction of Al(III) with **4** in an ML species was estimated[12] to be 8700 ($\pm$15) M^{-1}.

^1H NMR studies were conducted to locate the binding site of Al(III) in **4**. The spectrum of the free ligand (Fig. 3a) and that in the presence of an excess of $Al(ClO_4)_3 \cdot nD_2O$ (Fig. 3b) show marked differences only in the chemical shifts of the *tren* CH_2 protons, with threefold symmetry seemingly

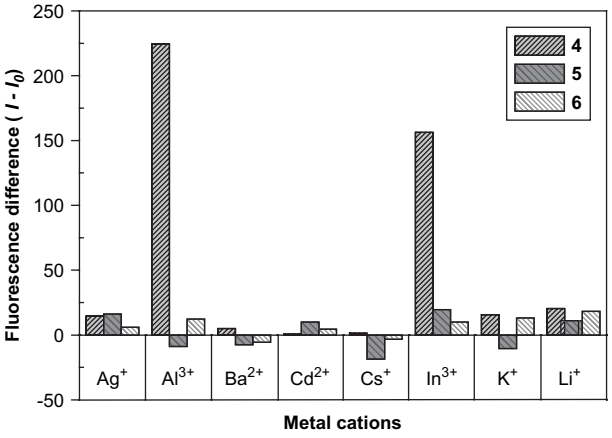


Figure 1. Bar profiles of fluorescence changes (I–I_0) of 1.0 μM solutions of **4**, **5** and **6** in CH_3CN upon addition of 500 equiv of various metal ions. Excitation at 343 nm; I_0: fluorescence emission intensity of free ligands; I: fluorescence emission intensity of metal complexes of ligands.

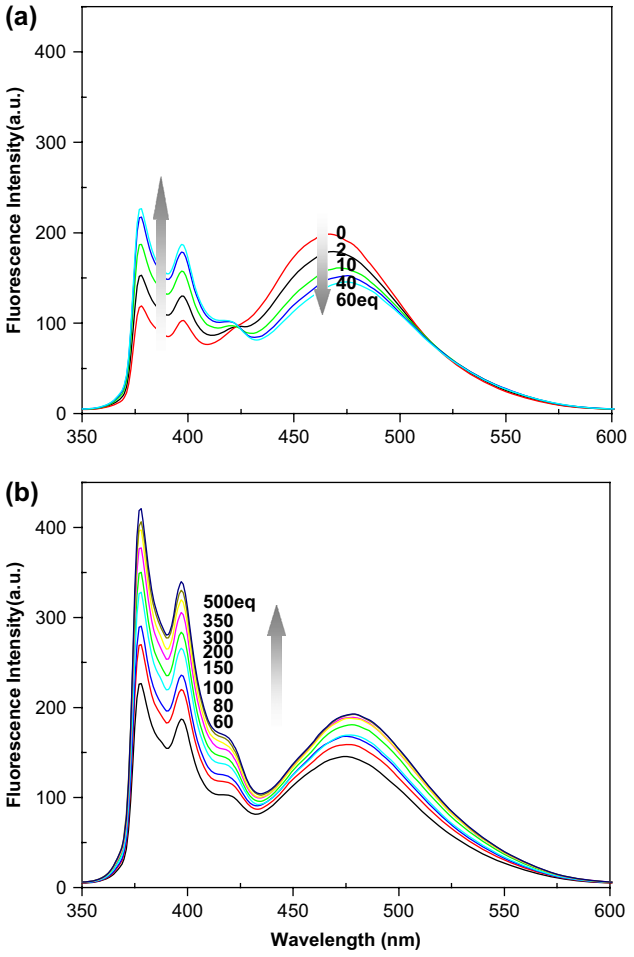


Figure 2. Fluorescence emission spectra change of **4** with increasing Al^{3+} (a) from 0 equiv to 60 equiv and (b) from 60 equiv to 500 equiv in CH_3CN. The excitation wavelength is 343 nm.

maintained. Similar observations of strong downfield shifting of the *tren* CH_2 signals were made during the complexation of parent *tren-N*-tricalix **1** with zinc.[5]

