Supplementary information

1. Special details relating to single crystal X-ray diffraction data

2. Experimental details

1. Special details for single crystal X-ray data

Compound 5: Due to the presence of a badly disordered chloroform molecule that could not be modeled appropriately, the routine SQUEEZE was applied to the data.[S1] This had the effect of dramatically improving the agreement indices.

Compound 9·Py: A number of restraints were applied to the data due to disordered pyridine molecules. As there was no way of identifying the position of the nitrogen atoms of these molecules due to the disorder, all atoms were modeled as C over disordered positions with partial occupancies.

Compound 10·Py: Restraints were applied due a calixarene carboxylate group that is disordered over two positions and is modeled at partial occupancies. Due to the presence of a badly disordered pyridine molecules in the interstitial voids between nanotubes (i.e. Py not taking part in direct - and therefore ordered - nanotube linking), the routine SQUEEZE was applied to the data to remove this diffuse electron density.[S1] This had the effect of dramatically improving the agreement indices.

2. Experimental

Microanalyses were repeatedly returned with values that suggested the inclusion of solvent within the calixarene cavity. As this is the case, these have not been included in this section. Notably all molecules were identified by ^{1}H and ^{13}C NMR, MS and IR spectroscopy.

25,27-Dihydroxy-26,28-di-ethoxycalix[4]arene (5)

Calix[4]arene (3.0066g, 7.22 mmol) was added to a solution of potassium carbonate (4.9768g, 36.01 mmol) and iodoethane (3.5 mL, 43.76 mmol) in acetone (150 mL). The solution was stirred at 80^{0}C for 24 h and then quenched with 1M HCl (100 mL) whereupon chloroform (2 × 50mL) was added to extract the product. The organic layer was washed with water (100mL), dried ($MgSO_4$) and solvent was removed under reduced pressure. Compound **5** was obtained as a pale yellow solid in a 36% yield. Recrystallisation from chloroform afforded single crystals that were suitable for X-ray diffraction studies.

^{1}H NMR ($CDCl_3$, 200MHz) δ 1.67 (2t, 6H, ^{3}J = 7 Hz), 3.41 (d, 4H, ^{2}J = 14 Hz), 4.13 (q, 4H, ^{3}J = 7 Hz), 4.36 (d, 4H, ^{2}J = 14 Hz), 6.70 (m, 4H), 6.95 (d, 4H, ^{3}J = 8 Hz), 7.08 (d, 4H, ^{3}J = 8 Hz), 8.30 (s, 2H).

25,27-Dihydroxy-26,28-di-n-propoxycalix[4]arene (6)

Calix[4]arene (3.00g, 7.1 mmol) was added to a solution of potassium carbonate (4.91g, 35.5 mmol) and iodopropane (3.1mL, 35.5 mmol) in acetone (150 mL). The solution was stirred at 80^{0}C for 24 h and then quenched with 1M HCl (100 mL) whereupon chloroform (2 × 50 mL) was added to extract the product. The organic layer was washed with water (100 mL), dried ($MgSO_4$), and solvent was removed under reduced pressure. The crude yellow solid was dissolved in acetone and left to crystallise. Compound **6** was obtained as colourless crystals in 93% yield.

^{1}H NMR ($CDCl_3$, 200MHz) δ1.30 (t, ^{3}J = 7.4 Hz, 3H), 1.95 – 2.16 (m 2H), 3.36 (d, ^{2}J = 12.9 Hz, 2H), 3.96 (t, ^{3}J = 6.2 Hz, 2H), 4.30 (d, ^{2}J = 12.9 Hz, 2H), 6.75 – 6.79 (m, 2H), 6.91 (d, ^{3}J = 7.5 Hz, 2H), 7.04 (d, ^{3}J = 7.5 Hz, 2H), 8.32 (s, 1H).

