

Supporting Information to

Self-Assembly of Hybrid Dendrons into Doubly-Segregated Supramolecular Polyhedral Columns and Vesicles

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1. Materials

4-Hydroxybiphenyl (97%), 3,4-dihydroxybenzoic acid (98%), 3,4-dihydroxy-phenylacetic acid (98%), 6-hydroxy-2-naphthoic acid (97%), 1-bromododecane (98%), 2-ethylhexyl bromide (98%), 2-methoxyethanol (99%), triphenyl phosphine (99%) (all from Acros), (S)-(+)-citronellylbromide (95%), thionyl chloride (99.5%), LiAlH₄ (95%), anhydrous K₂CO₃, diisopropyl azodicarboxylate (DAID, 95%), aluminum oxide (activated, basic, Brockmann I, standard grade, ~150 mesh, 58 Å) (all from Aldrich), silica gel (60 Å, 32-63 µm) (Sorbent Technology), DMF, MeOH, EtOH, MgSO₄, H₂SO₄, acetone, diethyl ether, ethyl acetate (all from Fisher, ACS reagents) were used as received. Dichloromethane (Fisher, ACS reagent grade) was refluxed over CaH₂ and freshly distilled before use. THF (Fisher, ACS reagent grade) was refluxed over sodium/benzophenone until the solution turned purple and distilled before use. All other chemicals were commercially available and were used as received. Methyl 4'-hydroxy-4-biphenyl carboxylate has been synthesized according to a modified literature procedure.¹ Methyl 6-hydroxy-2-naphthoate, methyl 3,4-dihydroxybenzoate, and methyl 2-(3,4-dihydroxyphenyl) acetate were synthesized from the corresponding acids by Fisher esterification in refluxing MeOH in presence catalytic amount of H₂SO₄. The synthesis of methyl 3-(3,4-dihydroxyphenyl)-propanoate was reported previously.² (S)-1-bromo-3,7-Dimethyloctane was synthesized by a procedure reported by Swager et al.³ (4)12G0-CH₂Cl (1), (6Np)12G0CH₂Cl (8), (4-3,4)12G1-CO₂CH₃, (4-3,4)12G1-CH₂OH, (6Np-3,4)12G1-CO₂CH₃ and (6Np-3,4)12G1-CH₂OH were synthesized following the procedures previously reported from our laboratory.^{4,5,6}

2. Techniques

¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded on a Bruker DRX 500 instrument. The purity of the products was determined by a combination of thin-layer chromatography (TLC) on silica gel coated aluminum plates (with F₂₅₄ indicator; layer thickness, 200 µm; particle size, 2-25 µm; pore size 60Å, SIGMA-Aldrich) and high pressure liquid chromatography (HPLC) using THF as mobile phase at 1 mL/min, on a Shimadzu LC-10AT high pressure liquid chromatograph equipped with a Perkin Elmer LC-100 oven (40 °C), containing two Perkin-Elmer PL gel columns of 5 X 10² and 1 X 10⁴ Å, a Shimadzu SPD-10A UV detector (λ = 254 nm), a Shimadzu RID-10A RI-detector, and a PE Nelson Analytical 900 Series integrator data station.

Thermal transitions were determined on a TA Instruments Q100 differential scanning calorimeter (DSC) equipped with a refrigerated cooling system with 10 °C min⁻¹ heating and cooling rates. Indium was used as calibration standard. The transition temperatures were calculated as the

maxima and minima of their endothermic and exothermic peaks. An Olympus BX51 optical microscope (100 X magnifications) equipped with a Mettler FP82HT hot stage and a Mettler Toledo FP90 Central Processor was used to verify thermal transitions and to characterize anisotropic textures. Melting points were measured using a uni-melt capillary melting point apparatus (Arthur H. Thomas Company) and were uncorrected. Density (ρ_{20}) measurements were carried out by flotation in gradient columns at 20 °C.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a PerSeptive Biosystems-Voyager-DE (Framingham, MA) mass spectrometer equipped with a nitrogen laser (337 μm) and operating in linear mode. Internal calibration was performed using Angiotensin II and Bombesin as standards. The analytical sample was obtained by mixing the THF solution of the sample (5-10mg/ml) and THF solution of the matrix (3,5-dimethoxy-4-hydroxy-trans-cinnamic acid or 4-hydroxybenzylidenemalononitrile, 10mg/mL) in a 1/5 v/v ratio. The prepared solution of the sample and the matrix (0.5 μL) was loaded on the MALDI plate and allowed to dry at 23 °C before the plate was inserted into the vacuum chamber of the MALDI instrument. The laser steps and voltages applied were adjusted depending on both the molecular weight and the nature of each analyzed compound.

X-ray diffraction (XRD) measurements were performed using Cu- $K_{\alpha 1}$ radiation ($\lambda = 1.54178 \text{ \AA}$) from a Bruker-Nonius FR-591 rotating anode X-ray source equipped with a $0.2 \times 0.2 \text{ mm}^2$ filament operated at 3.4 kW. The Cu radiation was collimated and focused with Osmic™ confocal optics followed by circular pinholes, and the scattered radiation was detected using a Bruker Hi-Star™ multiwire (area) detector. To minimize attenuation and background scattering, an integral vacuum was maintained along the length of the flight tube and within the sample chamber. Samples were held in thin-wall glass capillaries (0.7 – 1.0 mm in diameter), mounted in a temperature-controlled oven (temperature precision: $\pm 0.1 \text{ }^\circ\text{C}$, temperature range from -120 °C to 270 °C). The distance between the sample and the detector was 11.0 cm for wide angle diffraction experiments and 54.0 cm for intermediate angle diffraction experiments respectively. Aligned samples for fiber XRD experiments were prepared using a custom made extrusion device. The powdered sample ($\sim 10 \text{ mg}$) was heated inside the extrusion device above isotropization temperature. After slow cooling from the isotropic phase, the fiber was extruded in the liquid crystal phase and cooled to 23 °C. Typically, the aligned samples had a thickness of $\sim 0.3\text{-}0.7 \text{ mm}$ and a length of $\sim 3\text{-}7 \text{ mm}$. All XRD measurements were done with the aligned sample axis perpendicular to the beam direction. Primary data analysis was performed using Datasqueeze Software (version 2.1.4). Molecular models were built using the Materials Studio Modeling version 3.1 software from Accelrys.

Simulations of the powder X-ray diffraction data of the bilayer cubic phases followed the methodology described in the article. The numerical calculation of the Fourier transform of the polyhedral domains generated by the described scaled Voronoi tessellation procedure, were performed using 3-dimensional numerical integration based on the midpoint rule and also on the Monte Carlo methods. The presented final fits were performed using the midpoint rule based on a 64×64×64 3-dimensional numerical grid. The accuracy of the grid was tested by calculating the volume of the Voronoi polyhedrons of the cubic phase. The 64×64×64 numerical grid provided these volumes with an error of 0.5%.

3. Synthesis of the Hybrid Dendrons

Methyl 2-[3,4-bis{4'-(dodecyloxy)benzyloxy}phenyl]acetate, (4-3,4Et)12G1-CO₂CH₃ (4): To a thoroughly degassed suspension of anhydrous K₂CO₃ (1.38 g, 10.0 mmol) in DMF (25 mL) was added methyl 2-(3,4-dihydroxyphenyl) acetate, **2** (0.46 g, 2.5 mmol) and the resulting mixture was heated to 80 °C with continuous degassing. (4)12G0-CH₂Cl (1.56 g, 5.0 mmol) was added and the reaction was stirred at 80 °C under N₂ for overnight. The reaction was cooled to room temperature and poured into cold water. The precipitate was collected by vacuum filtration and the wet solid was passed through basic alumina using DCM as an eluent. The crude product was then purified by column chromatography (SiO₂, EtOAc:Hexane = 1:9) followed by precipitation in MeOH to give the title compound, **4** as a white solid: 1.17 g (64%). HPLC: 99+%; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.88 (t, 6H, J = 7.0 Hz), 1.20-1.39 (overlapped m, 32H), 1.45 (m, 4H), 1.77 (m, 4H), 3.51 (s, 2H), 3.66 (s, 3H), 3.94 (overlapped t, 4H, J = 6.5 Hz), 5.03 (s, 2H), 5.04 (s, 2H), 6.76 (dd, 1H, J = 2.0, 8.0 Hz), 6.69 (m, 6H), 7.32 (m, 4H); ¹³C NMR (125 MHz, CDCl₃, 27 °C, TMS): δ = 14.3, 22.8, 26.2, 29.4, 29.5, 22.5, 29.7, 29.7, 29.8, 29.8, 32.1, 40.8, 52.1, 68.14, 71.3, 71.4, 114.5, 115.6, 116.5, 122.3, 127.3, 129.1, 129.2, 129.2, 129.3, 137.2, 148.4, 149.2, 158.9, 159.0, 172.3; MALDI-TOF m/z: 753.20 ([M+Na]⁺ calculated for C₄₇H₇₀NaO₆ 753.51).

2-[3,4-Bis{4-(dodecyloxy)benzyloxy}phenyl]ethanol, (4-3,4Et)12G1-CH₂OH (5): To a slurry of LiAlH₄ (23 mg, 0.60 mmol) in dry THF at 0 °C was added slowly (4-3,4Et)12G1-CO₂CH₃, **4** (0.29 g, 0.40 mmol) in dry THF (25 mL) under N₂, and the resulting mixture was allowed to stir at room temperature for 2 h. The reaction was cooled to 0 °C and quenched by successive addition of H₂O (1x mL), 15% aq. NaOH (1x mL), and H₂O (3x mL) with continuous stirring until H₂ evolution ceased. The reaction mixture was filtered through celite and the lithium salts rinsed generously with THF. The filtrate was dried over anhydrous Na₂SO₄, filtered and concentrated to dryness. After precipitation in

MeOH from CH₂Cl₂, the title compound **5** (0.26 g, 93%) was obtained as white solid. HPLC: 99+%; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.88 (t, 6H, J = 7.0 Hz), 1.20-1.39 (overlapped m, 32H), 1.45 (m, 4H), 1.77 (m, 4H), 2.76 (t, 2H, J = 6.5 Hz), 3.78 (q, 2H, J = 6.0 Hz), 3.95 (t, 4H, J = 6.5 Hz), 5.04 (s, 2H), 5.06 (s, 2H), 6.72 (dd, 1H, J = 2.0, 8.0 Hz), 6.81 (d, 1H, J = 2.0 Hz), 6.87 (overlapped peaks, 5H), 7.32 (m, 4H); ¹³C NMR (125 MHz, CDCl₃, 27 °C, TMS): δ = 14.3, 22.9, 26.3, 29.5, 29.5, 29.6, 29.8, 29.8, 29.8, 29.9, 32.1, 38.9, 63.9, 68.2, 71.5, 71.6, 114.6, 115.9, 116.7, 122.1, 129.2, 129.3, 129.5, 131.9, 148.1, 149.3, 159.1, 159.1; MALDI-TOF m/z: 725.39 ([M+Na]⁺ calculated for C₄₆H₇₀NaO₅ 725.51).

Methyl 3-[3,4-bis{4-(dodecyloxy)benzyloxy}phenyl]propanoate, (4-3,4Pr)12G1-CO₂CH₃ (6): This compound was synthesized by the same procedure described for the synthesis of **4**. From methyl 3-(3,4-dihydroxyphenyl)-propanoate (0.67 g, 3.42 mmol), K₂CO₃ (2.8 g, 20 mmol) and (4)12G0-CH₂Cl (2.13 g, 6.8 mmol) in DMF (80 mL), 1.53 g (60%) of the title compound **6** was obtained as white powder after purification by gravity column chromatography (basic alumina, CH₂Cl₂) followed by recrystallization from acetone/MeOH. HPLC: 99+%; ¹H NMR (500 MHz, CDCl₃, 27 °C) δ = 0.93 (t, 9H, J = 6.9 Hz), 1.22-1.60 (m, 40H), 1.75-1.88 (m, 4H), 2.61 (t, 2H, J = 7.8 Hz), 2.89 (t, 2H, J = 7.8 Hz), 3.70 (s, 3H), 3.99 (m, 4H), 5.07 (s, 4H), 6.74 (dd, 1H, J = 2.0, 8.2 Hz), 6.84 (d, 1H, J = 1.9 Hz), 6.86-6.98 (m, 5H), 7.32-7.45 (m, 4H); ¹³C NMR (125 MHz, CDCl₃, 27 °C) δ = 14.0, 22.6, 25.9, 29.2, 29.3, 29.4, 29.5, 29.5, 29.5, 29.6, 30.4, 31.8, 35.8, 51.5, 67.9, 71.2, 114.3, 115.8, 120.9, 128.9, 129.0, 133.9, 147.6, 149.0, 158.8, 158.8, 173.3; MALDI-TOF m/z: 767.38 ([M+Na]⁺ calculated for C₄₈H₇₂NaO₆ 767.23).