The NMR solution was used to obtain a MALDI-TOF mass spectrum, providing evidence for a 1:1 complex in the solution with m/z=3051.541 (**4**+Al^{3+}−2H^+). A plausible model of the coordination mode of Al(III) when bound to **4**, which explains all these data is shown in Figure 4. Similar binding modes have been proposed for various tripodal systems based on *tren*.[1b]

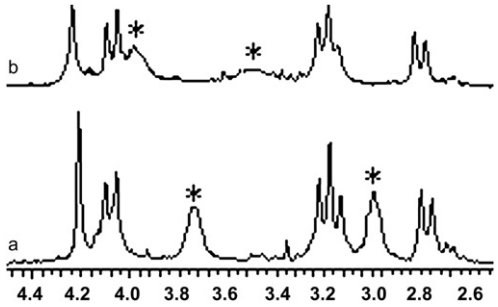


Figure 3. Partial ^1H NMR spectra of (a) free ligand **4** and (b) **4** in the presence of an excess of $Al(ClO_4)_3 \cdot nD_2O$.

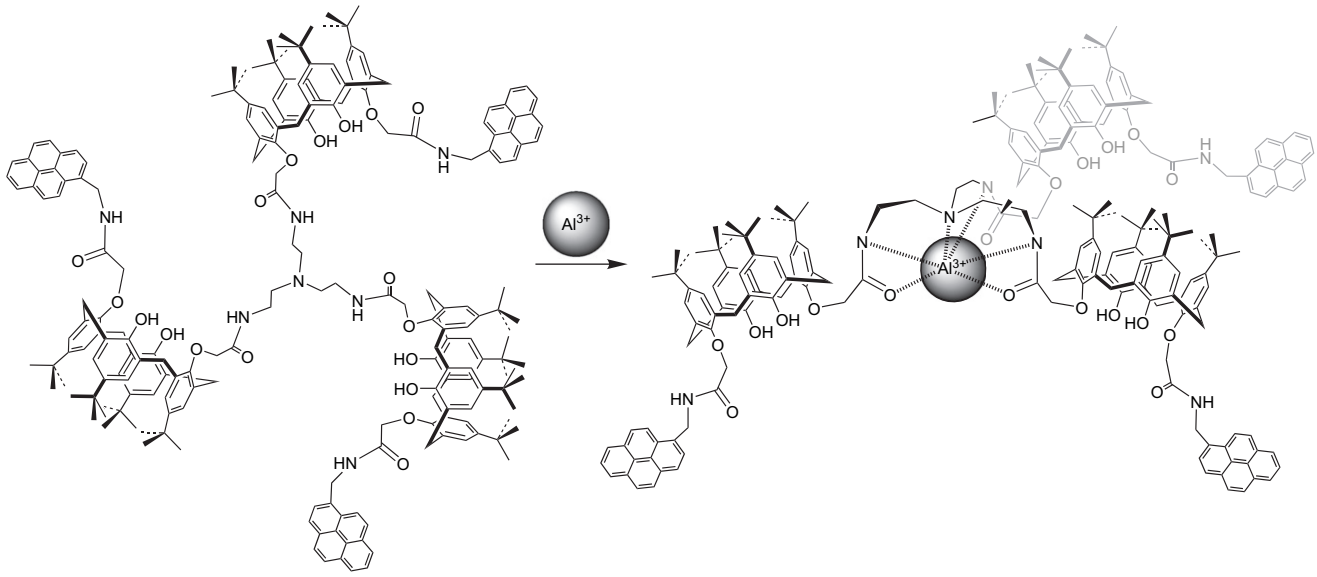


Figure 4. Tentative mode of complexation of Al^{3+} cation by **4**.

3. Conclusions

Aluminium is the most widely distributed and abundant metal in the environment and is extensively used in modern life.[13] It is neurotoxic and can induce many diseases, such as Alzheimer's disease, Parkinson's disease, amyotrophic lateral sclerosis, etc.[13] Compared to other metal cations, chemosensors aimed to detect and evaluate concentrations of aluminium are not so developed and the need to prepare molecular probes for this metal exists.[10] In the present paper we have synthesised a novel pyrenyl-appended tricalix[4]arene (**4**) which shows enhanced fluorescence in the presence of Al(III). We have shown the need for the receptor to be tripodal for complexation to occur. Of importance seems the fact that the chelating part of the receptor is separated from the signalling moieties.[9] In our case the separation is made by the use of calixarenes, which are selectively 1,3-dialkylated. On this line we prepared related tripodal sensors and bearing various photoreactive antennae to use other kinds of fluorescence properties.