25,27-Dihydroxy-26,28-di-ethoxy-3,9,15-triformylcalix[4]arene (7)

Compound **5** (1.4700g, 3.06 mmol) was added to a mixture of hexamethylenetetramine (7.2618g, 51 mmol) in trifluoroacetic acid (15 mL, 201 mmol),. The solution was stirred at 125 ^{0}C for 24 h and was quenched with ice water (100 mL) whereupon $CHCl_3$ (2 × 50mL) was added to extract the product. The organic layer was washed with water (100mL), dried ($MgSO_4$) and solvent was removed under reduced pressure. Compound **7** was obtained as a bright yellow solid which was crystallised from chloroform in a 15 % yield. **MS** [M]+ = 564.35. **^{1}H NMR** (200MHz, $CDCl_3$): δ 1.67 (2t, 6H, ^3J = 7 Hz, C$\underline{H}_3$), 3.51 and 3.57 (2d, 4H, ^2J = 14 Hz and 14 Hz, ArC$\underline{H}_2$Ar), 4.10 (2q, 4H, ^3J = 5.3 Hz, -OC$\underline{H}_2$), 4.26 and 4.34 (2d, 4H, ^2J = 14 Hz and 14 Hz, ArC$\underline{H}_2$Ar), 6.77 (t, 1H, ^3J = 7.5 Hz, Ar$\underline{H}$), 6.95 (d, 2H, ^3J = 8 Hz, Ar$\underline{H}$), 7.47 and 7.65 (2s, 6H, Ar$\underline{H}$), 8.95, 9.66 and 9.80 (3s, 3H, C$\underline{H}$O). **^{13}C NMR** (100.6MHz, $CHCl_3$): δ 15.17, 15.43 (C$\underline{H}_3$), 31.30, 31.47 (C$\underline{H}_2$), 72.53, 72.93 (C$\underline{H}_2$), 127.78, 128.65, 128.76, 132.27, 134.06 (Ar$\underline{C}$), 125.63, 129.35, 130.88, 131.00 (Ar$\underline{C}$H), 151.54, 156.89 (Ar$\underline{C}$OCH$_2$), 159.24 (Ar$\underline{C}$OH), 191.11, 191.23 (H$\underline{C}$O).

25,27-Dihydroxy-26,28-di-propoxy-3,9,15-triformylcalix[4]arene (8)

Compound **6** (1.5109g, 2.97 mmol) was added to a mixture of hexamethylenetetramine (7.2323g, 51.59 mmol) in trifluoroacetic acid (25 mL, 335 mmol). The solution was stirred at 125 ^{0}C for 24 h and was quenched with ice water (100 mL) whereupon $CHCl_3$ (2 × 50mL) was added to extract the product. The organic layer was washed with water (100mL), dried ($MgSO_4$) and solvent was removed under reduced pressure. Compound **8** was obtained as a bright yellow solid in 69 % yield. **MS** [M]+ = 592.37. **^{1}H NMR** (200MHz, $CDCl_3$): δ 1.30 (2t, ^3J = 7.5 Hz, 6H, C$\underline{H}_3$), 2.10 (m, 4H, -OCH$_2$C$\underline{H}_2$CH$_3$), 3.58 (2d, , ^2J = 14 Hz, 4H, ArC$\underline{H}_2$Ar), 4.02 (m, 4H, -OC$\underline{H}_2$), 4.29 (2d, 4H, ^2J = 14 Hz, ArC$\underline{H}_2$Ar), 6.77 (t, 1H, ^3J = 7, Ar$\underline{H}$), 6.95 (d, 2H, ^3J = 8.0, Ar$\underline{H}$), 7.49 and 7.65 (2s, 6H, Ar$\underline{H}$), 9.67 and 9.79 (2s, 3H, C$\underline{H}$O).

25,27-Dihydroxy-26,28-di-ethoxy-3,9,15-tricarboxylatocalix[4]arene (9)

Compound **7** (0.07g, 0.12 mmol) was dissolved in a 1:1 mixture of dimethyl sulfoxide:water and cooled to 0^{0}C where sodium chlorate (0.12g, 1.31 mmol) and

monosodium phosphate (0.23g, 1.92 mmol) were added. The solution was made basic with a solution of sodium carbonate then washed with ethyl acetate (50 mL) and acidified with conc HCl to afford **9** as an orange solid (49 %). Small single crystals of **9·Py** were obtained by slow evaporation of a pyridine solution of **9** over a period of several days.

