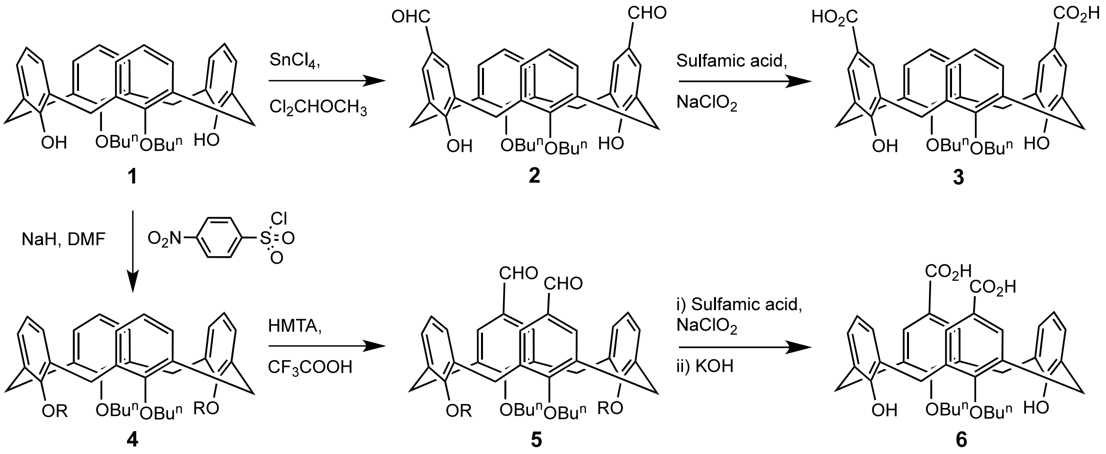
Supporting Information: Directed assembly via selectively positioned host functionality

Experimental Procedures

The synthesis of **3** - **5** was carried out according to literature or slightly modified literature procedures for related compounds.[S1-S3] All materials were purchased from Aldrich and used as supplied. All reactions were carried out under nitrogen atmosphere.



Scheme 1. Synthetic routes to building blocks **3**[S1] and **6.**[S2-S3]

Synthesis of Di-*O*-butoxy-di-*O*-bis(*p*-nitrobenezenesulfonyloxy)-calix[4]arene, 4: Compound **1** (5.00 g, 9.32 mmol) was dissolved in anhydrous DMF (200 mL). Sodium hydride (1.60 g, 40.0 mmol, 60% suspension in mineral oil) was added to the mixture and stirred at 0°C for 30 minutes. *p*-Nitrobenzene sulfonyl chloride (8.71 g, 39.2 mmol) was added to the cooled solution and the mixture was stirred at room temperature for 7 days. The mixture was then acidified with 1M HCl and extracted with DCM (4x100 mL), washed with deionised water, brine, and dried over $MgSO_4$. Solvent was removed under reduced pressure and the oily residue was dissolved in DCM (20 mL). Addition of methanol (150 mL) resulted in a precipitate which was filtered and washed with methanol to give pale yellow solid in 90% yield (7.62 g), mp: 255-258 °C. **^{1}H NMR** (300MHz, $CDCl_3$) δ = 8.36 – 8.33 (m, 4H, Ar-<u>H</u> (Nos)), 7.96 – 7.93 (m, 4H, Ar-<u>H</u>(Nos)), 7.00 – 6.95 (m, 4H, Ar-<u>H</u>), 6.87 – 6.82 (m, 2H, Ar-<u>H</u>), 6.40 – 6.34 (m, 2H, Ar-<u>H</u>), 6.16 – 6.09 (m, 4H, Ar-<u>H</u>), 3.92 (d, *J* = 13.2 Hz, 4H, Ar-$\underline{CH_2}$-Ar), 3.87 – 3.79 (m, 4H, -O-$\underline{CH_2}$-), 2.74 (d, *J* = 13.2 Hz, 4 H, Ar-$\underline{CH_2}$-Ar), 1.91 – 1.79 (m, 4 H, -O-CH_2-$\underline{CH_2}$-), 1.32 – 1.18 (m, 4H, -$\underline{CH_2}$-CH_3) 0.96 (t, *J* = 7.4 Hz, 6H, -$\underline{CH_3}$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 155.4, 152.6, 142.3, 134.0, 132.7, 130.3, 129.8, 128.9, 127.6, 126.9, 123.3, 119.4, 76.4, 31.8 30.3, 18.8, 13.9. **MS** *m/e* 930 (M + Na$^+$). **EA** calc for

$C_{48}H_{46}N_2O_{12}S_2$, C, 63.56; H, 5.11; N, 3.09%. Found C, 62.89; H, 5.24, N, 3.13%. **IR** ν_{max} 2961 cm^{-1} and 2943 cm^{-1} (C-H), 1531 cm^{-1} and 1367 cm^{-1} (N-O).