In addition, preliminary investigation showed that the fluorescence enhancement observed with Al(III) is significantly affected by the counter-anion, indicating that the complex **4**–Al^{3+} might find further application in anion sensing. Work is also currently under development in this direction in our laboratories.

4. Experimental section

4.1. General

Uncorrected melting points (Mps), Büchi 500. ^{1}H NMR, Bruker SY 200 (300 MHz, δ in parts per million from TMS, J in hertz in $CDCl_3$ or CD_3CN, TMS as standard). MALDI-TOF mass spectra, Biflex Bruker. All the reactions were run under N_2 atmosphere. SiO_2 (Geduran 1.11567) was used for column chromatography. All reagents and solvents were commercial and used without further purification. Fluorescence spectra were recorded with an RF-5301PC spectrofluorophotometer. Stock solutions (1.00 mM) of the metal perchlorate salts were prepared in CH_3CN. Stock solutions of **4**, **5** and **7** (0.06 mM) were prepared in CH_3CN as well. For all measurements, excitation was at 343 nm with excitation and emission slit widths at 3.0 nm. Fluorescence titration experiments were performed using 6.0 μM solutions of **4** in CH_3CN and various concentrations of metal perchlorate in CH_3CN.

4.2. Preparation of 4

Compound **1** (680 mg, 0.307 mmol), K_2CO_3 (339 mg, 2.456 mmol), **3**[6] (0.377 g, 1.228 mmol), an excess of KI and acetonitrile (13 mL) were refluxed for four days. After evaporation under reduced pressure, the residue was dissolved in CH_2Cl_2 and washed with aqueous 1 N HCl. The organic layer was dried over Na_2SO_4, filtrated and evaporated. Chromatography on an SiO_2 column (90:10 CH_2Cl_2/acetone) gave pure **4**. White solid. Mp=275–276 °C. ^{1}H NMR ($CDCl_3$): 9.17 (t, 3H, J=7.1 Hz, N*H*CO), 8.86 (t, 3H, J=7.3 Hz, N*H*CO-pyrenyl), 8.27–7.37 (m, 27H, pyrene-*H*), 6.93 (s, 6H, ArO*H*), 6.78–6.52 (m, 24H, Ar*H*), 5.33 (s, 6H, OCH_2CO-pyrenyl), 4.87 (s, 6H, OCH_2CO), 4.22 (s, 4H, NHCH_2-pyrenyl), 4.07 (d, 6H, J=13.2 Hz, AB system, ArCH_2Ar), 3.70–3.73 (m, 6H, NCH_2CH$_2$NHCO), 3.21 (d, 6H, J=13.2 Hz, AB system, ArCH_2Ar), 3.23 (d, 6H, J=13.5 Hz, AB system, ArCH_2Ar), 3.02–2.96 (m, 6H, NCH$_2$CH_2NHCO), 2.77 (d, 6H, J=13.5 Hz, AB system, ArCH_2Ar), 1.06 (s, 54H, *tert*-butyl), 0.918 (s, 27H, *tert*-butyl), 0.865 (s, 27H, *tert*-butyl). ^{13}C NMR ($CDCl_3$): 206.913, 168.416, 148.871, 147.669, 142.062, 132.402, 132.023, 131.167, 130.884, 130.566, 128.085, 127.343, 127.215, 126.678, 126.391, 125.933, 125.676, 125.324, 124.838, 124.698, 124.469, 122.720, 74.752, 54.051, 53.253, 43.218, 37.744, 33.944, 33.889, 33.575, 32.191, 31.501, 31.033, 30.865, 30.814. MW=3027.03 calculated for $C_{201}H_{225}N_7O_{18}$, (MALDI-TOF) m/z=3027.81. Yield 23%.

