Self-assembled, Cogged Hexameric Nanotubes Formed from Pyrogallol[4]arenes with a Unique Branched Side Chain

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Supporting Information

Experimental Details

C-isopropylpyrogallol[4]arene (1). Yield (16%); mp. 320°C (dec.). ¹H-NMR (DMSO-d₆): 0.78-0.88 (m, 24H, C₃H₃), 2.88-3.12 (m, 4H, CH₂Me₂), 3.72 (d, J = 11.9 Hz, 4H, CH₂Ar), 6.65-7.02 (m, 4H, ArH), 8.09 (s, 4H, ArOH), 8.51-8.77 (m, 7H, ArOH). ¹³C-NMR (DMSO-d₆): 21.59, 21.64, 21.73, 21.80, 22.44, 26.08, 28.92, 29.06, 29.35, 42.29, 42.78, 61.25, 114.31, 114.63, 123.33, 123.59, 124.10, 124.36, 124.60, 132.89, 133.35, 138.86, 139.61, 139.73, 139.78, 140.40. FT-IR (solid): δ = 926, 970, 1008, 1074, 1123, 1310, 1386, 1480, 1501, 1622, 2871, 2959, 3315 cm⁻¹. FAB MS (CH₃OH, NBA matrix): Calculated for M = C₄₀H₄₈O₁₂Na (m/z = 743.3043). Observed m/z = 743.3037 (100%).

Compound 1 was crystallized from the mixture 20:19:1 (v/v/v) EtOAc:EtOH:H₂O in bilayer motif (gg11508). All solvent molecules were refined with isotropic displacement parameters and bond distance restraints (DFIX). A total of 8 water molecules and 7.5 molecules of EtOH (disordered and some refined with partial occupancy atoms) were modeled as solvents in the lattice. 3 of the i-Pr groups were disorder and the disorder was modeled with partial occupancy positions.

C₁₉₀H₃₁₄O₇₉, M = 3862.41, triclinic, a = 15.8184(5), b = 17.1252(6), c = 21.4783(10) Å, U = 5158.9(3) Å³, µ = 0.096 mm⁻¹, T = 100(2) K, space group P-1, Z = 1, GOF = 1.487, final R-indices (R₁ = 0.1428, ⁰R₂ = 0.4391), 65492 reflections collected, 18166 unique (Rint = 0.0588), CCDC 731660.

C-(3-pentyl)pyrogallol[4]arene (2). Yield (19%); mp. 276-278°C (dec.). ¹H-NMR (DMSO-d₆): 0.76 (t, J = 8.9 Hz, 24H, CH₃), 1.17-1.39 (m, 16H, CHCH₂Me), 2.67-2.91 (m, 4H, CH₂Et₂), 3.64 (d, 8.9 Hz, 1H, CH₂Ar), 3.97 (d, 8.9 Hz, 3H, CH₂Ar), 6.83-6.94 (m, 4H, ArH), 8.02-8.09 (m, 4H, ArOH), 8.45-8.82 (m, 6H, ArOH), 9.15 (s, 2H, ArOH). ¹³C-NMR (DMSO-d₆): 8.99, 9.32, 9.38, 9.60, 10.20, 20.70, 20.88, 21.34, 21.82, 36.11, 36.36, 36.94, 55.47, 114.75, 120.52, 123.00, 123.16,
123.76, 123.90, 124.23, 132.92, 133.31, 139.23, 139.69, 140.34. FT-IR (solid): \( \delta = 943, 970, 1030, 1080, 1206, 1260, 1315, 1381, 1474, 1633, 2877, 2959, 3299 \) cm\(^{-1}\).

FAB MS (CH\(_3\)OH, NBA matrix): Calculated for M = C\(_{48}\)H\(_{54}\)O\(_{12}\)Na (m/z = 855.4295). Observed m/z = 855.4293 (100%).

Compound 2 was crystallized from the mixture 20:19:1 (v/v/v) EtOAc:EtOH:H\(_2\)O in the nano-tubular motif (gg14408). 2 formed a solvate with 4 EtOH molecules, 10 full water and 4 half occupancy water (totally 12 water molecules). All solvent molecules were refined with similar ADP restraints ISOR and SIMU. Some solvents and side chain atoms were also refined with bond distance restraints (DFIX, SADI).

C\(_{152}\)H\(_{238}\)O\(_{52}\), M = 2897.42, triclinic, \( a = 12.5581(17), b = 29.097(5), c = 30.504(7) \) Å, \( U = 9743(3) \) Å\(^3\), \( \mu = 0.074 \) mm\(^{-1}\), \( T = 100(2) \) K, space group P\(-\)1, \( Z = 2, \) GOF = 1.129, final R-indices (\( R_1 = 0.1645, R_2 = 0.4975 \)), 103521 reflections collected, 33806 unique (\( R_{\text{int}} = 0.186 \)), CCDC 729499.

C-(4-heptyl)pyrogallol[4]arene (3). Yield (24%); mp. 262-265°C (dec.).