Synthesis of *p*-di-formyl-di-*O*-butoxy-di-*O*-bis(*p*-nitrobenezenesulfonyloxy)-calix[4]arene, 5: Compound **4** (2.50 g, 2.76 mmol), hexamethylenetetramine (12.0 g, 85.6 mmol) and trifluoroacetic acid (50 mL) were stirred together at 90°C for 24 hours. The reaction mixture was cooled to room temperature, poured onto 400 mL of cold water and extracted with DCM (3x100 mL). The combined organic layers were washed with water, brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the oily residue was dissolved in DCM (20 mL). Addition of methanol (150 mL) resulted in a precipitate which was filtered and washed with methanol to give pale yellow solid in 74% yield (1.95 g), mp > 300 °C. **^{1}H NMR** (300MHz, DMSO-d$_6$) δ = 9.88 (s, 2H, -CO$\underline{H}$), 8.54 – 849. (m, 4H, Ar-$\underline{H}$ (Nos)), 8.13 – 8.08 (m, 4H, Ar-$\underline{H}$(Nos)), 7.68 (s, 4H, Ar-$\underline{H}$), 6.57 – 6.52 (m, 2H, Ar-$\underline{H}$), 6.37 – 6.32 (m, 2H, Ar-$\underline{H}$), 6.16 – 6.09 (m, 4H, Ar-$\underline{H}$), 3.92 (d, *J* = 13.2 Hz, 4H, Ar-$\underline{CH_2}$-Ar), 3.88 – 3.80 (m, 4H, -O-$\underline{CH_2}$-), 3.13 (d, *J* = 13.2 Hz, 4 H, Ar-$\underline{CH_2}$-Ar), 1.83 – 1.76 (m, 4 H, -O-CH_2-$\underline{CH_2}$-), 1.28 – 1.16 (m, 4H, -$\underline{CH_2}$-CH_3) 0.92 (t, *J* = 7.4 Hz, 6H, -$\underline{CH_3}$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ = 192.2, 161.6, 152.7, 144.3, 141.2, 133.9, 131.1, 129.6, 128.8, 127.6, 126.8, 123.4, 119.6, 76.4, 31.9, 30.4, 18.9, 13.7. **MS** *m/e* 986 (M + Na$^+$). **EA** calc for $C_{50}H_{46}N_2O_{14}S_2$, C, 62.36; H, 4.81; N, 2.91%. Found C, 63.40; H, 5.01, N, 3.02%. **IR** ν_{max} 2961 cm^{-1} and 2943 cm^{-1} (C-H), 1684 cm^{-1} (C=O), 1531 cm^{-1} and 1367 cm^{-1} (N-O).

