Synthesis. TLC-analysis was performed on silica gel (Merck, F254), $^1$H and $^{13}$C NMR spectra were measured at 300MHz (Varian Unity Innova Spectrometer) or 400 MHz (Varian VXR 400S Spectrometer). 1H chemical shifts are given in ppm (δ) relative to tetramethylsilane (TMS) as an internal standard. All triphenylene derivatives have been purified by column chromatography on the silica gel, using CH$_2$Cl$_2$ and CH$_2$Cl$_2$/MeOH as an eluent.

Scheme 1. Synthesis of 1a-1d. (A) Br-C$_n$H$_{2n}$-OH; K$_2$CO$_3$ in acetone or acetonitrile at 60°C; (B) FeCl$_3$ in dry CH$_2$Cl$_2$ at RT precipitated in cold MeOH; (C) 1) NaH in dry THF for 1h, 2) MeI;

1-hexyloxy-2-(ω-hydroxyalkyloxy)benzenes (2b, 2c) have been made from 2-hexyloxyphenol 4 by alkylation with appropriate bromoalcohol in the presence of K$_2$CO$_3$ in acetone.
1-hexyloxy-2-(6-hydroxyhexyloxy)benzene 2b (6.6 g, yield 87%); ¹H NMR (CDCl₃) δ (ppm): 6.88 (4H, s, ArH), 3.99 (4H, t, J = 6.6 Hz, ArOCH₂), 3.63 (2H, t, J = 6.4 Hz, -CH₂-OH) 1.83-0.88 (19H, m, -CH₂-CH₃); ¹³C NMR (CDCl₃) δ (ppm): 149.278, 149.20 (2 ArC-O), 121.14, 121.05 (2 ArC), 114.29, 114.20 (2 ArC), 69.32, 69.20 (2 O-CH₂), 62.80, 62.68 (1 CH₂-OH) 32.69-14.03 (9 -CH₂-)

1-hexyloxy-2-(11-hydroxyundecyloxy)benzene 2a (6.5 g, 69%) ¹H NMR (CDCl₃) δ (ppm): 6.88 (4H, s, ArH), 3.98 (4H, t, J = 6.6 Hz, ArOCH₂), 3.62 (2H, t, J = 6.6 Hz, -CH₂-OH) 1.83-0.90 (29H, m, -CH₂-CH₃); ¹³C NMR (CDCl₃) δ (ppm): 149.30 (2 ArC-O), 121.05 (2 ArC), 114.25 (2 ArC), 69.33 (2 O-CH₂), 63.01 (1 CH₂-OH) 32.82-14.04 (14 -CH₂-)

1a and 1b were prepared by FeCl₃ mediated coupling of 3,3’,4,4’-tetrahexyloxybiphenyl 3 and 1-hexyloxy-2-(ω-hydroxyalkyloxy)benzenes 2b and 2c resulting products with a total yield between 40-60%.

11-(6-hydroxyhexyloxy)-2,3,6,7,10-pentakishexyloxytriphenylene 1b (1.75 g, 40 %) ¹H NMR (CDCl₃) δ (ppm): 7.84 (6H, s, ArH), 4.23 (12H, t, J=6.6 Hz, ArOCH₂), 3.68 (2H, t, J = 6.6 Hz, CH₂-OH), 1.98-1.35 (48H, m, -CH₂-), 0.96-0.91 (15H, m, -CH₃); ¹³C NMR (CDCl₃) δ (ppm): 149.05, 148.96 (6 ArC-O), 123.70, 123.66 (6 ArC), 107.48 (6 ArC), 69.78, 69.61 (6 O-CH₂), 62.93 (2 CH₂-OH) 32.76-14.63 (29 -CH₂-CH₃). Phase behavior on cooling: I 68.5ºC Col 47.8ºC Cr

11-(11-hydroxyundecanoxy)-2,3,6,7,10-pentakishexyloxytriphenylene 1a (2.9 g, 59 %) ¹H NMR (CDCl₃) δ (ppm): 7.84 (6H, s, ArH), 4.23 (12H, t, J=6.6 Hz, ArOCH₂), 3.62 (2H, t, J = 6.6 Hz, CH₂-OH), 1.98-1.31 (58H, m, -CH₂-), 0.96-0.93 (15H, m, -CH₃); ¹³C NMR (CDCl₃) δ (ppm): 149.04 (6 ArC-O), 123.67 (6 ArC), 107.48 (6 ArC), 69.78 (6 O-CH₂), 63.07 (2 CH₂-OH) 32.83-14.06 (34 -CH₂-CH₃). Phase behavior on cooling: I 60.8ºC Col₁ 35ºC Col₂ 30ºC Cr

11-hydroxy-2,3,6,7,10-pentakishexyloxytriphenylene 5 has been prepared by coupling 3,3’,4,4’-tetrahexyloxybiphenyl 3 with 2-hexyloxyphenol 4 in the presence of FeCl₃.⁴²
Alkylation of 11-hydroxy-2,3,6,7,10-pentakis(hexyloxy)triphenylene with appropriate bromoalkohol in the presence of K₂CO₃ in acetone gives products 1a-d.

11-(4-hydroxybuthyloxy)-2,3,6,7,10-pentakis(hexyloxy)triphenylene 1c (0.646 g, yield 47%) ¹H NMR (CDCl₃) δ (ppm): 7.84-7.81 (6H, m, ArH), 4.28-4.21 (12H, m, ArOCH₂), 3.79 (2H, t, J = 6.6 Hz, CH₂-OH), 1.96-1.39 (44H, m, -CH₂-), 0.93 (15H, m, -CH₃); ¹³C NMR (CDCl₃) δ (ppm): 149.12, 149.08, 148.75, 148.42 (6 ArC-O), 123.71, 123.66, 123.43 (6 ArC), 107.57, 107.44, 106.78, 106.50 (6 ArC), 69.77, 69.39 (6 O-CH₂), 62.35 (2 CH₂-OH) 31.7-14.06 (27 -CH₂-CH₃). Phase behavior on cooling: l 71.2ºC Col 40ºC Cr

Compound 1d has been made by O-alkylation of 1a with iodomethane preceded by sodium alkoxide formation with NaH.

1d (0.45 g, 90 %) ¹H NMR (CDCl₃) δ (ppm): 7.84 (6H, s, ArH), 4.23 (12H, t, J=6.6 Hz, ArOCH₂), 3.35 (2H, t, J = 6.6 Hz, CH₂-OH), 3.32 (3H, s, O-CH₃) 1.94-1.31 (58H, m, -CH₂-), 0.94 (15H, m, -CH₃); ¹³C NMR (CDCl₃) δ (ppm): 148.95 (6 ArC-O), 123.60 (6 ArC), 107.3 (6 ArC), 72.97 (1 O-CH₃) 69.69 (6 O-CH₂), 58.54 (1 -CH₂-O) 31.88-14.08 (34 -CH₂-CH₃)