\(^1\)H NMR (DMSO-\(d_6\)): 0.77 (m, 24H, CH\(_3\)), 1.26 (m, 32H, CH\(_2\)), 2.73-3.02 (m, 4H, (C\(_3\)H\(_7\))\(_2\)CH), 3.61 (d, \( J = 11.9 \) Hz, 1H, C\(_3\)H\(_2\)Ar), 3.98 (d, \( J = 11.9 \) Hz, 3H, C\(_3\)H\(_2\)Ar), 6.79-6.90 (m, 4H, ArH), 8.02-9.18 (m, 12H, ArO). \(^{13}\)C-NMR (DMSO-\(d_6\)): 14.74, 14.86, 14.92, 14.96, 17.70, 17.95, 31.89, 32.03, 32.43, 33.26, 34.22, 37.09, 37.24, 37.52, 37.80, 114.59, 120.46, 123.00, 123.19, 123.71, 123.86, 124.17, 132.82, 133.27, 139.16, 139.25, 139.70, 139.76, 140.28, 140.47. FT-IR (solid): \( \delta = 939, 976, 1086, 1262, 1241, \) 1311, 1474, 1503, 1625, 2872, 2929, 2953, 3317, 3530 cm\(^{-1}\). FAB MS (CH\(_3\)OH, NBA matrix): Calculated for M = C\(_{56}\)H\(_{80}\)O\(_{12}\)Na (m/z = 967.5547). Observed m/z = 967.5542 (100%).

Compound 3 was crystallized from 20:19:1 (v/v/v) EtOAc:EtOH:H\(_2\)O in the bilayer motif (gg12609). Some atoms of the solvent molecules and side chains were refined with similar ADP restraints ISOR and SIMU as well as bond distance restraints (DFIX, SADI). A total of 5 molecules of EtOH (disordered and some refined with partial occupancy atoms) were modeled as solvents in the lattice.

C\(_{66}\)H\(_{110}\)O\(_{17}\), M = 1175.54, monoclinic, \( a = 14.4537(9), b = 27.4829(16), c = 33.817(2) \) Å, \( U = 13284.1 \) (14) Å\(^3\), \( \mu = 0.083 \) mm\(^{-1}\), \( T = 100(2) \) K, space group C\(2/c\), \( Z = 8, \) GOF = 1.030, final R-indices (\( R_1 = 0.0960, R_2 = 0.2766, \)) 108097 reflections collected, 111594 unique (\( R_{\text{int}} = 0.041, \)) CCDC 739768.


\(^{13}\)H NMR (DMSO-\(d_6\)): 0.82-0.84 (m, 24H, CH\(_3\)), 1.17-1.18 (m, 48H, CH\(_2\)), 2.70-3.00 (m, 4H, (C\(_4\)H\(_9\))\(_2\)CH), 3.56 (d, \( J = 11.9 \) Hz, 1H, CHAr\(_2\)), 4.00 (d, \( J = 11.9 \) Hz, 3H,
Compound 4 was crystallized from the mixture 20:19:1 (v/v/v) EtOAc:EtOH:H$_2$O in bilayer motif (gg17008). The title compound formed solvate with 4 EtOH molecules of which two are disordered. Some atoms of the solvent molecules and the side chains were refined with similar ADP restraints EADP, ISOR and SIMU as well as bond distance restraints (DFIX, SADI).

C$_{72}$H$_{120}$O$_{16}$, M = 1241.68, triclinic, a = 13.3006(13), b = 16.1323(15), c = 17.8421(16) Å, $\mu$ = 0.080 mm$^{-1}$, $T$ = 100(2) K, space group P-1, Z = 2, GOF = 1.051, final R-indices ($R_1$ = 0.0930, $\bar{R}_2$ = 0.3101), 67630 reflections collected, 12268 unique ($R_{int}$ = 0.045), CCDC 731659.

Additional Crystallographic Experimental Discussion

Due to the nature of these compounds it is extremely difficult to obtain crystalline products suitable for single crystal x-ray diffraction studies. In general we were able to get only poor quality single crystals for the series of compounds described below and in most cases, multiple data sets were collected and the best data set has been presented in this paper. As a result, the residual values are high (compounds 1 and 2) for all the data sets and these structural data were only used to supplement information from other sources. The number and types of solvent molecules in the lattices are the best models that could be refined using the available data. The number of solvent molecules even varied slightly from data set to data set of the same compound. In almost all cases the H atoms for the solvent water molecules have been omitted as it is not possible to locate these from difference Fourier maps. In some cases the H atoms for the side chains were not calculated as these resulted in short contacts with other disordered motifs.

Monolayer studies. HPLC grade chloroform from Aldrich (St. Louis, MO) was used to prepare amphiphile solutions with a concentration of ~1 mg mL$^{-1}$ as determined by mass. Solutions of 1, 2, 5 and 6 were heated to facilitate complete dissolution of compound. Surface pressure-area isotherm experiments were carried out on a Langmuir trough (Nima, UK). Pressure was measured with a Wilhelmy plate made out of filter paper. Subphase temperature was maintained at 23.0 ± 0.1 °C by an Isotemp 3016 circulating thermostat. The subphase contained ultrapure water with a resistivity of 18.2 MΩ (Millipore). Monolayers
were formed by spreading 50 μL of a CHCl₃ solution of compounds 1, 2, 5, and 6 (1.0 mg mL⁻¹) onto the subphase and allowing 10 minutes for the solvent to evaporate. Trough barriers were compressed at a constant speed of 20 cm²·mlc⁻¹ min⁻¹. Data are plotted as surface pressure (mN m⁻¹) vs. molecular area (Å²). Isotherm data were collected in triplicate on each of 3 separate days, resulting in a total of 9 individual trials for each compound to obtain accurate isotherm information. An average of these 9 trials appear in this communication.

**Brewster angle microscopy (BAM).** BAM images were collected using a MicroBAM2 (Nanofilm Technology, Göttingen, Germany) fitted over the Langmuir trough. The light source is a 659 nm laser diode with 30 mW maximum optical power. The images were captured by a CCD camera and stored on a PC. Field of view for raw image is approximately 3.6 mm wide x 4.1 mm high. Images were adjusted using GIMP 2 software to show a field of view of 2.0 mm x 2.0 mm in Figure 3. Barrier compression speed was ≈5 Å² molecule⁻¹ min⁻¹.