Methyl 2-[3,4-bis{(6-(dodecyloxy)naphthalen-2-yl)methoxy}phenyl]acetate, (6Np-3,4Et)12G1-CO₂CH₃ (8): This compound was synthesized by the same procedure described for the synthesis of **4**. From methyl 2-(3,4-dihydroxyphenyl) acetate (0.46 g, 2.5 mmol), K₂CO₃ (1.38 g, 10.0 mmol) and (6Np)12G0-CH₂Cl, **7** (1.81 g, 5.0 mmol) in DMF (50 mL), 0.75 g (36%) of the title compound **8** was obtained as white solid after purification by column chromatography (SiO₂, EtOAc:Hexane = 1:9) followed by precipitation in MeOH. HPLC: 99+%; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.88 (t, 6H, J = 6.5 Hz), 1.20-1.42 (overlapped m, 32H), 1.50 (m, 4H), 1.84 (m, 4H), 2.51 (s, 2H), 3.61 (s, 3H), 4.01 (t, 4H, J = 6.5 Hz), 5.25 (s, 2H), 5.27 (s, 2H), 6.78 (dd, 1H, J = 1.5, 8.0 Hz), 6.93 (d, 1H, J = 8.5 Hz), 6.96 (d, 1H, J = 1.5 Hz), 7.12 (m, 4H), 7.51 (m, 2H), 7.63 (m, 2H), 7.69 (dd, 2H, J = 5.5, 8.5 Hz), 7.80 (d, 2H, J = 11.0 Hz); ¹³C NMR (125 MHz, CDCl₃, 27 °C, TMS): δ = 14.3, 22.8, 26.3, 29.4, 29.5, 29.6, 29.7, 29.8, 29.8, 29.8, 32.1, 40.8, 52.1, 68.2, 71.7, 71.8, 106.6, 115.5, 116.4, 119.3, 122.4, 125.9, 126.1, 126.3, 126.5, 127.2, 127.4, 128.8, 129.5, 129.6, 132.4, 132.5, 134.4, 134.4, 148.5, 149.3, 157.4, 172.3; MALDI-TOF m/z: 853.94 [M+Na]⁺ calculated for C₅₅H₇₄NaO₆ 853.54).

Methyl 3-[3,4-bis{(6-(dodecyloxy)naphthalen-2-yl)methoxy}phenyl]propanoate, (6Np-3,4Pr)12G1-CO₂CH₃ (9): This compound was synthesized by the same procedure described for the synthesis of **4**. From methyl 3-(3,4-dihydroxyphenyl)-propanoate (0.24 g, 1.2 mmol), K₂CO₃ (0.68 g, 4.9 mmol) and (6Np)12G0-CH₂Cl (0.88 g, 2.4 mmol) in DMF (50 mL), 0.62 g (60%) of the title compound **9** was obtained as white powder after purification by column chromatography (SiO₂, EtOAc:Hexane = 1:9) followed by recrystallization from acetone. HPLC: 99+%; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.88 (t, 6H, J = 6.8 Hz), 1.20-1.40 (overlapped m, 32H), 1.45-1.52 (m, 4H), 1.85 (m, 4H), 2.57 (t, 2H, J = 7.5 Hz), 2.85 (t, 2H, J = 7.5 Hz), 3.62 (s, 3H), 4.07 (m, 4H), 5.24 (s, 2H), 5.30 (s, 2H), 6.71 (dd, 1H, J = 2.0, 8.1 Hz), 6.87 (d, 1H, J = 2.0 Hz), 6.91 (d, 1H, J = 8.2 Hz), 7.11 (m, 4H), 7.51 (m, 2H), 7.62 (m, 2H), 7.70 (m, 2H), 7.79 (m, 2H); ¹³C NMR (125 MHz, CDCl₃, 27 °C, TMS): δ = 14.3, 22.8, 26.3, 29.4, 29.5, 29.6, 29.7, 29.8, 29.8, 30.6, 30.1, 35.9, 51.7, 68.2, 71.8, 71.9, 106.6, 115.7, 115.8, 119.3, 121.3, 126.0, 126.1, 126.3, 126.4, 127.1, 128.7, 128.8, 129.5, 129.5, 132.5, 132.6, 134.2, 134.3, 134.4, 137.3, 142.2, 147.8, 149.3, 157.4, 157.4, 173.5; MALDI-TOF m/z: 868.25 ([M+Na]⁺ calculated for C₅₆H₇₆NaO₆ 867.55).

3-[3,4-Bis{(6-(dodecyloxy)naphthalen-2-yl)methoxy}phenyl]propan-1-ol, (6Np-3,4Pr)12G1-CH₂OH (10): This compound was synthesized by the same general procedure described for the synthesis of compound **5** from LiAlH₄ (30 mg, 0.64 mmol) and (6Np-3,4Pr)12G1-CO₂CH₃, **9** (0.36 g, 0.43 mmol) in dry THF (8 mL). After purification by column chromatography (SiO₂, EtOAc:Hexane = 3:7) followed by crystallization in acetone, the title compound **10** (0.26 g, 74%) was obtained as white solid. HPLC: 99+%; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.88 (t, 6H, J = 6.9 Hz), 1.12 (br s, 1H), 1.20-1.41 (overlapped m, 32H), 1.50 (m, 4H), 1.82 (m, 6H), 2.60 (t, 2H, J = 7.4 Hz), 3.57 (m, 2H), 4.07 (t, 4H, J = 6.6 Hz), 5.24 (s, 2H), 5.26 (s, 2H), 6.70 (dd, 1H, J = 2.0, 8.1 Hz), 6.85 (d, 1H, J = 2.0 Hz), 6.92 (d, 1H, J = 8.2 Hz), 7.11 (m, 4H), 7.51 (m, 2H), 7.63 (m, 2H), 7.69 (dd, 2H, J = 3.3, 8.5 Hz), 7.79 (s, 2H); ¹³C NMR (125 MHz, CDCl₃, 27 °C, TMS): δ = 14.3, 22.9, 26.4, 29.5, 29.6, 29.7, 29.8, 29.8, 29.9, 31.8, 32.2, 34.4, 62.4, 68.4, 72.1, 72.3, 106.8, 106.9, 116.1, 116.5, 119.4, 119.5, 121.6, 126.2, 126.3, 126.4, 126.5, 127.2, 128.9, 129.6, 132.7, 132.9, 134.5, 135.7, 147.8, 149.4, 157.5, 157.6; MALDI-TOF m/z: 839.44 ([M+Na]⁺ calculated for C₅₅H₇₆NaO₅ 839.56).

(S)-Methyl 6-(3,7-dimethyloctyloxy)-2-naphthoate, (6Np)dm8*G0-CO₂CH₃ (12): To a thoroughly degassed suspension of anhydrous K₂CO₃ (9.5 g, 0.068 mol) in DMF (136 mL) was added methyl 6-hydroxy-2-naphthoate (6.88 g, 0.034 mol) and the resulting mixture was heated to 80 °C with continuous degassing. At 80 °C was then added (S)-3,7-dimethyloctyl bromide (7.52 g, 0.034 mol) and the reaction allowed to stir at 80 °C under N₂ for 4 h (TLC controlled). The reaction mixture was cooled to room temperature and poured into ice-cold water. The precipitate was collected by vacuum filtration

and the solid was passed through a short column of basic alumina using DCM as eluent. 10.5 g (90%) of the title compound **12** was obtained as shiny white powder after recrystallization from MeOH. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.69; ^1H NMR (500 MHz, CDCl_3 , 27 °C, TMS): δ = 0.87 (d, 6H, J = 6.6 Hz), 0.98 (d, 3H, J = 6.6 Hz), 1.16-1.19 (m, 3H), 1.34-1.36 (m, 3H), 1.53-1.62 (m, 1H), 1.64-1.72 (m, 2H), 1.90 (m, 1H), 3.96 (s, 3H), 4.11-4.15 (t, 2H, J = 6.7 Hz), 7.15 (s, 1H), 7.19 (dd, 1H, J = 6.5, 2.4 Hz), 7.75 (d, 1H, J = 8.6 Hz), 7.84 (d, 1H, J = 8.7 Hz), 8.28 (dd, 1H, J = 6.9, 1.6 Hz), 8.52 (s, 1H); ^{13}C NMR (125 MHz, 27 °C, CDCl_3): δ = 19.9, 22.8, 22.9, 24.9, 28.2, 30.1, 36.3, 37.5, 39.5, 52.3, 66.7, 106.6, 120.2, 125.3, 126.1, 127.0, 128.0, 131.1, 137.4, 159.3, 167.6.

(S)-[6-(3,7-dimethyloctyloxy)naphthalen-2-yl]methanol, (6Np)dm8*G0-CH₂OH (13): This compound was synthesized by the same general procedure described for the synthesis of compound **5**. From LiAlH_4 (1.7 g, 0.045 mol) and (6Np)dm8*G0-CO₂CH₃, **12** (10.3 g, 0.03 mol) in dry THF (120 mL), the title compound **13** (9.1 g, 97%) was obtained as white solid. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.37; ^1H NMR (500 MHz, CDCl_3 , 27 °C, TMS): δ = 0.89 (d, 6H, J = 6.6 Hz), 0.99 (d, 3H, J = 6.6 Hz), 1.17-1.19 (m, 3H), 1.34-1.37 (m, 3H), 1.51-1.57 (m, 1H), 1.61-1.64 (m, 1H), 1.67-1.74 (m, 2H), 1.81-1.84 (m, 1H), 4.09-4.14 (m, 2H), 4.81 (d, 2H, J = 5.6 Hz), 7.13-7.17 (overlapped d, 2H), 7.45 (d, 1H, J = 6.9 Hz), 7.73 (overlapped peaks, 3H); ^{13}C NMR (125 MHz, CDCl_3 , 27 °C, TMS): δ = 19.9, 22.8, 22.9, 24.9, 28.2, 30.2, 36.4, 37.5, 39.5, 65.8, 66.6, 106.7, 119.6, 125.8, 126.0, 127.4, 128.9, 129.5, 134.4, 136.1, 157.5.

(S)-2-(chloromethyl)-6-(3,7-dimethyloctyloxy)naphthalene, (6Np)dm8*G0-CH₂Cl (14): To a 0 °C solution of (6Np)dm8*G0-CH₂OH, **13** (8.96 g, 28.5 mmol) in dry CH_2Cl_2 (135 mL) containing catalytic amount of dry DMF was added slowly SOCl_2 (2.6 mL, 35.6 mmol in 36 mL of dry CH_2Cl_2) under N_2 , and the resulting mixture was allowed to stir at room temperature for 30 min after which TLC showed completion. CH_2Cl_2 was removed in a rotary evaporator and the crude solid was dried under vacuum for 1 h. The title compound **14** (8.6 g, 91%) was obtained as white solid after recrystallization from hexane. TLC (EtOAc/hexane = 3/7): R_f = 0.77; ^1H NMR (500 MHz, CDCl_3 , 27 °C, TMS): δ = 0.88 (d, 6H, J = 6.5 Hz), 0.97 (d, 3H, J = 6.6 Hz), 1.16-1.19 (m, 3H), 1.34-1.37 (m, 3H), 1.53-1.54 (m, 1H), 1.61-1.63 (m, 1H), 1.67-1.73 (m, 1H), 1.89 (m, 1H), 4.09-4.14 (m, 2H), 4.73 (s, 2H), 7.13-7.17 (overlapped d, 2H), 7.46 (d, 1H, J = 6.7 Hz), 7.73 (overlapped peaks, 3H); ^{13}C NMR (125 MHz, 27 °C, CDCl_3): δ = 19.9, 22.8, 22.9, 24.9, 28.2, 30.2, 36.4, 37.5, 39.5, 47.1, 66.6, 106.7, 119.8, 127.0, 127.7, 128.7, 129.6, 132.6, 134.7, 157.9.

