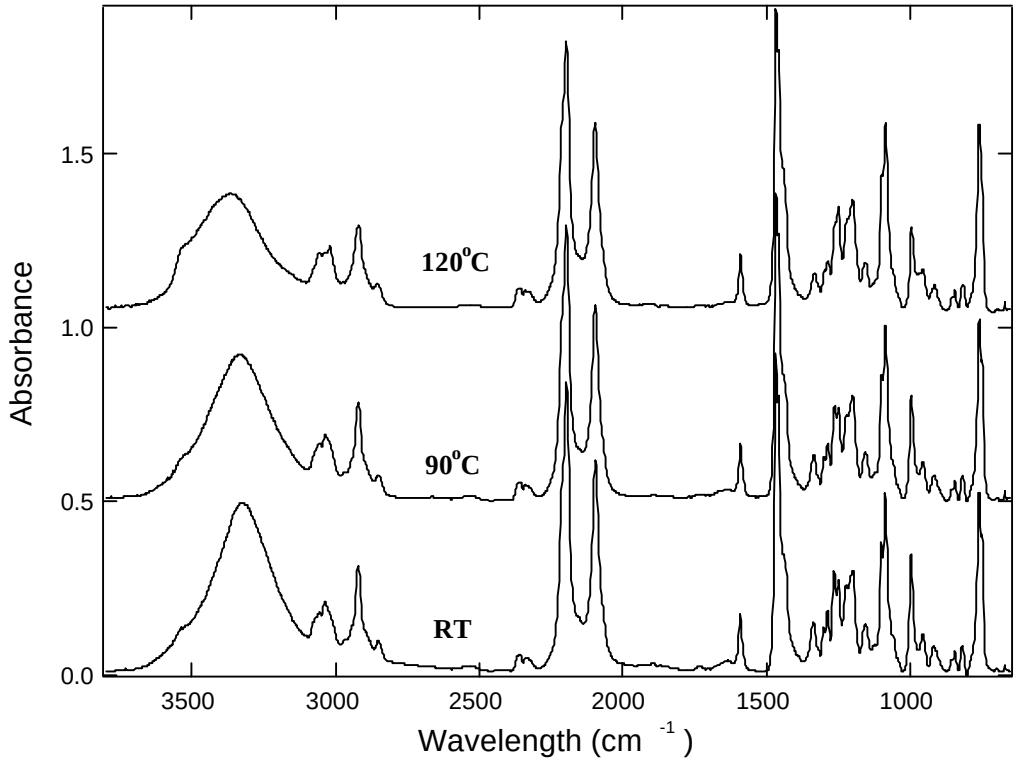
Supporting Information

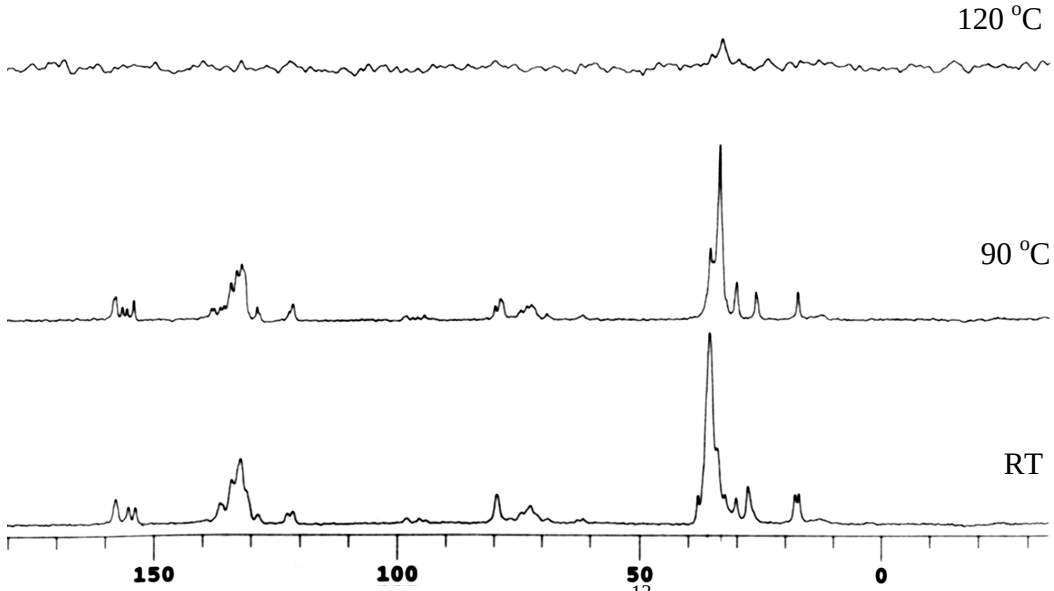
Experimental Procedure

1,3-O,O'-bis(dodecyl)calix[4]arene: A solution of calix[4]arene (1g, 2.36 mmol), 1-bromododecane (2.35g, 9.44 mmol), and K_2CO_3 (1.30g, 9.44 mmol) in DMF (100 ml) were stirred for 18 hrs at 95 ^oC. Once the reaction was stopped, the product mixture was concentrated under reduced pressure, and then extracted with methylene chloride (100 ml) / water (100 ml). The desired product was crystallized from methylene chloride solution by adding ethanol (200ml). Yield: 91%. ^{1}HNMR ($CDCl_3$) δ (ppm) showed characteristic of 1,3-bis-substitution. 7.03 (4H, d), 6.90 (4H, d), 6.72 (2H, t), 6.62 (2H, t), 8.17 (2H, s, Ar-OH) 4.30 (4H, d, Ar-CH_2-Ar), 3.35 ppm (4H, d, Ar-CH_2-Ar); alkyl chains (C_{12}). 3.98 (4H, t, Ar-O-CH_2-R)), 2.06 (4 H, t), 1.68 (4H, t), 1.44 (16 H, t), and 0.86 (6H, t). ^{13}C NMR ($CDCl_3$-d) δ (ppm): 153 & 151 (Ar-OR), 133 & 128 (Ar, *ortho* to OR), 127 & 126 (Ar, *meta* to OR), 122 & 121 (Ar, *para* to OR), 76.7 (CH_2-O-Ar), 31.9 (Ar-CH_2-Ar), 31.4-29.4 (Alkyl chains), 26.0 (γ'-CH_2), 22.7 (β-CH_2), 14.1 (α-CH_3). Mass spectrometry MALDI, Empirical Formula: $C_{52}H_{72}O_4$, m/z (%): 783.5 (100) [M + Na^+], 760.5 (23) [M^+]. IR(KBr): υ = 3300 (O-H), 3025-3070 (Ar-H, weak), 2922 (C-H, as), 2853 (C-H, s), 1466, 1440, 1267, 1248, 1216, 1196, 1159, 1089, 1008, 762 (1,2,3-sub-Ar), 753 (1,2,3-sub-Ar).

