**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$_2$CO$_3$ (1.30g, 9.44 mmol) in DMF (100 ml) were stirred for 18 hrs at 95 °C. 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 ($\gamma'$-CH$_2$), 22.7 ($\beta$-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): $\nu = 3300$ (O-H), 3025-3070 (Ar-H, weak), 2922 (C -H, as), 2853 (C -H, s), 2196 (C-D, as), 2094 (C-D, s), 1590, 1545, 1440, 1265, 1249, 1220, 1200, 1157, 1087, 995, 760 (1,2,3-sub-Ar), 748 (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 were calix[4]arene (0.426g, 1.00 mmol), 1-bromododecane-d$_{25}$ (1.00g, 3.65 mmol), and K$_2$CO$_3$ (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): $\nu = 3326$ (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 $T_2$. 