Methyl 3,4-bis-[(6-((S)-3,7-dimethyloctyloxy)naphthalen-2-yl)methoxy]-benzoate, (6Np-3,4)dm8*G1-CO₂CH₃ (15): This compound was synthesized by the same general procedure described for the synthesis of compound **4**. From methyl 3,4-dihydroxybenzoate (1.01 g, 6.0 mmol), K_2CO_3 (3.32

g, 24.0 mmol) and (6Np)dm8*G0-CH₂Cl, **14** (4.0 g, 12.0 mmol) in DMF (60 mL), compound **15** (3.8 g, 83%) was obtained as white solid. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.66; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.88 (d, 12H, *J* = 6.6 Hz), 0.99 (d, 6H, *J* = 6.6 Hz), 1.17-1.20 (m, 6H), 1.33-1.39 (m, 6H), 1.53-1.57 (m, 2H), 1.59-1.67 (m, 2H), 1.69-1.74 (m, 2H), 1.84-1.90 (m, 2H), 3.87 (s, 3H), 4.09-4.14 (m, 4H), 5.32 (s, 2H), 5.34 (s, 2H), 7.01 (d, 1H, *J* = 8.5 Hz), 7.14 (overlapped peaks, 4H), 7.55 (dd, 2H, *J* = 6.4, 2.0 Hz), 7.64 (overlapped peaks, 3H), 7.71 (overlapped peaks, 3H), 7.81 (s, 1H), 7.85 (s, 1H); ¹³C NMR (125 MHz, 27 °C, CDCl₃): δ = 19.9, 22.8, 22.9, 24.9, 28.2, 29.9, 30.1, 36.5, 37.5, 39.5, 52.2, 66.6, 70.9, 71.3, 113.6, 115.0, 115.8, 123.3, 124.3, 127.0, 127.1, 127.9, 128.2, 128.3, 128.6, 133.2, 133.3, 135.0, 135.3, 140.8, 148.6, 153.2, 159.0, 167.0; MALDI-TOF *m/z*: 760.81 (M⁺, calculated for C₅₀H₆₄O₆ 760.41), 783.69 ([M+Na]⁺, calculated 783.40).

Methyl 4'-(dodecyloxy)biphenyl-4-carboxylate, (4Bp)12G0-CO₂CH₃ (17a): This compound was synthesized by the same procedure described for the synthesis of **12**. From methyl 4'-hydroxy-4-biphenylcarboxylate (2.85 g, 12.5 mmol), K₂CO₃ (3.46 g, 25 mmol), and 1-bromododecane (3.12 g, 12.5 mmol) in DMF (40 mL), 4.63 g (93%) of the title compound **17a** was obtained as a white solid after recrystallization from acetone-CH₂Cl₂ mixture. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.73; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.90 (t, 3H, CH₃, *J* = 7.0 Hz), 1.27-1.37 (m, 16H, CH₃(CH₂)₈), 1.46-1.49 (m, 2H, CH₃(CH₂)₈CH₂), 1.79-1.82 (m, 2H, CH₂CH₂O), 3.93 (s, 3H, CO₂CH₃), 4.02 (t, 2H, OCH₂, *J* = 6.6 Hz), 6.99 (dd, 2H, 3',5', *J* = 4.8, 2.1 Hz), 7.57 (dd, 2H, 2',6', *J* = 4.6, 2.1 Hz), 7.63 (dd, 2H, 2, 6, *J* = 4.8, 1.9 Hz), 8.08 (dd, 2H, 3, 5, *J* = 4.8, 1.9 Hz); ¹³C NMR (125 MHz, CDCl₃, 27 °C, TMS): δ = 14.3, 22.9, 26.3, 29.5-29.9, 32.1, 52.3, 68.4, 115.2, 126.6, 128.4, 128.5, 130.3, 132.4, 145.5, 159.7, 167.3.

Methyl 4'-(2-ethyl-hexyloxy)-biphenyl-4-carboxylate, (4Bp)Et6G0-CO₂CH₃ (17b): This compound was synthesized by the identical procedure described for the synthesis of **12**. From methyl 4'-hydroxy-4-biphenylcarboxylate (1.94 g, 8.5 mmol), K₂CO₃ (2.35 g, 17 mmol) and 2-ethylhexyl bromide (1.64 g, 8.5 mmol) in DMF (35 mL), 2.62 g (91%) of the title compound **17b** was obtained as white solid. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.69; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.96 (t, 6H, *J* = 7.6 Hz), 1.34-1.36 (m, 2H), 1.43-1.54 (m, 6H), 1.75 (m, 1H), 3.90 (d, 2H, *J* = 5.6 Hz), 3.93 (s, 3H), 7.00 (d, 2H, *J* = 8.7 Hz), 7.57 (d, 2H, *J* = 8.7 Hz), 7.63 (d, 2H, *J* = 8.4 Hz), 8.08 (d, 2H, *J* = 8.4 Hz); ¹³C NMR (125 MHz, CDCl₃, 27 °C, TMS): δ = 11.3, 14.3, 23.3, 24.1, 29.3, 30.8, 39.6, 52.3, 70.9, 115.2, 126.7, 128.4, 128.5, 130.3, 132.4, 145.6, 159.9, 167.3.

Methyl 4'-((S)-3,7-dimethyl-octyloxy)-biphenyl-4-carboxylate, (4Bp)dm8*G0CO₂CH₃ (17c): This compound was synthesized by the identical procedure described for the synthesis of **12**. From methyl 4'-hydroxy-4-biphenylcarboxylate (2.74 g, 12 mmol), K₂CO₃ (3.32 g, 24 mmol) and (S)-3,7-dimethyloctyl

bromide (2.65 g, 12 mmol) in DMF (60 mL), 4.20 g (95%) of the title compound **17c** was obtained as white solid after recrystallization from acetone. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.68; ^1H NMR (500 MHz, CDCl_3 , 27 °C, TMS): δ = 0.89 (d, 6H, J = 6.6 Hz), 0.97 (d, 3H, J = 6.6 Hz), 1.16-1.19 (m, 3H), 1.34-1.36 (m, 3H), 1.50-1.53 (m, 1H), 1.57-1.64 (m, 1H), 1.64-1.72 (m, 1H), 1.81-1.84 (m, 1H), 3.93 (s, 3H), 4.02-4.06 (m, 2H), 6.99 (dd, 2H, J = 4.6, 2.1 Hz), 7.57 (dd, 2H, J = 4.6, 2.1 Hz), 7.63 (dd, 2H, J = 4.8, 1.9 Hz), 8.08 (dd, 2H, J = 4.8, 1.9 Hz); ^{13}C NMR (125 MHz, 27 °C, CDCl_3): δ = 19.9, 22.8, 22.9, 24.9, 28.2, 30.1, 36.4, 37.5, 39.5, 52.3, 66.7, 115.2, 126.6, 128.4, 128.5, 130.3, 132.4, 145.5, 159.6, 167.3.

[4'-(Dodecyloxy)biphenyl-4-yl]methanol (4Bp)12G0-CH₂OH (18a): This compound was synthesized by the identical procedure described for the synthesis of compound **5**. From LiAlH_4 (0.66 g, 17.4 mmol) and (4Bp)12G0CO₂CH₃, **17a** (4.60 g, 11.6 mmol) in dry THF, the title compound **18a** (3.8 g, 94%) was obtained as white solid. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.35; ^1H NMR (500 MHz, CDCl_3 , 27 °C, TMS): δ = 0.91 (t, 3H, J = 7.0 Hz), 1.29-1.37 (m, 16H), 1.46-1.50 (m, 2H), 1.60 (t, 1H, J = 5.9 Hz), 1.79-1.82 (m, 2H), 4.02 (t, 2H, J = 6.6 Hz), 4.73 (d, 2H, J = 5.9 Hz), 6.98 (dd, 2H, J = 4.6, 2.1 Hz), 7.42 (d, 2H, J = 8.3 Hz), 7.50-7.56 (overlapped d, 4H); ^{13}C NMR (125 MHz, CDCl_3 , 27 °C, TMS): δ = 14.3, 22.9, 26.3, 29.6-29.9, 32.2, 65.5, 68.5, 115.2, 127.1, 127.7, 128.3, 133.5, 139.5, 140.7, 159.1.

[4'-(2-Ethyl-hexyloxy)-biphenyl-4-yl]-methanol, (4Bp)Et6G0-CH₂OH (18b): This compound was synthesized by the identical procedure described for the synthesis of compound **5**. From LiAlH_4 (0.38 g, 10 mmol) and (4Bp)Et6G0-CO₂CH₃, **17b** (2.30 g, 6.75 mmol) in dry THF (60 mL), the title compound **18b** (2.0 g, 95%) was obtained as waxy solid. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.34; ^1H NMR (500 MHz, CDCl_3 , 27 °C, TMS): δ = 0.91-0.97 (overlapped t, 6H), 1.33-1.36 (m, 4H), 1.44-1.47 (m, 4H), 1.53 (s, 1H), 1.76 (m, 1H), 3.86-3.92 (m, 2H), 4.73 (s, 2H), 6.99 (d, 2H, J = 8.8 Hz), 7.42 (d, 2H, J = 8.4 Hz), 7.53 (d, 2H, J = 8.8 Hz), 7.56 (d, 2H, J = 8.3 Hz); ^{13}C NMR (125 MHz, CDCl_3 , 27 °C, TMS): δ = 11.4, 14.3, 23.3, 24.1, 29.3, 30.6, 30.8, 39.6, 65.4, 70.8, 115.1, 127.1, 127.7, 128.3, 133.3, 139.4, 140.6, 159.3.

[4'-((S)-3,7-Dimethyl-octyloxy)-biphenyl-4-yl]-methanol, (4Bp)dm8*G0CH₂OH (18c): This compound was synthesized by the identical procedure described for the synthesis of compound **5**. From LiAlH_4 (0.63 g, 16.5 mmol) and (4Bp)dm8*G0CO₂CH₃, **17c** (4.06 g, 11 mmol) in dry THF (40 mL), the title compound **18c** (3.3 g, 88%) was obtained as white powder after recrystallized from acetone. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.27; ^1H NMR (500 MHz, CDCl_3 , 27 °C, TMS): δ = 0.88 (d, 6H, J = 6.6 Hz), 0.96 (d, 3H, J = 6.6 Hz), 1.16-1.19 (m, 3H), 1.34-1.37 (m, 3H), 1.51-1.54 (m, 1H), 1.61-1.64 (m, 2H), 1.67-1.72 (m, 1H), 1.81-1.84 (m, 1H), 4.01-4.06 (m, 2H), 4.74 (d, 2H, J = 6.0

Hz), 6.98 (dd, 2H, $J = 4.6, 2.1$ Hz), 7.42 (d, 2H, $J = 8.1$ Hz), 7.50-7.56 (overlapped d, 4H); ^{13}C NMR (125 MHz, 27 °C, CDCl_3): $\delta = 19.9, 22.8, 22.9, 24.9, 28.2, 30.1, 36.4, 37.5, 39.5, 65.4, 66.7, 115.1, 127.1, 127.7, 128.3, 132.9, 139.4, 140.6, 159.0$.

4-(Chloromethyl)-4'-(dodecyloxy)biphenyl, (4Bp)12G0-CH₂Cl (19a): This compound was synthesized by the identical procedure described for the synthesis of compound **14**. From SOCl_2 (0.9 mL, 12.5 mmol) in 18 mL of dry CH_2Cl_2 and (4Bp)12G0-CH₂OH, **18a** (3.69 g, 10 mmol) in dry CH_2Cl_2 (60 mL), the title compound **19a** (3.65 g, 94%) was obtained as white solid after precipitation in cold MeOH from concentrated CH_2Cl_2 solution. TLC (EtOAc/hexane = 3/7): $R_f = 0.74$; ^1H NMR (500 MHz, CDCl_3 , 27 °C, TMS): $\delta = 0.90$ (t, 3H, $J = 7.0$ Hz), 1.28-1.37 (m, 16H), 1.46-1.49 (m, 2H), 1.78-1.84 (m, 2H), 4.01 (t, 2H, $J = 6.6$ Hz), 4.63 (s, 2H), 6.98 (d, 2H, $J = 8.6$ Hz), 7.44 (d, 2H, $J = 8.1$ Hz), 7.50-7.56 (overlapped d, 4H); ^{13}C NMR (125 MHz, CDCl_3 , 27 °C, TMS): $\delta = 14.3, 22.9, 26.3, 29.5, 29.9, 32.1, 46.4, 68.3, 115.1, 127.2, 128.3, 129.2, 133.0, 135.9, 141.3, 159.2$.

