Supplementary Material (ESI) for Chemical Communications

Supporting information

For

Amphiphilic Behavior of an Apparently Non-polar Calix-arene

Patrick Shahgaldian, Anthony W. Coleman, Srinivasan S. Kuduva and Michael. J. Zaworotko

Table of content:

Langmuir isotherm experiment and Brewter Angle Microscopy.

The experiment was carried out on a Nima 601 trough on de-ionized purified water (resistivity>18 MΩ.cm). The spreading solution was prepared in chloroform (HPLC grade) and deposited on the water surface (30 min were allowed for the evaporation of the solvent and equilibration of the monolayer). Compressions and decompressions were performed at a continuous rate of 20 cm²/min.

Brewster Angle Microscopy imaging was carried out using a miniBAM (NanoFilm Technology, Germany) during the compression of the monolayer of **1** as described above.

Synthesis of 25,26,27,28 tetradodecyloxy-calix[4]arene

General: NMR spectra were recorded on a Varian 500 MHz in $CDCl_3$ with TMS as internal standard; values are expressed in ppm. Electrospray Mass spectrum was recorded on a Perkin-Elmer Sciex API 165 in positive mode. All chemicals were purchased from ACROS Organics, and used without further purification.

Under nitrogen atmosphere and magnetic stirring, in dry DMF, was added sodium hydride (0.66 g, 27 mmol) and 25,26,27,28-tetrahydroxycalix[4]arene (1.14 g, 2.7 mmol). After one minute stirring, bromododecane (6.7 g, 27 mmol) was added slowly. After 12 hours, the sodium hydride was neutralized with 14 mL of HCl 2M, the white precipitate was filtered and recrystallized from chloroform/methanol to yield **1** (93 %), as a colorless crystalline solid suitable for X-ray crystallography (mp= 187 °C).

^{1}H NMR: 6.68 (d, H_{meta}-Ar, 8H), 6.62 (t, H_{para}-Ar-OR, 4H), 4.52 and 3.21 (2d, Ar-CH_2-Ar, 8H), 3.96 (t, O-CH_2-, 8H), 1.99 (m, O-CH$_2$-CH_2, 8H), 1.46 (m, O-CH$_2$-CH$_2$-CH_2, 8H), 1.36 (m, CH_2, 64H), 0.92 (t, CH_3, 12H).

^{13}C NMR: 14.28 (*C*H$_3$), 23.05 (CH$_3$*C*H$_2$), 26.73 (CH$_3$CH$_2$*C*H$_2$), 29.00, 29.15, 29.80, 30.19, 30.38, 30.70, 30.89, 31.42((*C*H$_2$)$_8$), 32.29 (Ar-*C*H$_2$-Ar), 75.47 (O-*C*H$_2$), 121.60, 122,76, 127,81, 128,98, 135. 45, 156.92 (Ar).

ES/MS m/z = 1099 [M+H$^+$] ; 1121 [M+Na$^+$]

Colloidal suspension preparation and Photon Correlation Spectroscopy experiment

1 was dissolved in tetrahydrofuran (THF) at a concentration of 5 mg/mL. Under magnetic stirring (500 rpm), in a conical flask, to a volume of 3 mL of the THF solution, was added 100 mL of pure water (resistivity > 18 MΩ) at a constant flow rate of 300 mL/min. The slightly milky suspension was stirred for an additional minute. After evaporation of the solvent at 40°C under reduced pressure the final volume was adjusted at 100 mL.

Photon Correlation Spectroscopy measurements were carried out using a Malvern 4700 spectrometer and a Malvern 71320, 256 channel correlator with a 40 mW He-Ne (633 nm) laser source. All values were measured at an angle of 90° in 10 mm diameter cells. The system was thermostated at 25°C. All measurements were repeated five times, and the variance of the measurements was less than 5%. The

analysis of the measurements was performed using the computer program Contin (Malvern).

AFM imaging

Imaging was carried out using a Explorer AFM (Thermomicroscopes Inc. Santa Clara, USA) equipped with a 100 μm tripod scanner, in non-contact mode, using high resonant frequency (F_0=320 KHz) pyramidal cantilevers with silicon probes at a scan frequency of 1 Hz. Images are processed with the SPM Lab 5.01 software package and presented unfiltered.

The samples were prepared by depositing a suspension of **1**-based SLN on freshly cleaned microscope glass plates and dried overnight at room temperature.

Crystallographic Data

Intensity data for **1** were collected at 175 K on a Bruker SMART-APEX diffractometer using Mo_{ka} radiation (λ = 0.7107 Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structure was solved using direct methods and refined by full-matrix least-squares on $|F|^2$. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms.

Crystal data for **1**: Orthorhombic, Pbca, a = 18.760(1), b = 19.969(3), c = 36.601(6) Å, volume = 13711(4) $Å^3$, Z = 8, r_{cal} = 1.064 g cm^{-3}, μ = 0.063 mm^{-1}, F(000)= 4864, $2\theta_{max}$= 56.72° (-24<=h<=24, -26<=k<=-26, -48<=l<=44). Final residuals (for 722 parameters) were R1= 0.985 for 16731 reflections with I > 2σI, and

R1 = 0.2121, wR2 = 0.1870, GooF = 0.875 for all 118361 data. Residual electron density was 0.402 and –0.330 eÅ^{-3}.