4.3. Preparation of 7

Compound **2** (0.334 g, 0.46 mmol), $(CH_3)_2NCH_2CH_2NH_2$ (0.081 g, 0.92 mmol) and (1:1) methanol/toluene (25 mL) were refluxed for 14 h. After evaporation of the solvents, **7** was isolated by SiO_2 column chromatography (CH_2Cl_2). White solid. Mp=213–214 °C. ^{1}H NMR ($CDCl_3$): 9.10 (t, 1H, *J*=6.0 Hz, N*H*), 7.10–7.01 (m, 8H, Ar*H*), 4.57 (s, 2H, ArOCH_2), 4.27 (d, 2H, *J*=13.8 Hz, AB system, ArCH_2Ar), 4.22 (d, 2H, *J*=13.2 Hz, A′B′ system, ArCH_2Ar), 3.65 (q, 2H, *J*=5.7 Hz, NHCH_2), 3.50 (s, 2H, *J*=13.8 Hz, AB system, ArCH_2Ar), 3.45 (s, 2H, *J*=13.2 Hz, A′B′ system, ArCH_2Ar), 2.65 (t, 2H, *J*=6.3 Hz, NCH_2), 2.38 (s, 6H, N–(CH_3)$_2$), 1.24 (s, 9H, *tert*-butyl), 1.23 (s, 18H, *tert*-butyl), 1.18 (s, 9H, *tert*-butyl). Yield 52%.

4.4. Preparation of 5

Same procedure as for **4**. Compound **7** (358 mg, 0.460 mmol), K_2CO_3 (63 mg, 0.460 mmol), **3** (212 mg, 0.691 mmol), KI (excess), acetonitrile (10 mL), reflux for three days, SiO_2 column (95:5 CH_2Cl_2/acetone). White solid. Mp=262–264 °C. ^{1}H NMR ($CDCl_3$): 10.18 (br s, 1H, N*H*), 9.66 (s, 1H, O*H*), 9.39 (br s, 1H, N*H*), 9.12 (s, 1H, O*H*), 8.38–7.95 (m, 9H, pyrene-*H*), 7.09–6.99 (m, 8H, Ar*H*), 5.15 (d, 2H, *J*=6.0 Hz, CH_2–NH pyrene), 4.78 (s, 2H, OCH_2CO), 4.72 (s, 2H, OCH_2C=O), 4.23 (d, 2H, *J*=15.0 Hz, AB system, ArCH_2Ar), 4.03 (d, 2H, *J*=15.0 Hz, A′B′system, ArCH_2Ar), 4.03 (br s, 2H, $(CH_3)_2$NCH_2), 3.90 (q, 2H, *J*=6.0 Hz, HNCH_2), 3.45 (d, 2H, *J*=15.0 Hz, AB system, ArCH_2Ar), 3.41 (s, 6H, N(CH_3)$_2$), 3.38 (d, 2H, *J*=15.0 Hz, A′B′ system, ArCH_2Ar), 1.23 (s, 9H, *tert*-butyl), 1.21 (s, 18H, *tert*-butyl), 1.17 (s, 9H, *tert*-butyl). ^{13}C NMR ($CDCl_3$): 169.464, 162.380, 148.677, 147.901, 143.891, 132.742, 131.173, 131.027, 130.691, 130.299, 128.649, 128.220, 127.649, 127.486, 127.409, 126.772, 126.002, 125.911, 125.319, 125.272, 124.888, 123.005, 74.754, 65.028, 63.354, 53.387, 52.671, 41.521, 34.275, 34.050, 33.949, 33.691, 33.229, 32.190, 31.645, 31.486, 31.461, 31.116, 29.702. MW=1048.41 calculated for $C_{69}H_{81}N_3O_6$, *m*/*z*=1048.22. Yield 21%.

4.5. Preparation of 8

Same procedure as for **7**. Compound **1** (3.00 g, 4.16 mmol), $NH(CH_2CH_2NH_2)_2$ (0.141 g, 1.38 mmol), 1:1 methanol/toluene (40 mL), reflux for six days, SiO_2 column (95:5 CH_2Cl_2/acetone). White solid. Mp=154–156 °C. ^{1}H NMR ($CDCl_3$): 9.17 (t, 2H, *J*=5.3 Hz, N*H*CO), 7.07 (d, 4H, *J*=2.3 Hz, Ar*H*), 7.05 (d, 8H, *J*=7.3 Hz, Ar*H*), 6.98 (d, 4H, *J*=2.3 Hz, Ar*H*), 4.56 (s, 4H, OCH_2CO), 4.21 (q, 8H, *J*=13.2 Hz, AB system, ArCH_2Ar), 3.68 (q, 4H, *J*=5.7 Hz, NHCH_2CH$_2$NHCO), 3.41 (t, 8H, *J*=13.2 Hz, AB system, ArCH_2Ar), 3.15 (t, 4H, *J*=6.0 Hz, NHCH$_2$CH_2NHCO), 1.23 (s, 18H, *tert*-butyl), 1.22 (s, 36H, *tert*-butyl), 1.17 (s, 18H, *tert*-butyl). Yield 68%.