4'-Chloromethyl-4-(2-ethyl-hexyloxy)biphenyl, (4Bp)Et6G0-CH₂Cl (19b): This compound was synthesized by the identical procedure described for the synthesis of compound **14**. From SOCl_2 (0.55 mL, 7.5 mmol) and (4Bp)Et6G0-CH₂OH, **18b** (1.88 g, 6 mmol) in dry CH_2Cl_2 (60 mL), the title compound **19b** (1.93 g, 97%) was obtained as gummy solid. TLC (EtOAc/hexane = 3/7): $R_f = 0.78$; ^1H NMR (500 MHz, CDCl_3 , 27 °C, TMS): $\delta = 0.93$ -0.99 (overlapped t, 6H), 1.35-1.37 (m, 4H), 1.46-1.54 (m, 4H), 1.78 (m, 1H), 3.88-3.92 (m, 2H), 4.64 (s, 2H), 7.00 (d, 2H, $J = 8.8$ Hz), 7.46 (d, 2H, $J = 8.3$ Hz), 7.53 (d, 2H, $J = 8.8$ Hz), 7.57 (d, 2H, $J = 8.3$ Hz); ^{13}C NMR (125 MHz, CDCl_3 , 27 °C): $\delta = 11.3, 14.3, 23.3, 24.1, 29.3, 30.5, 30.8, 39.6, 46.4, 70.8, 115.1, 126.9, 127.2, 128.3, 128.5, 129.2, 132.9, 135.9, 141.3, 159.4$.

4'-Chloromethyl-4-((S)-3,7-Dimethyl-octyloxy)-biphenyl, (4Bp)dm8*G0CH₂Cl (19c): This compound was synthesized by the identical procedure described for the synthesis of compound **14**. From SOCl_2 (0.82 mL, 11.3 mmol) in 16 mL of dry CH_2Cl_2 and (4Bp)dm8*G0-CH₂OH, **18c** (3.2 g, 9.4 mmol) in dry CH_2Cl_2 (60 mL), the title compound **19c** (3.0 g, 89%) was obtained as white solid after precipitation in cold MeOH. TLC (EtOAc/hexane = 3/7): $R_f = 0.80$; ^1H NMR (500 MHz, CDCl_3 , 27 °C, TMS): $\delta = 0.89$ (d, 6H, $J = 6.6$ Hz), 0.97 (d, 3H, $J = 6.6$ Hz), 1.16-1.19 (m, 3H), 1.34-1.37 (m, 3H), 1.53-1.54 (m, 1H), 1.61-1.64 (m, 1H), 1.67-1.72 (m, 1H), 1.81-1.86 (m, 1H), 4.01-4.08 (m, 2H), 4.63 (s, 2H), 6.98 (dd, 2H, $J = 4.6, 2.1$ Hz), 7.44 (d, 2H, $J = 8.0$ Hz), 7.50-7.55 (overlapped d, 4H); ^{13}C NMR (125 MHz, CDCl_3 , 27 °C): $\delta = 19.9, 22.8, 22.9, 24.9, 28.2, 30.1, 36.4, 37.5, 39.5, 46.4, 66.7, 115.1, 127.2, 128.3, 129.3, 133.0, 136.0, 141.3, 159.2$.

Methyl 3,4-bis-[(4'-(dodecyloxy)biphenyl-4-yl)methoxy] benzoate, (4Bp-3,4)12G1-CO₂CH₃ (21a): This compound was synthesized by the same general procedure described for the synthesis of compound

4. From methyl 3,4-dihydroxybenzoate, **20** (0.76 g, 4.5 mmol), K₂CO₃ (2.5 g, 18 mmol) and (4Bp)12G0-CH₂Cl, **19a** (3.49 g, 9 mmol) in DMF (100 mL), compound **21a** (3.5 g, 90%) was obtained as white solid after purification by column chromatography (silica gel, EtOAc-hexane = 3:7) followed by precipitation in MeOH from concentrated solution of CH₂Cl₂. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.71; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.90 (t, 6H, *J* = 7.0 Hz), 1.27-1.36 (m, 32H), 1.46-1.49 (m, 4H), 1.79-1.82 (m, 4H), 3.88 (s, 3H), 4.01 (t, 4H, *J* = 6.6 Hz), 5.25 (s, 4H), 6.98 (overlapped peaks), 7.47-7.56 (overlapped, 12H), 7.67 (dd, 1H, *J* = 6.5, 1.9 Hz), 7.69 (s, 1H); ¹³C NMR (125 MHz, CDCl₃, 27 °C, TMS): δ = 14.3, 22.9, 26.3, 29.5-29.9, 32.1, 52.2, 68.3, 71.0, 71.4, 113.6, 115.0, 115.9, 123.3, 124.3, 127.0, 127.1, 127.9, 128.2, 128.3, 133.2, 133.3, 135.0, 135.3, 140.8, 148.6, 153.2, 159.0, 159.1, 167.0; MALDI-TOF *m/z*: 868.82 (M⁺, calculated for C₅₈H₇₆O₆ 868.56), 891.69 ([M+Na]⁺, calculated 891.55).

3,4-Bis-[4'-(2-ethyl-hexyloxy)-biphenyl-4-ylmethoxy]-benzoic acid methyl ester, (4Bp-3,4)Et6G1-CO₂CH₃ (21b): This compound was synthesized by the same general procedure described for the synthesis of compound **4**. From methyl 3,4-dihydroxybenzoate, **20** (454 mg, 2.7 mmol), K₂CO₃ (1.49 g, 10.8 mmol) and (4Bp)Et6G0-CH₂Cl, **19b** (1.79 g, 5.4 mmol) in DMF (30 mL), compound **21b** (1.65 g, 81%) was obtained as white solid after purification by column chromatography (silica gel, EtOAc-hexane = 3:7) followed by precipitation in MeOH from concentrated solution of CH₂Cl₂. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.56; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.90-0.96 (overlapped t, 12H, *J* = 7.4 Hz), 1.33-1.36 (m, 8H), 1.45-1.54 (m, 8H), 1.75 (m, 2H), 3.88 (d, 4H, *J* = 5.2 Hz), 3.89 (s, 3H), 5.25 (s, 4H), 6.96-6.99 (overlapped peaks, 5H), 7.46-7.60 (overlapped peaks, 12H), 7.67 (d, 1H, *J* = 6.4 Hz), 7.69 (s, 1H); ¹³C NMR (125 MHz, 27 °C, CDCl₃): δ = 11.1, 14.1, 23.1, 23.9, 29.1, 30.5, 39.4, 52.0, 57.1, 70.6, 70.7, 71.1, 113.4, 114.8, 115.6, 123.1, 124.0, 126.8, 127.6, 127.9, 128.0, 132.9, 133.0, 134.8, 135.1, 140.6, 140.8, 148.4, 153.0, 159.1, 166.8; MALDI-TOF *m/z*: 756.74 (M⁺, calculated for C₅₀H₆₀O₆ 756.44), 779.37 ([M+Na]⁺, calculated 779.43).

[3,4-Bis-(4'-dodecyloxy-biphenyl-4-ylmethoxy)phenyl]methanol, (4Bp-3,4)12G1-CH₂OH (22a): This compound was synthesized by the same general procedure described for the synthesis of compound **5**. From LiAlH₄ (60 mg, 1.58 mmol) and (4Bp-3,4)12G1-CO₂CH₃, **21a** (0.91 g, 1.05 mmol) in dry THF (100 mL), the title compound **22a** (0.81 g, 91%) was obtained as white solid. HPLC: 99+%; TLC (CH₂Cl₂/MeOH = 9/1): R_f = 0.54; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.90 (t, 6H, *J* = 7.0 Hz), 1.27-1.36 (overlapped m, 33H,), 1.46-1.49 (m, 4H), 1.79-1.82 (m, 4H), 4.01 (t, 4H, *J* = 6.6 Hz), 4.60 (d, 2H, *J* = 5.8 Hz), 5.20 (s, 4H), 6.89 (dd, 1H, *J* = 6.7, 1.9 Hz), 6.96 (overlapped peaks, 5H), 7.04 (s, 1H), 7.46-7.55 (overlapped, 12H); ¹³C NMR (125 MHz, CDCl₃, 27 °C, TMS): δ = 14.3, 22.9, 26.3, 29.5-29.9, 32.1, 65.5, 68.3, 71.4, 71.5, 114.4, 115.0, 115.6, 120.5, 127.0, 128.0, 128.1, 128.3, 133.3,

134.7, 135.7, 135.8, 140.6, 148.2, 149.5, 159.0; MALDI-TOF m/z : 840.91 (M^+ , calculated for $C_{57}H_{76}O_5$ 840.57), 863.48 ($[M+Na]^+$, calculated 863.56).

3,4-Bis[4'-(heptan-3-yloxy)biphenyl-4-yl]methoxyphenyl]methanol, (4Bp-3,4)Et6G1-CH₂OH (22b): This compound was synthesized by the same general procedure described for the synthesis of compound **5** from $LiAlH_4$ (34 mg, 0.90 mmol) and (4Bp-3,4)Et6G1-CO₂CH₃, **21b** (0.45 g, 0.60 mmol) in dry THF (18 mL). After purification by column chromatography (SiO₂, EtOAc:Hexane = 3:7) and precipitation in cold MeOH, the title compound **22b** (0.32 g, 73%) was obtained as white solid. HPLC: 99+%; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.89-0.98 (overlapped t, 12H, J = 7.5 Hz), 1.28-1.40 (m, 8H), 1.37-1.59 (m, 8H), 1.75 (m, 2H), 3.87 (d, 4H, J = 6.0 Hz), 4.59 (d, 2H, J = 6.0 Hz), 5.17 (s, 2H), 5.21 (s, 2H), 6.88 (dd, 1H, J = 2.0, 8.5 Hz), 6.94-7.00 (overlapped peaks, 5H), 7.04 (d, 1H, J = 1.5 Hz), 7.45-7.56 (overlapped peaks, 12H); ¹³C NMR (125 MHz, CDCl₃, 27 °C): δ = 11.3, 14.3, 23.3, 24.1, 29.3, 30.8, 39.6, 65.5, 70.8, 71.3, 71.5, 114.4, 115.0, 115.5, 120.4, 126.98, 127.9, 128.1, 128.2, 133.2, 134.6, 135.7, 135.8, 140.7, 148.7, 149.4, 159.3; MALDI-TOF m/z : 756.74 (M^+ , calculated for $C_{50}H_{60}O_6$ 756.44), 779.37 ($[M+Na]^+$, calculated 779.43).

Methyl 2-[3,4-Bis-4'-(dodecyloxy)-biphenyl-4-yl]-methoxyphenyl]-acetate, (4Bp-3,4Et)12G1-CO₂CH₃ (23a): This compound was synthesized by the same general procedure described for the synthesis of compound **4**. From methyl 2-(3,4-dihydroxyphenyl) acetate, **2** (0.22 g, 1.2 mmol), K₂CO₃ (0.66 g, 4.8 mmol) and (4Bp)12G0-CH₂Cl, **19a** (0.93 g, 2.4 mmol) in DMF (20 mL), compound **23a** (0.78 g, 74%) was obtained as white solid after purification by column chromatography (silica gel, EtOAc-hexane = 3:7) followed by precipitation in MeOH from concentrated solution of CH₂Cl₂. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.51; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.90 (t, 6H, J = 7.0 Hz), 1.27-1.37 (m, 32H), 1.46-1.50 (m, 4H), 1.79-1.82 (m, 4H), 3.53 (s, 2H), 3.66 (s, 3H), 4.01 (t, 4H, J = 6.5 Hz), 5.19 (s, 4H), 6.81 (d, 1H, J = 6.4 Hz), 6.91 (s, 1H), 6.93-6.97 (overlapped peaks, 5H), 7.48-7.54 (overlapped peaks, 12H); ¹³C NMR (125 MHz, 27 °C, CDCl₃): δ = 14.3, 22.9, 26.3, 29.5-29.9, 32.1, 40.9, 52.2, 68.3, 71.4, 71.5, 115.0, 115.5, 116.5, 122.5, 127.0, 127.5, 128.0, 128.1, 128.3, 133.3, 135.8, 135.9, 140.6, 148.5, 149.3, 159.0, 172.4; MALDI-TOF m/z : 883.16 (M^+ , calculated for $C_{59}H_{78}O_6$ 883.25), 806.21 ($[M+Na]^+$, calculated 906.24).

