Supplemental Information for manuscript:


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Information comprises:

- Crystal data and structural description of (1·MeCN)₂-ethylene glycol.
- Structural description of dimer found in 1·1.5EtOAc.
- ¹H and ¹³C NMR characterisation data for 1 and 2.
- X-ray powder diffraction patterns (XRPD’s) of 1·MeCN and 1·AqMeCN (Figure S5) compared with the calculated powder patterns of 1·MeOH and 1·EtOAc (Figure S6).
- XRPD of 2·MeOH compared with the calculated powder patterns of 2·MeCN (Figure S7).
Crystal data and structural description of (1·MeCN₂)-ethylene glycol.

The bi-layer structure of crude C-chlorobutylpyrogallol[4]arene (PgC₄Cl) co-crystallised with ethylene glycol (bi-product from synthesis) in acetonitrile.

Crystal data. C₉₈H₁₂₂Cl₈N₄O₂₆, M = 2055.60, triclinic, a = 12.663(4), b = 19.072(7), c = 21.232(7) Å, α = 102.169(6), β = 95.612(6), γ = 92.779(6)°, U = 4976(3) Å³, μ = 1.372 mm⁻¹, T = 173 K, space group P\textbar 1 (no. 2), Z = 2, Mo-Kα radiation (λ = 0.71073 Å), Final GOF = 1.006, R₁ = 0.0691, 35217 reflections measured, 21312 unique (R_int = 0.0294) which were used in all calculations. The final ωR(F²) was 0.2008 (all data). Minimum and maximum residual electron density (e Å⁻³) are –0.62 and 0.951 respectively.

Structural description.

The asymmetric unit of the structure contains two PgC₄Cl molecules, one molecule of ethylene glycol, and a total of four acetonitrile molecules, one of which is disordered (Figure S1). The ethylene glycol molecules form hydrogen bonds with the calixarene upper rim hydroxyl groups in the hydrophilic section of the bi-layer arrangement (Figure S2); two CH₂OH···OAr hydrogen bonds with distances of 1.977 and 2.061 Å, and one ArO···OHCH₂ hydrogen bond with a distance of 1.891 Å. The extended structure shows the distortion of the calixarene chlorobutyl groups within the hydrophobic section of the bi-layer arrangement (Figure S3).

Figure S1. The asymmetric unit showing the co-crystallisation of ethylene glycol, the disordered acetonitrile molecule and the disordered chlorobutyl chains of the calixarenes.
**Figure S2.** The hydrogen bonding interactions found between the ethylene glycol and the upper rim hydroxyl groups of the calixarenes (solvent molecules and calixarene chlorobutyl chains omitted for clarity).

**Figure S3.** Partial packing diagram showing the bi-layer arrangement and the distortion of the chlorobutyl chains. The disordered chlorobutyl chains have only been shown in one position and hydrogen atoms, solvent molecules and ethylene glycol have been omitted for clarity.
• Structural description of dimer found in 1·1.5EtOAc.

**Figure S4.** Skewed dimeric capsule arrangement found in 1·1.5EtOAc showing hydrogen bonding interactions (dashed red lines) and the disordered ethyl acetate molecule. Hydrogen atoms have been omitted for clarity.

**Brief structural description.**

The skewed dimeric capsule arrangement contains half of an ethyl acetate molecule that is disordered over two positions. The assembly is stabilised by three crystallographically unique hydrogen bonding interactions with OH···O distances of 2.732, 2.744, and 3.170 Å.
• $^1$H and $^{13}$C NMR, IR and MS characterisation data for 1 and 2.

C-Chlorobutylpyrogallol[4]arene, 1:
$^1$H NMR (500 MHz, CD$_3$CN) $\delta_H$: 6.89 (s, 1H, Ha), 4.27 (t, 1H, Hb, $^3J = 5$ Hz), 3.64 (2H, t, Hf, $^3J = 5$ Hz), 2.30 (2H, m, He), 1.86 (2H, m, He), 1.41 (2H, m, Hd).
$^{13}$C NMR (500 MHz, CD$_3$CN) $\delta_C$: 139.9, 133.5, 125.6, 114.4, 46.0, 35.0, 33.4, 32.8, 26.0.

C-Bromoocetylpyrogallol[4]arene, 2:
$^1$H NMR (500 MHz, CDCl$_3$) $\delta_H$: 8.7s (s, 1H, OH/Ha), 7.49 (s, 1H, OH/Ha), 6.88 (s, 1H, OH/Ha), 6.83 (s, 1H, OH/Ha), 4.37 (t, 1H, Hb, $^3J = 5$ Hz), 3.38 (2H, t, Hj, $^3J = 5$ Hz), 2.29 (2H, m, Hc), 1.86 (2H, m, Hi), 1.43 (10H, m, Hd – Hh).
$^{13}$C NMR (500 MHz, CDCl$_3$) $\delta_C$: 139.3, 138.1, 132.2, 126.1, 124.8, 114.5, 46.0, 35.1, 33.9, 33.6, 30.5, 30.3, 29.8, 28.9, 27.7.
• X-ray powder diffraction patterns (XRPD’s) of 1·MeCN and 1·AqMeCN compared with the calculated powder patterns of 1·MeOH and 1·EtOAc.

**Figure S5.** XRPDs of 1·MeCN and 1·AqMeCN.

The two powder patterns are similar with respect to a number of reflections.
Figure S6. Calculated XRPDs of 1·MeOH and 1·EtOAc.

When the experimental and calculated XRPD’s are compared, the strong low angle reflection is present in all experiments, although significant difference is observed in all four samples at higher angle. On the basis of the strong low angle reflection, all structures are assumed to be bi-layer arrangements.
- XRPD of 2-MeOH compared with the calculated powder patterns of 2-MeCN.

Figure S7. Experimental and calculated XRPD’s of 2-MeOH and 2-MeCN.

The experimental XRPD appears to show amorphous material and cannot be compared well with the calculated diffraction pattern from the crystal structure of 2-MeCN.