Synthesis of p-di-carboxylato-di-*O*-butoxy-di-*O*-bis(*p*-nitrobenezenesulfonyloxy)-calix[4]arene. Compound **5** (0.50 g, 0.52 mmol) was dissolved in a mixture of acetone (25 mL) and DCM (75 mL) and was cooled to 0°C. Sulfamic acid (0.20 g, 2.06 mmol) dissolved in water (3 mL) and sodium chlorite (0.16 g, 1.77 mmol) dissolved in water (3 mL) were added to the cooled solution and the mixture was stirred at room temperature for 24 h. Solvents were removed under reduced pressure and the solid was taken up with 1M HCl, filtered, washed with deionised water and dried to give pale yellow solid in 95% yield (0.49 g), mp (decomp): > 270°C. **^{1}H NMR** (300MHz, DMSO-d$_6$) δ = 12.78 (s, 2H, -COO$\underline{H}$), 8.56 – 8.52 (m, 4H, Ar-$\underline{H}$ (Nos)), 8.14 – 8.10 (m, 4H, Ar-$\underline{H}$(Nos)), 7.82 (s, 4H, Ar-$\underline{H}$), 6.58 – 6.52 (m, 2H, Ar-$\underline{H}$), 6.36 – 6.30 (m, 4H, Ar-$\underline{H}$), 3.94 – 3.88 (m, 4H, Ar-$\underline{CH_2}$-Ar), 3.85 – 3.82 (m , 4H, -O-$\underline{CH_2}$-), 3.15 – 3.09 (m, 4H, Ar-$\underline{CH_2}$-Ar), 1.85 – 1.73 (m, 4H, -O-CH_2-$\underline{CH_2}$-), 1.22 – 1.12 (m, 4H, -$\underline{CH_2}$-CH_3) 0.92 (t, *J* = 7.3 Hz, 6H, -$\underline{CH_3}$). **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d$_6$) δ = 166.3, 155.4, 152.6, 134.9, 134.0, 130.3, 128.9, 128.7, 127.6, 127.4, 126.9, 123.3, 119.4, 76.4, 31.4, 30.3, 18.8, 13.9. **MS** *m/e* 1018 (M + Na$^+$). **EA** calc for $C_{50}H_{46}N_2O_{16}S_2$, C, 60.35; H, 4.66; N, 2.82%. Found C, 60.47; H, 4.91, N, 2.90%. **IR** ν_{max} 2961 cm^{-1} and 2943 cm^{-1} (C-H), 3000 – 2760 cm^{-1} (broad COOH), 1680 cm^{-1} (C=O), 1602 cm^{-1} (C-O), 1531 cm^{-1} and 1367 cm^{-1} (N-O).

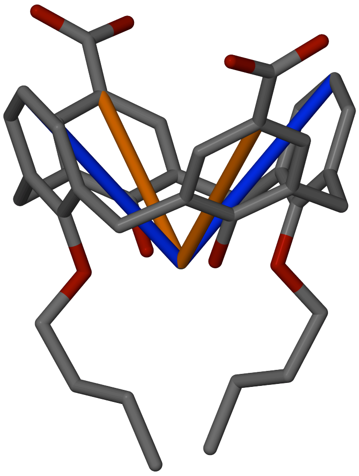
Synthesis of *p*-di-carboxylato-di-*O*-butoxy-calix[4]arene, 6: *p*-di-carboxylato-di-*O*-butoxy-di-*O*-bis(*p*-nitrobenezenesulfonyloxy)-calix[4]arene (0.50 g, 0.50 mmol) was dissolved in a mixture of ethanol (80 mL), DCM (80 mL) and 50 molar equivalent of potassium hydroxide (1.47 g, 26.0 mmol). The mixture was stirred at room temperature for 24 h, then acidified with 1M HCl and extracted with DCM (3x100 mL). Combined organic layers were washed with deionised water, brine and dried over $MgSO_4$. Solvents were removed under reduced pressure. The solid was taken up with hexane and filtered to give pale yellow solid in 87% yield (1.96 g); mp: > 300°C. **^{1}H NMR** (300MHz, DMSO-d_6) δ = 12.75 (s, 2H, -COO$\underline{H}$), 8.26 (s, 2H, -O$\underline{H}$), 7.62 (s, 4H, Ar-$\underline{H}$), 7.24 – 7.18 (m, 4H, Ar-$\underline{H}$), 6.69 – 6.62 (m, 2H, Ar-$\underline{H}$), 4.18 (d, *J* = 13.0 Hz, 4H, Ar-$\underline{CH_2}$-Ar), 3.98 (t, *J* = 6.0 , 4H, -O-$\underline{CH_2}$-), 3.59 (d, *J* = 13.0 Hz, 4H, Ar-$\underline{CH_2}$-Ar), 2.08 – 1.94 (m, 4H, -O-CH_2-$\underline{CH_2}$-), 1.82 – 1.74 (m, 4 H, -$\underline{CH_2}$-CH_3), 1.10 (t, *J* = 7.4 Hz, 6 H, -$\underline{CH_3}$). **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ = 166.3, 155.4, 152.6, 134.0, 130.3, 128.9, 127.6, 127.3, 119.4, 76.4, 31.8, 30.3, 18.8, 13.9. **MS** *m/e* 648 (M + Na^+). **EA** calc for $C_{38}H_{40}O_8$, C, 73.06; H, 6.45%. Found C, 72.58; H, 6.48%. **IR** ν_{max} 3330 cm^{-1} (OH), 2957 cm^{-1} and 2929 cm^{-1} (C-H), 3000 – 2760 cm^{-1} (COOH), 1686 cm^{-1} (C=O), 1600 cm^{-1} (C-O).