MS *m/z* = 635.2 Found = 635.2 **^{1}H NMR** (200MHz, CD_3OD): δ 1.57 (2t, 6H, ^{3}J= 7.5 Hz, $C\underline{H}_3$), 3.50 and 3.57 (2d, 4H, ^{2}J= 10 Hz and 10 Hz, $ArC\underline{H}_2Ar$), 4.07 (m, 4H, $-OC\underline{H}_2$), 4.25 and 4.33 (2d, 4H, ^{2}J = 10 Hz and 10 Hz, $ArC\underline{H}_2Ar$), 6.65 (t, 1H, ^{3}J = 7.5 Hz, Ar<u>H</u>), 6.92 (d, 2H, ^{3}J = 4 Hz, Ar<u>H</u>), 7.62 and 7.87 (3s, 6H, Ar<u>H</u>). **^{13}C NMR** (100.6MHz, CD_3OD): δ 15.68 ($\underline{C}H_3$), 32.21, 32.25 (2 × $\underline{C}H_2$), 73.97, 74.05 (2 × $\underline{C}H_2$), 122.62, 129.09, 129.49, 134.21, 134.95 (Ar<u>C</u>), 126.70, 130.45, 131.98, 132.21 (Ar<u>C</u>H), 153.14, 157.51 ($Ar\underline{C}OCH_2$), 159.16 (Ar<u>C</u>OH), 169.23, 170.26 (<u>C</u>OOH).

25,27-Dihydroxy-26,28-di-propoxy-3,9,15-tricarboxylatocalix[4]arene (10)

Compound **8** (0.9945g, 1.68 mmol) was dissolved in a 1:1 mixture of dimethyl sulfoxide:water and cooled to 0^0C where sodium chlorate (1.29g, 14.02 mmol) and monosodium phosphate (2.35g, 17.03 mmol) were added. The solution was made basic with a solution of sodium carbonate then washed with ethyl acetate (100 mL) and acidified with conc HCl to afford 10 as a yellow solid (61 %). Thin needle shaped single crystals of **10·Py** were obtained by slow evaporation of a pyridine solution of **10** over a period of several days.

MS *m/z* = 640.36 Found = 663.4 **^{1}H NMR** (200MHz, CD_3OD): δ 1.15 (2t, 6H, ^{3}J= 7.2 Hz, $C\underline{H}_3$), 2.01 (m, 4H, $-OCH_2C\underline{H}_2CH_3$), 3.51 and 3.58 (2d, 4H, ^{2}J = 12 Hz and 12 Hz, $ArC\underline{H}_2Ar$), 3.85 (m, 4H, $-OC\underline{H}_2$), 4.26 and 4.33 (2d, 4H, ^{2}J = 7 Hz and 7 Hz, $ArC\underline{H}_2Ar$), 6.74 (t, 1H, ^{3}J = 7.5 Hz, Ar<u>H</u>), 6.94 (d, 2H, ^{3}J = 9 Hz, Ar<u>H</u>), 7.63 and 7.87 (2s, 6H, Ar<u>H</u>). **^{13}C NMR** (100.6MHz, CD_3OD): δ 11.55 ($\underline{C}H_3$), 11.62 ($\underline{C}H_3$), 24.69 (2 × $\underline{C}H_2$), 32.13 ($\underline{C}H_2$), 32.17 ($\underline{C}H_2$), 79.70 ($\underline{C}H_2$), 79.90 ($\underline{C}H_2$), 122.59, 128.87, 129.42, 134.22, 134.93 (Ar<u>C</u>), 126.77, 130.53, 132.01, 132.25 (Ar<u>C</u>H), 153.16 ($Ar\underline{C}OCH_2$), 157.37 ($Ar\underline{C}OCH_2$), 159.28 (2 × Ar<u>C</u>OH), 169.10 (<u>C</u>OOH), 170.24 (<u>C</u>OOH).

References:

S1. 1. A. L. Spek, *Acta Cryst. A46* 1990, C34.