4.6. Preparation of 9

Compound **8** (502 mg, 0.337 mmol), $(Boc)_2O$ (147 mg, 0.675 mmol), CH_2Cl_2 (10 mL) were stirred at rt for 12 h. The solvents were evaporated under reduced pressure. After workup as for **4**, pure **9** was precipitated with methanol. White solid. Mp=169–171 °C. ^{1}H NMR ($CDCl_3$): 10.13–9.29 (m, 8H, O*H* and N*H*CO), 7.06 (s, 2H, Ar*H*), 7.05 (s, 8H, Ar*H*), 7.04 (s, 2H, Ar*H*), 6.99 (s, 4H, Ar*H*), 4.54 (s, 4H, OCH_2CONH), 4.25 (d, 4H, *J*=12.0 Hz, AB system, ArCH_2Ar), 4.15 (d, 4H, *J*=12.0 Hz, A′B′ system, ArCH_2Ar), 3.76 (br s, 4H, NHCH_2CH$_2$NHCO), 3.69 (br s, 4H, NHCH$_2$CH_2NHCO), 3.41 (d, 8H, *J*=12.0 Hz, AB and A′B′systems, ArCH_2Ar), 1.47 (s, 9H, *tert*-butyl-Boc), 1.23 (s, 18H, *tert*-butyl), 1.22 (s, 36H, *tert*-butyl), 1.17 (s, 18H, *tert*-butyl). Yield 58%.

4.7. Preparation of 10

Same procedure as for **4**. Compound **9** (500 mg, 0.31 mmol), K_2CO_3 (218 mg, 1.58 mmol), **3** (243 mg, 0.79 mmol), KI (excess), acetonitrile (10 mL), reflux for 24 h. Pure **10** was precipitated with EtOH. White solid. Mp=185–186 °C. ^{1}H NMR ($CDCl_3$): 9.09 (br s, 2H, N*H*CO), 8.87 (br s, 1H, N*H*CO-pyrenyl), 8.70 (br s, 1H, N*H*CO-pyrenyl), 8.27–7.68 (m, 18H, pyrene-*H*), 6.87 (br s, 2H, Ar*H*), 6.75 (s, 12H, Ar*H*), 6.57 (s, 4H, Ar*H*), 6.51 (s, 4H, Ar*H*), 5.33 (s, 4H, OCH_2CONH-pyrenyl), 4.78 (s, 4H, OCH_2CO), 4.11 (br s, 4H, NHCH_2–pyrene), 4.07 (s, 4H, NHCH_2CH$_2$NHCO), 3.79 (s, 4H, NHCH$_2$CH_2NHCO), 3.58 (d, 4H, *J*=11.6 Hz, AB system, ArCH_2Ar), 3.25 (d, 4H, *J*=11.6 Hz, AB system, ArCH_2Ar), 3.01 (d, 4H, *J*=12.0 Hz, A′B′ system, ArCH_2Ar), 2.69 (d, 4H, *J*=12.0 Hz, A′B′ system, ArCH_2Ar), 1.55 (s, 3H, *tert*-butyl-Boc), 1.49 (s, 6H, *tert*-butyl-Boc), 1.13 (s, 36H, *tert*-butyl), 0.93 (s, 18H, *tert*-butyl), 0.86 (s, 18H, *tert*-butyl). Yield 35%.