Synthesis of coordination polymer, 7: Compound **3** (28.1 mg, 0.045 mmol) and $Cd(NO_3)_2.4H_2O$ (138.7 mg, 0.45 mmol) were dissolved in 2 mL of DMF, followed by layering of 1,10-Phenanthroline (48.5 mg, 0.27 mmol) dissolved in 1 mL of MeOH. Slow evaporation of the solvents over several weeks resulted in the formation of colourless blocks suitable for X-ray diffraction studies.

Synthesis of metal-organic capsule, 8: Compound **6** (29.4 mg, 0.047 mmol) and $Cd(NO_3)_2.4H_2O$ (144.9 mg, 0.47 mmol) were dissolved in 2 mL of DMF, followed by layering of 1,10-phenanthroline (50.6 mg, 0.28 mmol) dissolved in 1 mL of MeOH. Slow evaporation of the solvents over several weeks resulted in the formation of colourless blocks suitable for X-ray diffraction studies.

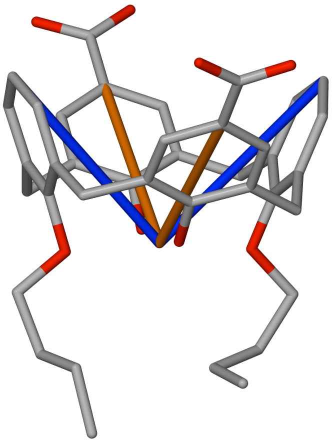
Additional Figures

Additional Figures showing the angles associated with the partially pinched-cone conformers observed **3·dmf**, **7** and **8**. In order to measure these angles we have generated a centroid between the four lower-rim O atoms and measured the angles from the top of distal phenyl rings within the molecules.



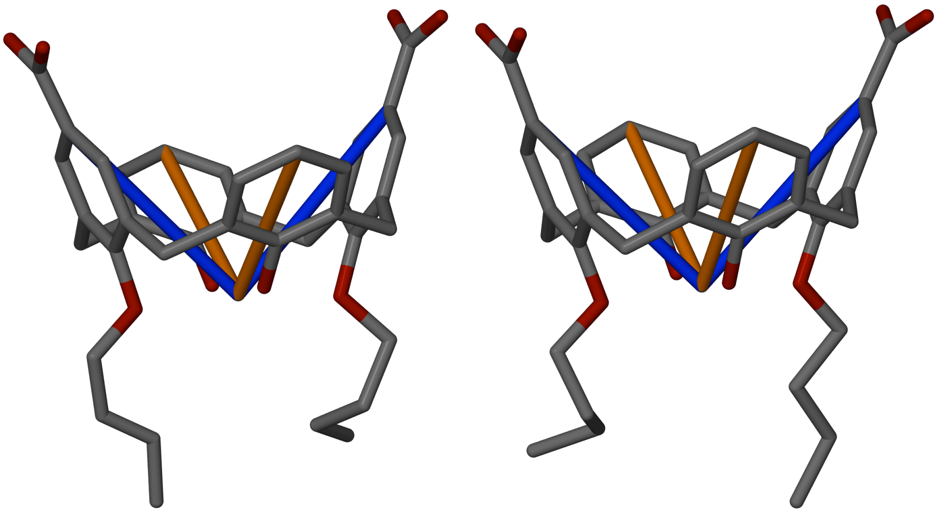
Orange: 107.8°
Blue: 88.4°

Figure S1. The *C*$_2$-Symmetric partial pinched-cone conformer of **3** found in **3·dmf**. The co-crystallised DMF and H atoms are omitted for clarity.



Orange: 111.2
Blue: 88.2

Figure S2. The partially pinched-cone conformer of **3** found in **7**.



Orange: 106.5
Blue: 91.0

Orange: 113.2
Blue: 88.6

Figure S3. Partial pinched-cone conformers found in **8**. The left and right hand calixarenes are those in the top and bottom of Figure 3A respectively.

References

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