Methyl 2[3,4-bis4'-(S)-3,7-dimethyloctyloxy)biphenyl-4-yl]methoxyphenyl]acetate, (4Bp-3,4Et)dm8*G1-CO₂CH₃:(23c): This compound was synthesized by the same general procedure described for the synthesis of compound **4**. From methyl 2-(3,4-dihydroxyphenyl) acetate, **2** (0.27 g, 1.5 mmol), K₂CO₃ (0.83 g, 6.0 mmol) and (4Bp)dm8*G0-CH₂Cl, **19c** (1.08 g, 3.0 mmol) in DMF (25 mL), compound **23c** (0.88 g, 71%) was obtained as white solid after purification by column chromatography (silica gel, EtOAc-hexane = 3:7) followed by precipitation in MeOH from concentrated solution of

CH₂Cl₂. HPLC: 99+%; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.87 (d, 12H, *J* = 6.5 Hz), 0.95 (d, 6H, *J* = 6.5 Hz), 1.13-1.23 (m, 6H), 1.26-1.40 (m, 6H), 1.50-1.60 (m, 2H), 1.61-1.64 (m, 2H), 1.66-1.70 (m, 2H), 1.82-1.84 (m, 2H), 3.53 (s, 2H), 3.65 (s, 3H), 3.99-4.07 (m, 4H), 5.17 (s, 2H), 5.19 (s, 2H), 6.80 (dd, 1H, *J* = 2.0, 8.0 Hz), 6.91 (d, 1H, *J* = 8.0 Hz), 6.93 (d, 1H, *J* = 1.5 Hz), 6.96 (m, 4H), 7.46-7.55 (overlapped peaks, 12H); ¹³C NMR (125 MHz, 27 °C, CDCl₃): δ = 19.9, 22.8, 22.9, 24.9, 28.2, 30.1, 36.4, 37.5, 39.5, 40.1, 52.2, 66.6, 71.4, 71.4, 100.2, 100.6, 114.9, 115.4, 116.4, 122.5, 126.9, 127.5, 127.9, 128.1, 128.3, 135.7, 135.8, 137.3, 140.6, 148.4, 149.2, 158.9, 172.4; MALDI-TOF *m/z*: 849.56 ([M+Na]⁺, calculated for C₅₅H₇₀NaO₆ 849.51).

Methyl 3-[3,4-Bis-{{4'-(dodecyloxy)-biphenyl-4-yl}-methoxy}-phenyl]-propanoate, (4Bp-3,4Pr)12G1-CO₂CH₃ (24): This compound was synthesized by the same general procedure described for the synthesis of compound 4. From methyl 3-(3,4-dihydroxyphenyl)-propanoate, **3** (0.26 g, 1.3 mmol), K₂CO₃ (0.72 g, 5.2 mmol) and (4Bp)12G0-CH₂Cl, **19a** (1.01 g, 2.6 mmol) in DMF (40 mL), compound **24** (0.85 g, 73%) was obtained as white solid after purification by column chromatography (silica gel, EtOAc-hexane = 3:7) followed by precipitation in MeOH from concentrated solution of CH₂Cl₂. HPLC: 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.61; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.90 (t, 6H, *J* = 7.0 Hz), 1.27-1.37 (m, 32H), 1.46-1.50 (m, 4H), 1.79-1.82 (m, 4H), 2.58 (t, 2H), 2.86 (t, 2H), 3.65 (s, 3H), 4.01 (t, 4H, *J* = 6.5 Hz), 5.17 (s, 4H), 6.72 (d, 1H, *J* = 6.4 Hz), 6.84 (s, 1H), 6.91 (d, 1H, *J* = 6.4 Hz), 6.96 (overlapped peaks, 4H), 7.46-7.55 (overlapped peaks, 12H); ¹³C NMR (125 MHz, 27 °C, CDCl₃): δ = 14.3, 22.9, 26.3, 29.5-29.9, 30.7, 32.1, 36.1, 51.8, 68.3, 71.5, 71.6, 115.0, 115.8, 115.9, 121.4, 127.0, 128.0, 128.1, 128.3, 133.4, 134.3, 135.9, 136.0, 140.6, 147.8, 149.3, 159.0, 173.6; MALDI-TOF *m/z*: 896.90 (M⁺, calculated for C₆₀H₈₀O₆ 897.27), 919.74 ([M+Na]⁺, calculated 920.26).

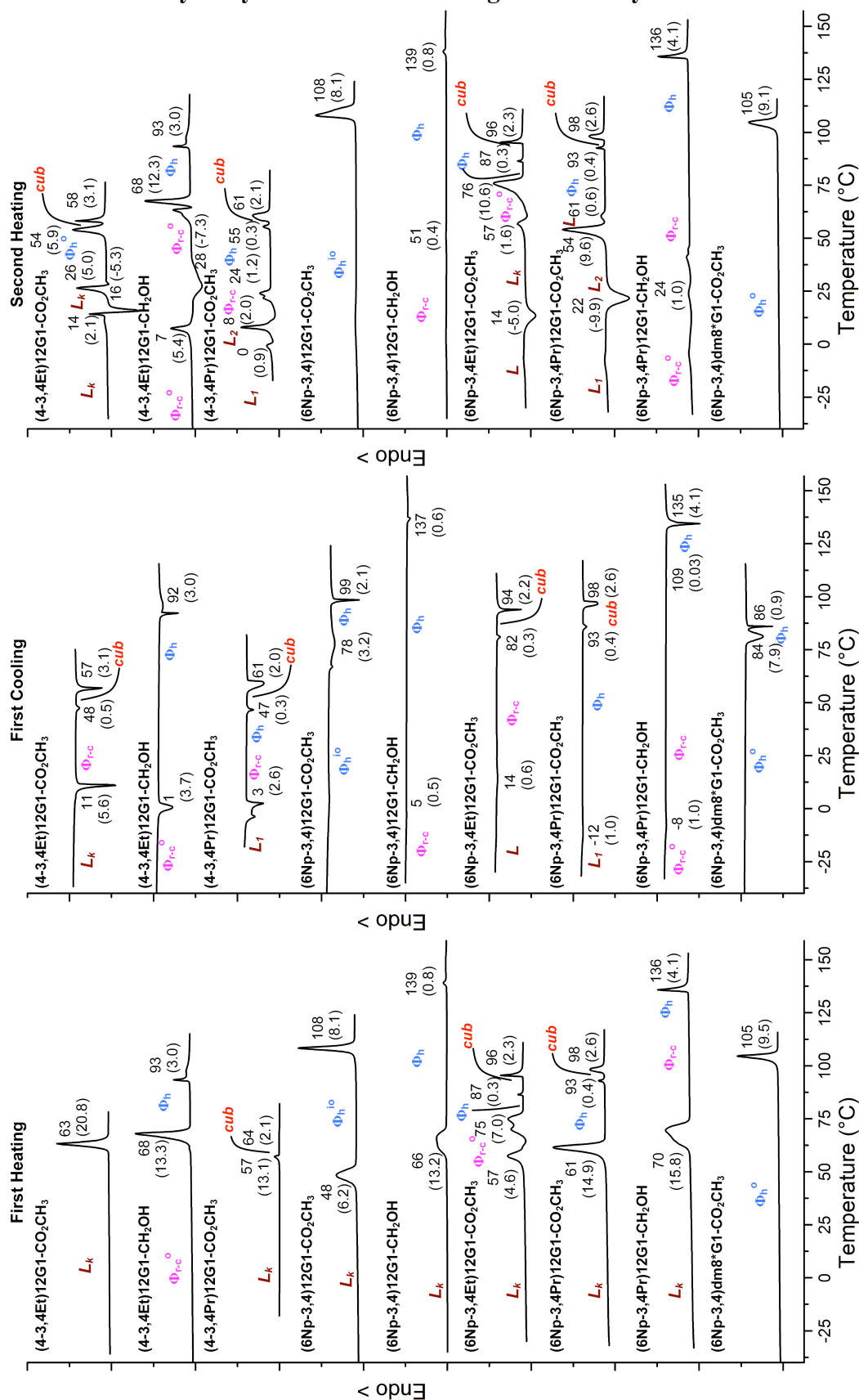
3-[3,4-bis{{4'-(dodecyloxy)biphenyl-4-yl}methoxy}phenyl]propan-1-ol, (4Bp-3,4Pr)12G1-CH₂OH (25): This compound was synthesized by the same general procedure described for the synthesis of compound 5 from LiAlH₄ (20 mg, 0.45 mmol) and (4Bp-3,4Pr)12G1-CO₂CH₃, **24** (0.20 g, 0.22 mmol) in dry THF (5 mL). After purification by column chromatography (SiO₂, EtOAc:Hexane = 3:7) and recrystallization in CH₂Cl₂-acetone, the title compound **25** (0.14 g, 74%) was obtained as white solid. HPLC: 99+%; ¹H NMR (500 MHz, CDCl₃, 27°C, TMS): δ = 0.88 (t, 6H, *J* = 6.4 Hz), 1.14 (br s, 1H), 1.20-1.40 (overlapped m, 32H), 1.46 (m, 4H), 1.81 (m, 6H), 2.62 (t, 2H, *J* = 7.4 Hz), 3.61 (m, 2H), 3.99 (t, 4H, *J* = 6.5 Hz), 5.15 (s, 2H), 5.20 (s, 2H), 6.72 (dd, 1H, *J* = 2.0, 8.1 Hz), 6.82 (d, 1H, *J* = 2.0 Hz), 6.90 (d, 1H, *J* = 8.1 Hz), 6.94 (d, 4H, *J* = 8.7 Hz), 7.50 (m, 12H); ¹³C NMR (125 MHz, CDCl₃, 27°C, TMS): δ = 14.3, 22.9, 26.2, 29., 29.5, 29.6, 29.7, 29.8, 29.8, 31.7, 32.1, 34.3, 62.3, 68.3, 71.4, 71.6,

114.9, 115.7, 116.1, 121.4, 126.9, 127.9, 128.1, 128.1, 128.2, 133.3, 135.5, 135.9, 136.0, 140.5, 147.5, 149.5, 158.9; MALDI-TOF m/z : 891.56 ($[M+Na]^+$ calculated for $C_{59}H_{80}NaO_5$ 891.59).