1,3-O,O'-bis(dodecyl)calix[4]arene-d_{50} with deuterated dodecyl ($C_{12}D_{25}$), 98%D: The exact same procedure as above was followed except that deuterated 1-bromododecane-d_{25} was used. Materials used are calix[4]arene (0.426g, 1.00 mmol), 1-bromododecane-d_{25} (1.00g, 3.65 mmol), and K_2CO_3 (0.553g, 2.22 mmol) in DMF (40 ml). Yield: 81%. ^{1}HNMR ($CDCl_3$) δ (ppm) 1,3-bis-substitution 7.04 (4H, d), 6.92 (4H, d), 6.78 (2H, t), 6.64 (2H, t), 8.28 (2H, s, Ar-OH) 4.30 (4H, d, Ar-CH_2-Ar), 3.35 ppm (4H, d, Ar-CH_2-Ar); no alkyl chains peaks since they are deuterated. Mass spectrometry MALDI, Empirical Formula: $C_{52}H_{23}D_{49}O_4$ (note: 98%D), m/z (%): 833.4 (100) [M + Na^+]. IR(KBr): υ = 3326 (O-H), 3025-3070 (Ar-H, weak), 2922 (C-H, as), 2852 (C-H, s), 2196 (C-D, as), 2094 (C-D, s), 1590, 1465, 1440, 1265, 1249, 1220, 1200, 1157, 1087, 995, 760 (1,2,3-sub-Ar), 748 (1,2,3-sub-Ar).



Supporting Information, Figure 1. Variable-temperature FTIR spectra of 1,3-O,O'-dodecylcalixarene-d_{50} with deuterated dodecyl chains. The vibration bands from 2800 to 3000 cm^{-1} are due to C-H vibration only, while the two vibration bands in the region of 2000 to 2500 cm^{-1} are due to C-D vibrations.



Supporting Information, Figure 2. Solid-state CP/MAS ^{13}C NMR of 1,3-O,O'-dodecylcalixarene at various temperatures. The alkyl chain resonances shift 2 ppm after T_1 and another 1 ppm after T_2.