4.8. Preparation of 11

Compound **10** (500 mg, 0.235 mmol) and 1:1 trifluoroacetic acid/dichloromethane (10 mL) were stirred at rt for 4 h. The solvents were evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4, filtrated and evaporated to give pure **5**. White solid. Mp=181–182 °C. ^{1}H NMR ($CDCl_3$): 9.23 (t, 2H, *J*=6.0 Hz, N*H*CO), 9.14 (t, 2H, *J*=3.0 Hz, N*H*CO-pyrenyl), 8.24–8.01 (m, 18H, pyrene-*H*), 6.92 (s, 4H, ArO*H*), 6.83 (d, 4H, Ar*H*), 6.77 (s, 4H, Ar*H*), 6.65 (s, 4H, Ar*H*), 6.60 (d, 4H, Ar*H*), 5.32 (d, 4H, *J*=3.1 Hz, NHCH_2–pyrene), 4.73 (s, 4H, OCH_2CO), 4.11 (s, 4H, OCH_2CO-pyrenyl), 4.05 (d, 4H, *J*=13.2 Hz, AB system, ArCH_2Ar), 3.87 (q, 4H, NHCH_2CH$_2$NHCO), 3.35 (t, 4H, NHCH$_2$CH_2NHCO), 3.28 (d, 4H, *J*=13.5 Hz, A′B′ system, ArCH_2Ar), 3.08 (d, 4H, *J*=13.2 Hz, AB system, ArCH_2Ar), 2.84 (d, 4H, *J*=13.5 Hz, A′B′ system, ArCH_2Ar), 1.16 (s, 36H, *tert*-butyl), 0.95 (s, 18H, *tert*-butyl), 0.91 (s, 18H, *tert*-butyl). MW=2023.69 calculated for $C_{134}H_{151}N_5O_{12}$, (MALDI-TOF) *m*/*z*=2023.57. Quantitative yield.

4.9. Preparation of 6

Same procedure as for **4**. Compound **11** (297 mg, 0.148 mmol), K_2CO_3 (30 mg, 0.22 mmol), C_2H_5I (34 mg, 0.22 mmol), acetonitrile (4 mL), reflux for three days, SiO_2 column (85:15 dichloromethane/acetone). White solid. Mp=186–187 °C. ^{1}H NMR ($CDCl_3$): 9.12 (t, 2H, *J*=3.6 Hz, N*H*CO), 8.62 (t, 2H, *J*=5.4 Hz, N*H*CO-pyrenyl), 8.24–7.72

(m, 18H, pyrene–*H*), 6.76 (d, 4H, *J*=2.1 Hz, Ar*H*), 6.74–6.70 (m, 8H, Ar*H* and ArO*H*), 6.56 (s, 4H, Ar*H*), 6.52 (d, 4H, *J*=2.1 Hz, Ar*H*), 5.32 (d, 4H, *J*=3.3 Hz, NHCH_2–pyrene), 4.73 (s, 4H, OCH_2CO), 4.14 (s, 4H, OCH_2-CONH-pyrenyl), 4.02 (d, 4H, *J*=13.5 Hz, AB system, ArCH_2Ar), 3.62–3.68 (m, 6H, CH_2CH_2), 3.67 (q, 2H, *J*=6.2 Hz, NCH_2CH_3), 3.24 (d, 4H, *J*=13.5 Hz, AB system, ArCH_2Ar), 3.05 (d, 4H, *J*=13.2 Hz, A′B′ system, ArCH_2Ar), 2.85 (t, 4H, *J*=7.5 Hz, CH_2–CH_2), 2.71 (d, 4H, *J*=13.2 Hz, A′B′ system, ArCH_2Ar), 2.70 (t, 3H, *J*=6.2 Hz, CH_2CH_3), 1.12 (s, 36H, *tert*-butyl), 0.91 (s, 18H, *tert*-butyl), 0.85 (s, 18H, *tert*-butyl). ^{13}C NMR ($CDCl_3$): 170.865, 168.593, 149.095, 148.656, 148.207, 148.148, 142.671, 132.312, 131.960, 130.876, 130.530, 129.872, 128.095, 127.552, 126.885, 126.248, 126.068, 125.834, 125.772, 125.498, 125.093, 124.848, 74.738, 74.331, 48.194, 43.199, 36.448, 34.003, 33.975, 33.697, 32.098, 31.531, 31.166, 30.861, 30.842. MW=2052.75 calculated for $C_{136}H_{155}N_5O_{12}$, (MALDI-TOF) *m*/*z*=2051.63. Yield 62%.

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