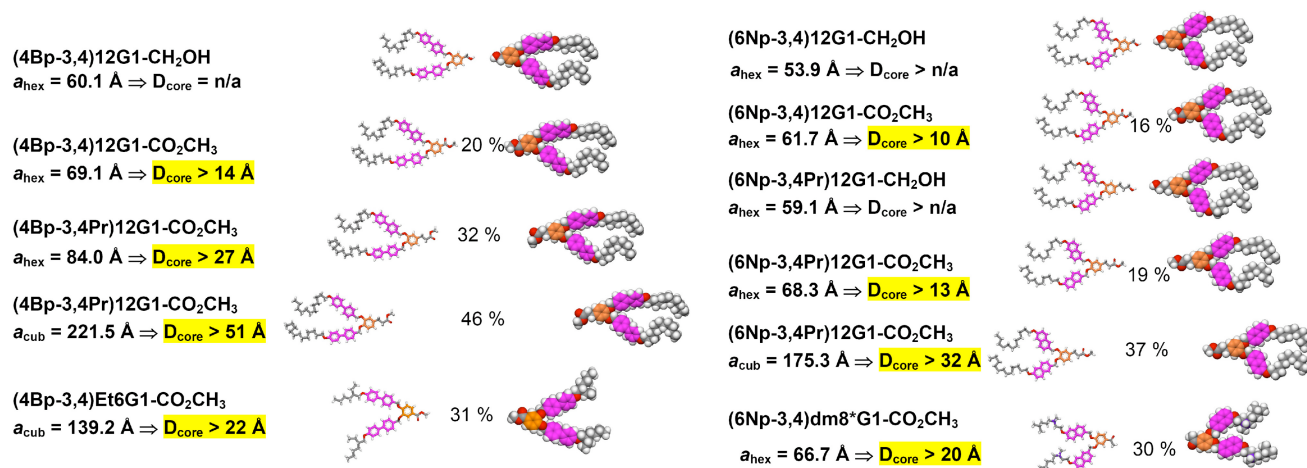
3,4-Bis-(4'-dodecyloxy-biphenyl-4-ylmethoxy)-benzoic acid, (4Bp-3,4)12G1CO₂H (26): To a clear solution of (4Bp-3,4)12G1-CO₂CH₃, **21a** (2.61 g, 3 mmol) in EtOH (95%, 60 mL) and THF (40 mL) mixture at 65 °C, was added KOH (0.98 g, 15 mmol in 3 mL H₂O) and the solution was refluxed for 2 h after which the mixture was cooled to RT and diluted with THF. The solution was acidified with glacial acetic acid (pH $\approx$ 3) and poured into cold H₂O (300 mL) and stirred for 15 min. The precipitate was collected by vacuum filtration and air-dried. The crude product was dissolved in warm THF and precipitated in acetone (400 mL). The powdered solid (2.36 g, 92%) was collected by filtration and vacuum dried. ¹H NMR (500 MHz, CDCl₃, 50 °C, TMS): δ = 0.91 (t, 6H, J = 7.0 Hz), 1.28-1.40 (m, 32H), 1.47-1.50 (m, 4H), 1.79-1.82 (m, 4H), 4.02 (t, 4H, J = 6.6 Hz), 5.26 (s, 4H), 6.96 (d, 4H, J = 8.3 Hz), 7.02 (d, 1H, J = 8.4 Hz), 7.46-7.51 (overlapped d, 8H), 7.56 (d, 4H, J = 8.3 Hz), 7.71 (d, 1H, J = 2.0 Hz), 7.73 (dd, 1H, J = 4.4, 2.0 Hz); ¹³C NMR was not taken because of the insoluble nature of the compound. MALDI-TOF m/z : 877.36 ($[M+Na]^+$, calculated for $C_{57}H_{74}NaO_6$ 877.54).

3,4-Bis-(4'-dodecyloxy-biphenyl-4-ylmethoxy)-benzoic acid 2-methoxy ethyl ester, (4Bp-3,4)12G1-CO₂CH₂CH₂OCH₃ (27): To a stirred solution of (4Bp-3,4)12G1-CO₂H, **26** (214 mg, 0.25 mmol) in dry THF (30 mL), 2-methoxy ethanol (24 mg, 0.315 mmol) and PPh₃ (164 mg, 0.625 mol) was added at RT under N₂. To that solution, DIAD (125 μ L, 0.63 mmol) was added drop-wise and stirred for 6 h. The reaction mixture was concentrated in a rotary evaporator and poured into MeOH (100 mL) and precipitate was collected by vacuum filtration. Purification by column chromatography (SiO₂, CH₂Cl₂ as eluent) followed by precipitation in MeOH yielded the title compound **27** (0.16 g, 70%) as pure white solid. HPLC: 99+%; TLC (CH₂Cl₂/MeOH = 9/1): R_f = 0.92; ¹H NMR (500 MHz, CDCl₃, 27 °C, TMS): δ = 0.90 (t, 6H, J = 7.0 Hz), 1.27-1.37 (overlapped m, 32H), 1.46-1.49 (m, 4H), 1.79-1.82 (m, 4H), 3.41 (s, 3H), 3.71 (t, 2H, J = 4.8 Hz), 4.01 (t, 4H, J = 6.6 Hz), 4.43 (t, 2H, J = 4.8 Hz), 5.25 (s, 4H), 6.95-6.98 (overlapped peaks, 5H), 7.47-7.55 (overlapped d, 12H), 7.70 (overlapped peaks, 2H); ¹³C NMR (125 MHz, CDCl₃, 27 °C, TMS): δ = 14.3, 22.9, 26.3, 29.5-29.9, 32.1, 59.3, 64.1, 68.3, 70.9, 71.4, 113.6, 115.0, 116.1, 123.2, 124.4, 127.0, 127.1, 127.9, 128.2, 128.3, 133.3, 135.0, 135.3, 140.8, 148.6, 153.3, 159.0, 166.5; MALDI-TOF m/z : 935.16 ($[M+Na]^+$, calculated for $C_{60}H_{80}NaO_7$ 935.58).

4. Thermal Analysis by Differential Scanning Calorimetry

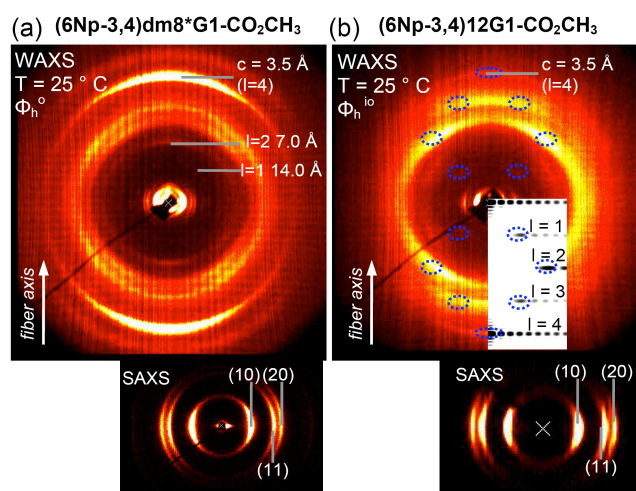


5. Structural and Retrostructural Analysis

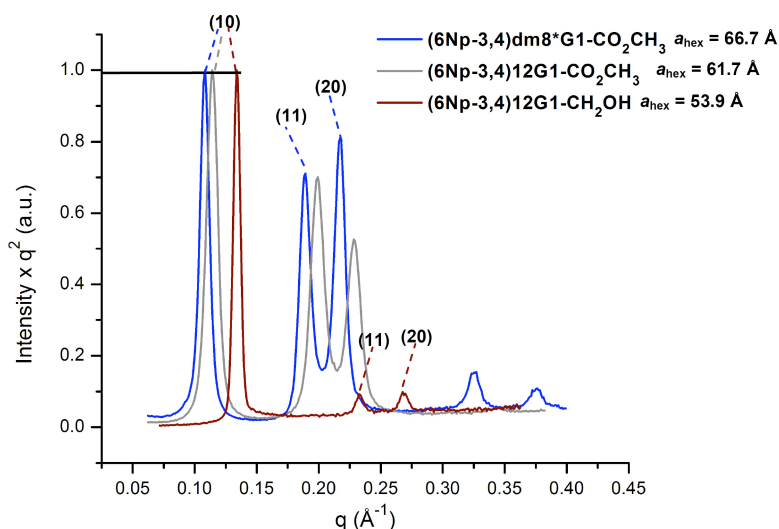


Supporting Figure SF4. Molecular models of the hybrid dendrons with alkyl chains in mixed *trans* and *gauche* conformation. The core diameter D_{core} was calculated assuming that there is no interdigitation between the supramolecular clusters. In all cases the percentages indicate the ratio $D_{\text{core}}/D_{\text{cluster}}$.

5.1. Analysis of the X-ray Powder and Fiber Patterns



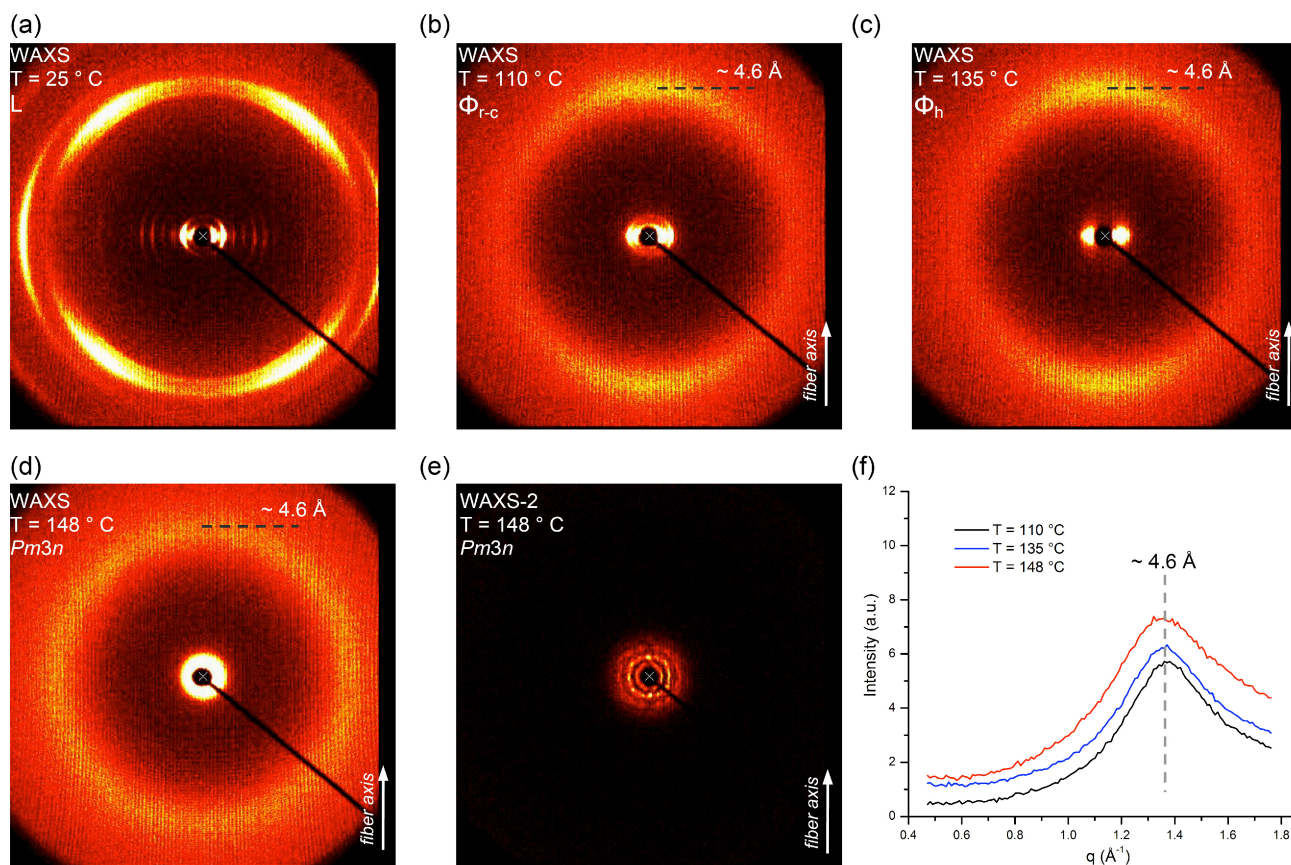
Supporting Figure SF5. WAXS and SAXS patterns collected from the oriented fibers of the hybrid naphthyl-benzyl dendrons functionalized with chiral (a) and achiral (b) alkyl chains. Compound, collection temperature and phase are indicated. In (b) the atomistic simulation of an *octa-36_I* helix,⁷ with the parameters $c = 3.5 \text{ \AA}$, $\varphi = 10^\circ$ and $R_{\text{helix}} = 20 \pm 4 \text{ \AA}$, is overlaid at scale on the WAXS fiber pattern.



Supporting Figure SF6. Small angle X-ray powder diffraction data collected at 100°C in the columnar hexagonal phases for the indicated naphthyl methyl ether hybrid dendrons.

Supporting Figure SF6 illustrates the significant difference of the powder X-ray diffraction intensity profiles of the first generation naphthyl methyl ether hybrid dendrons. Upon the change of the apex functionalization, the **(6Np-3,4)12G1-CO₂CH₃** exhibits a $D_{\text{col}} = 61.7 \text{ \AA}$ that corresponds to a 14% increase over the $D_{\text{col}} = 53.9 \text{ \AA}$ of the **(6Np-3,4)12G1-CH₂OH**. At the same time, the relative intensities of the higher order diffraction peaks exhibit a significant amplification: $\text{area}(20)/\text{area}(10) = 5\%$ for **(6Np-3,4)12G1-CH₂OH**, to $\text{area}(20)/\text{area}(10) = 70\%$ for **(6Np-3,4)12G1-CO₂CH₃**. Upon the change of the periphery functionalization, from achiral $R = \text{C}_{12}\text{H}_{25}$ to chiral $R = \text{dm8}^*$ alkyl chains, (Schemes 1,2), the intensity profiles shown in Supporting Figure SF6 are similar, both structures exhibiting comparable enhancements of the higher order diffraction peaks. Interestingly, the WAXS fiber patterns of the two naphthyl-benzyl hybrid dendritic esters shown in Supporting Figure SF5 suggest a helical packing. In the case of the **(6Np-3,4)dm8*G1-CO₂CH₃** the two stacking along the column axis features, marked in Supporting Figure SF5a at $7.0 \text{ \AA}$ on $L=2$ and at $3.5 \text{ \AA}$ on the $L=4$, together with the wide-angle off-meridional features observed on the $L=2$ suggest a possible supramolecular dimer structure. In addition, the wide-angle off-meridional features observed on $L=2$ and on $L=4$ suggest a dendron tilt correlation along the column axis. Molecular model based simulation of the WAXS fiber pattern combined with additional XRD experiments are needed to definitively assess these features as dendron tilt correlation or as column-to-column correlations. The wide angle features of the WAXS fiber pattern of the **(6Np-3,4)12G1-CO₂CH₃**, shown in Supporting Figure SF5b, were all in excellent agreement with the atomistic simulation of an *octa-36₁* helix,⁷ including the off-meridional wide angle features of the $L=2$. In comparison with the **(6Np-3,4)dm8*G1-CO₂CH₃**, the $L=4$ layer line of the **(6Np-3,4)12G1-CO₂CH₃** exhibits only a meridional maxima at $3.5 \text{ \AA}$, and no off-meridional features were observed. Similarly,

the L=4 layer line of the **(4Bp-3,4)12G1-CO₂CH₃** and **(4Bp-3,4)12G1-CO₂CH₂CH₂OCH₃** shown in Figure 3 exhibit only a meridional maxima.

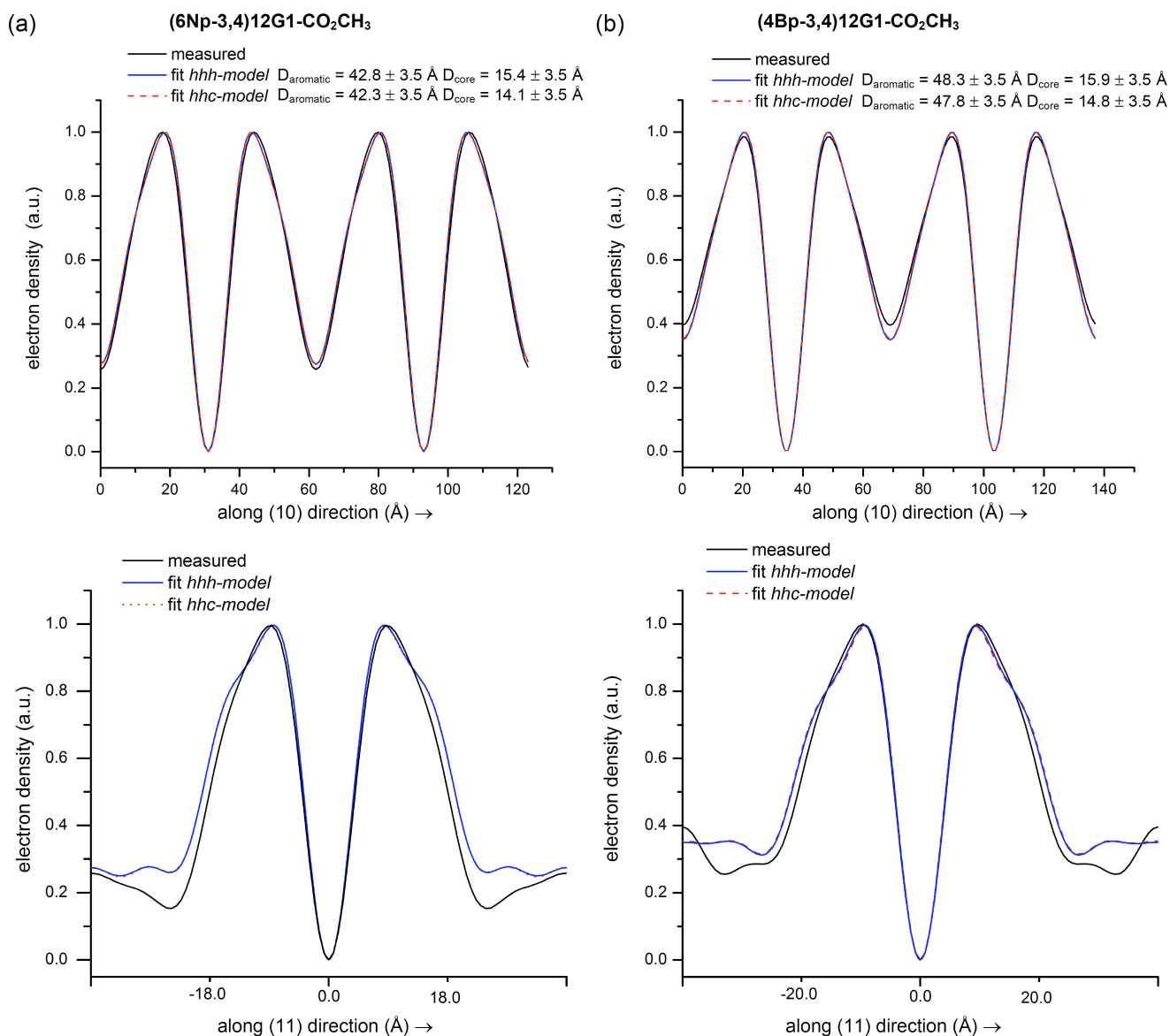


Supporting Figure SF7. Wide angle X-ray diffraction patterns collected from the oriented sample of **(4Bp-3,4Pr)12G1-CO₂CH₃** upon heating (a-d), and the corresponding WAXS-2 pattern (e) collected at larger detector to sample distance while the sample temperature was maintained constant at the value reached in (d). Corresponding meridional plots of the fiber patterns collected at the indicated temperatures (f).

The calculation of the number of dendrons forming the supramolecular stratum μ listed in Table 1 relies on four sets of parameters: molecular weight of the dendron, experimental density, lattice dimensions, and average thickness of the supramolecular stratum t . The average thickness t was extracted from the WAXS fiber and powder data. The value of t is 3.5 ± 0.2 Å for Φ_h^{i0} and Φ_h^0 phases, with the exception of **(4-3,4Et)12G1-CO₂CH₃** which has an average column strata thickness of 4.5 ± 0.2 Å. For Φ_h and $Pm\bar{3}n$ cubic phases the value of t ranges from 4.5 to 4.6 ± 0.2 Å. In the case of the $Pm\bar{3}n$ cubic phases the μ_c values listed in Table 1 are the number of dendrons forming the supramolecular “stratum”. This supramolecular stratum is defined by the cross-section through the plane $z = 0$ of the close-contact supramolecular clusters with the centers at $x = 1/4$ and $3/4$ as shown in Figure 11c, with an average diameter of $a/2$ and thickness t , where a is the $Pm\bar{3}n$ cubic phases lattice parameter. Supporting Figure

SF7f illustrates that upon the phase transition from the bilayer hexagonal to bilayer cubic, the value of t is unchanged for the **(4Bp-3,4)12G1-CO₂CH₃**. The difference of the value of t between the two groups of phases, $\{\Phi_h^{i0}$ and $\Phi_h^0\}$ and $\{\Phi_h$ and $Pm\bar{3}n\}$, is most probable caused by the average degree of order within the supramolecular stratum. In the group of liquid crystalline phases $\{\Phi_h$ and $Pm\bar{3}n\}$ the increased conformational freedom of the dendritic unit is most probable to generate an increase of the average supramolecular stratum thickness t .

5.2. Reconstruction of the Electron Density Distributions and Simulation of the Powder XRD



Supporting Figure SF8. Relative electron density profiles of the columnar hexagonal phase of the **(6Np-3,4)12G1-CO₂CH₃** (a) and **(4Bp-3,4)12G1-CO₂CH₃** (b) reconstructed from the measured, *hhh-model* and *hhc-model* fitted amplitudes along the (10) and the (11) direction, as indicated.

For all columnar and cubic phases the relative electron density distributions were calculated using

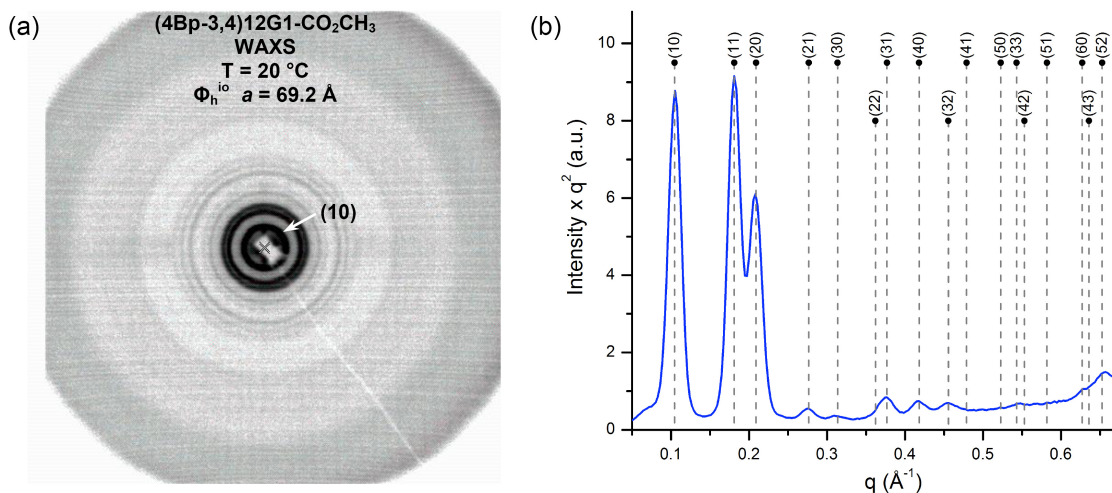
$$\rho(\vec{r}) = \sum_{j=1}^n F_j e^{i\vec{q}_j \cdot \vec{r}} \text{ where } F_j \text{ is the scaled amplitude of the } j^{\text{th}} \text{ powder diffraction peaks with the appropriate}$$

phase + or -, and n= total number of amplitudes included in the Fourier series reconstructions. The F_j were calculated from the square root of the area of the j^{th} powder diffraction peaks after applying the appropriate multiplicity corrections. Figures 8 and Supporting Figure SF8 show the relative electron density profiles reconstructed from a set of $n = 7$ amplitudes extracted from the small angle powder XRD patterns shown in Figures 1 and 8. Wide angle powder and fiber XRD patterns exhibit additional diffraction peaks, (Supporting Figure SF9), but due to the increased complexity of the phase problem the lower resolution of the peaks width and their overlap for the region $q_{(\text{hk})} > 0.4 \text{ \AA}^{-1}$ in WAXS that increases the error of the peak area, and their relatively small contribution to the Fourier reconstruction that is dominated by the F_{10} , F_{11} and F_{20} , they were not included in the analysis. Future work will address the phase problem for the case when additional higher order diffraction peaks are included.

The fitted amplitudes for all models and for all columnar and cubic phases, were based on the “aliphatic sea” model that considers a continuum for the outer aliphatic region of the supramolecular clusters.⁸ The diameter of the aliphatic region is provided directly by the lattice parameters. Therefore in all cases the only parameters that were fitted are the dimension of the aromatic and core regions, and whenever appropriate of the inner aliphatic region. The “aliphatic sea” model cancels the first term in the equations 3, 4 and 6.

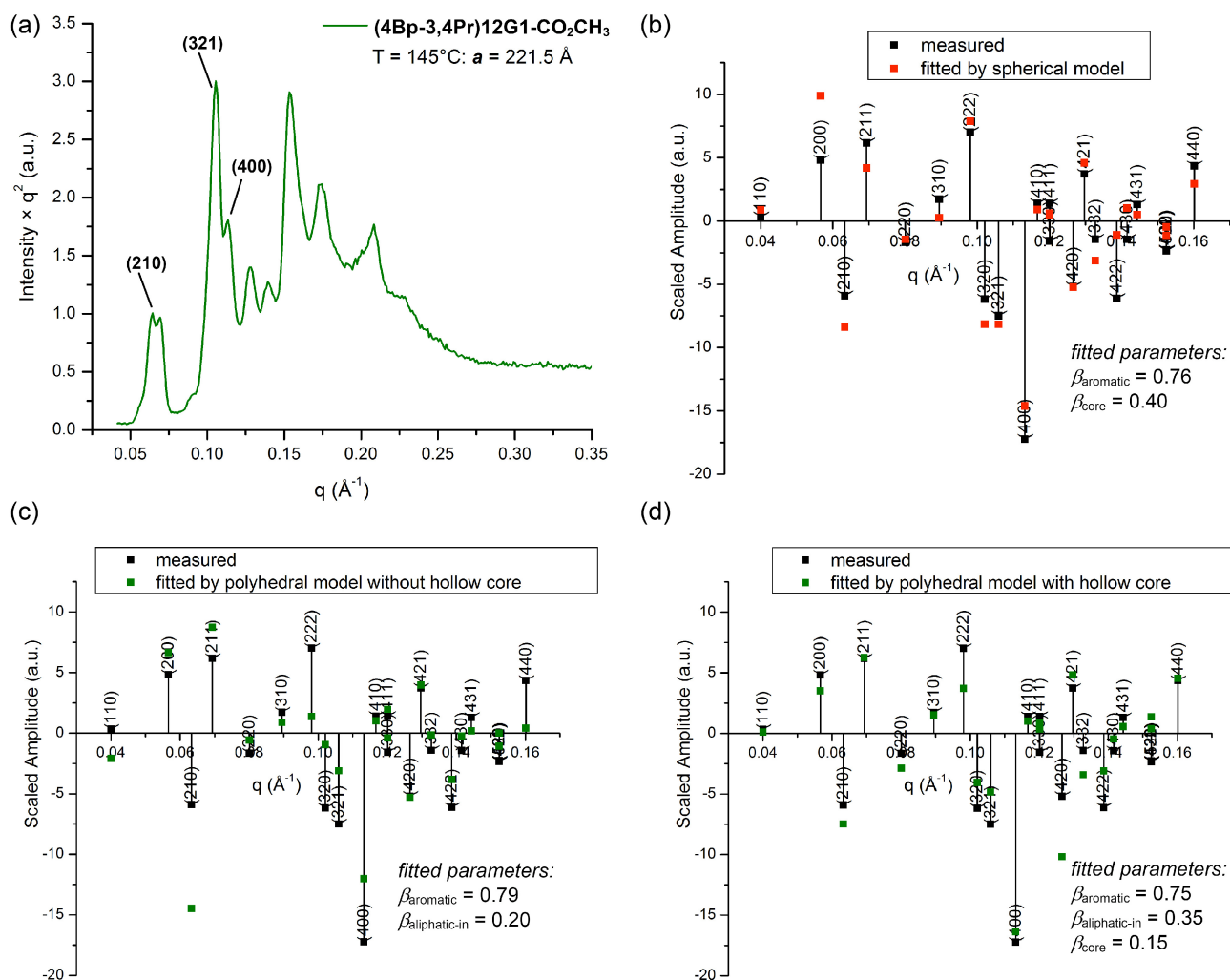
The Fourier transform given by eq 2 was tested for accuracy using a model of hexagonal shaped distribution of constant electron density that fills exactly unit cell of the hexagonal lattice. This model corresponds to the case when the side of the hexagon is equal with $a/(2 \sin 60^\circ)$, where a is the columnar hexagonal lattice dimension. The Fourier transform of this model is expected to generate zero scattering intensity for all $q_{(\text{hk}0)}$, except for $q=0$. The Fourier transform of this model calculated using eq 2 was obtained to be zero with a precision of $\pm 10^{-6}$.

The only exception to the “aliphatic sea” model was the spherical approximation⁹ described in this section. The electron densities used in the fits, ρ_{region} , were calculated from the number of electrons per region, marked for the aliphatic and aromatic regions in Figure 2, divided by the region volume. In all cases ρ_{core} is always zero. Considering that in all cases the experimental amplitudes are relative amplitudes, and not absolute ones, the fits have one an additional scaling parameter.



The powder XRD profile of the $Pm\bar{3}n$ cubic phase of **(4Bp-3,4Pr)12G1-CO₂CH₃** was collected in ultra-SAXS to improve the resolution, at the sample-detector distance of 120 cm. The resolution was improved compared with SAXS, but the area of the close-by diffraction peaks, shown in Supporting Figure SF10a, was still subject to larger errors. The amplitudes extracted from the powder XRD pattern are marked in Supporting Figure SF10b-d by the filled black squares. The parameters β marked in Figure 11 and Supporting Figure SF10 are defined as $\beta_{\text{core}} = D_{\text{core}} / (a/2)$, $\beta_{\text{aliphatic-in}} = D_{\text{aliphatic-in}} / (a/2)$ and $\beta_{\text{aromatic}} = D_{\text{aromatic}} / (a/2)$, where $a = Pm\bar{3}n$ cubic phase lattice parameter, D_{core} = diameter of the core region, $D_{\text{aliphatic-in}}$ = diameter of the inner aliphatic region, and D_{aromatic} = diameter of the aromatic region.

In comparison with the spherical model, the fit using scaled Voronoi tessellation based on a model with polyhedral aromatic and inner aliphatic regions, but no core region, matches better the experimental amplitudes, as shown in Supporting Figure SF10c. The best fit, shown in Supporting Figure SF11d, was obtained from the model with polyhedral aromatic and inner aliphatic regions, and an additional core region. The diameter of the core region was fitted to $\beta_{\text{core}} \times a / 2 = 0.15 \times 221.5 / 2 \text{ \AA} \sim 17 \text{ \AA}$, the thickness of the inner aliphatic region was fitted to $(\beta_{\text{aliphatic-in}} - \beta_{\text{core}}) \times a / 4 = 11.1 \text{ \AA}$ and the thickness of the outer aliphatic region was fitted to $(1 - \beta_{\text{aromatic}}) \times a / 4 = 13.9 \text{ \AA}$. Further adjustments of the numerical algorithms are needed to establish if the fit improved due to the presence of a core region or due to the addition of another parameter to the model.



Supporting Figure SF10. Powder diffraction collected from (4Bp-3,4Pr)12G1-CO₂CH₃ in the cubic phase (a) used to calculate the measured amplitudes from (b-d). Comparison of the measured amplitudes with the fitted amplitudes by the spherical model⁹ (b), polyhedral model without (c) and with (d) hollow core.

Supporting Table ST2. Structural and Retrostructural Analysis of the First Generation Dendritic Alcohols

Compound	T (°C)	Phase	$a, b(\text{\AA})^a$	$d_{10}, d_{11}, d_{20}, d_{21}, d_{30}(\text{\AA})^b$ $d_{10}, d_{01}, d_{11}, d_{20}, d_{21}, d_{31}, d_{12}, d_{22}(\text{\AA})^c$ $d_{001}, d_{002}, d_{003}, d_{004}(\text{\AA})^d$ $d_{20}, d_{11}, d_{31}, d_{40}, d_{02}, d_{22}(\text{\AA})^e$	$\gamma^f(^\circ)$
(4-3,4)12G1-CH ₂ OH	35	Φ_{r-s}^o	66.0, 38.9	-, 38.9, -, 33.0, 25.2, 19.2, 18.7, 16.8	
	90	Φ_h	49.9	43.2, 24.9, 21.6	
(4-3,4Et)12G1-CH ₂ OH	35	Φ_{r-c}	112.9, 48.0	56.6, 44.2, 29.6, 28.3, 24.0, 22.1	66.9
	90	Φ_h	52.3	45.3, 26.2, 22.7	
(6Np-3,4)12G1-CH ₂ OH	20	L^g	52.5	52.5, 26.3, 17.5	
	125	Φ_h	53.9	46.7, 26.9, 23.4	
	35	Φ_{r-c}	113.9, 50.5	57.0, 46.3, 30.4, 28.6, 25.3, 23.1	
	90	Φ_{r-c}	120.2, 53.6	60.2, 49.1, 32.1, 30.1, 26.8, 24.5	
(6Np-3,4Pr)12G1-CH ₂ OH	30	L^g	53.8	53.9, 26.9, 17.9	66.1
	90	Φ_{r-c}	120.2, 53.6	60.2, 49.1, 32.1, 30.1, 26.8, 24.5	
	130	Φ_h	59.1	51.2, 29.5, 25.6	
	35	Φ_{r-c}	130.7, 52.6	65.5, 48.9, 33.6, 32.7, 26.3, 24.4	
(4Bp-3,4)12G1-CH ₂ OH	20	L^g	59.5	59.5, 29.7, 19.8	69.1
	110	Φ_{r-c}	144.1, 54.9	72.2, 51.4, 36.3, 36.1, 27.5, 25.7	
	180	Φ_h	60.1	52.2, 30.1, 26.0	
	150	Φ_{r-c}	127.8, 56.1	63.9, 51.4, 33.9, 32.0, 28.1, 25.7	
	30	L	58.7	58.7, 29.3, 19.6	
(4Bp-3,4Pr)12G1-CH ₂ OH	30	L	61.5	61.5, 30.7, 20.5	67.4
	170	Φ_{r-c}	140.3, 58.3	70.4, 54.2, 36.5, 35.1, 29.1, 26.9	
(4Bp-3,4)Et6G1-CH ₂ OH	30	Φ_{r-s}^o	38.2, 33.1	38.2, 33.1, 25.0, 19.1, 16.5, -, 15.2	65.9
	100	Φ_{r-c}	103.9, 44.3	52.2, 40.9, 27.3, 26.0, 22.2, 20.4	
	145	Φ_{r-c}	97.1, 46.3	48.7, 41.9, 26.5, 24.3, 23.2, 20.9	
	160	Φ_h	50.2	43.5, 25.1, 21.7	

^a Lattice parameters calculated using $a = (2/\sqrt{3})(d_{10} + \sqrt{3}d_{11} + 2d_{20} + \sqrt{7}d_{21})/4$ for hexagonal phases, $a = (d_{001} + 2d_{002})/2$ for lamellar phases, $a = 2d_{20}$ and $b = d_{01}$ for simple rectangular phases, and $a = (2d_{20} + 4d_{40})/2$, $b = 2d_{02}$ for centered rectangular columnar phases. ^b d-spacing for columnar hexagonal phases. ^c d-spacing for simple rectangular phases. ^d d-spacing for lamellar phases. ^e d-spacing for centered rectangular columnar phases. ^f Angle defined by $\gamma = \angle(\vec{a} + \vec{b}, \vec{b})$ and calculated using $\gamma = \tan^{-1}(a/b)$. ^g Phase observed only in the first heating cycle of the as prepared compound.

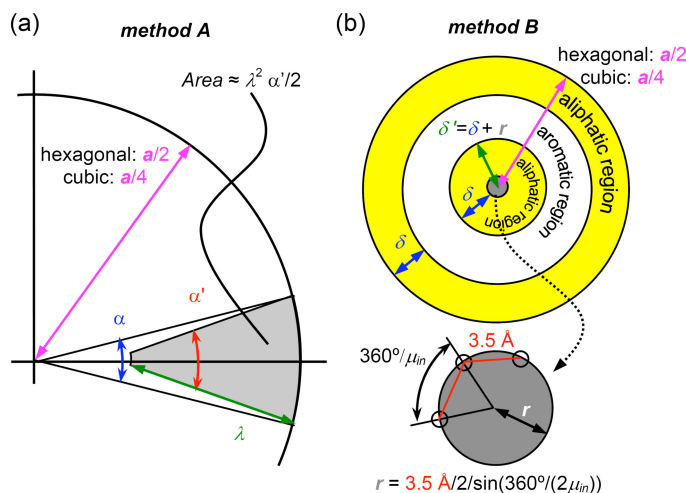
5.3. Calculation of the Number of Dendrons Forming the Outer and Inner Layers

For a cluster cross-section with thickness t , the total number of dendrons is calculated from the experimental density ρ , lattice parameter a , and molecular weight M_{wt} as shown in Table 1:

$$\mu^{(hexagonal)} = (a^2 t \sqrt{3} / 2) \rho N_A / M_{wt} \text{ and } \mu^{(cubic)} = (\pi a^2 t / 16) \rho N_A / M_{wt} \quad (\text{SE1})$$

For the bi-layer columnar and cubic phases the internal organization of the supramolecular clusters is characterized by two parameters: μ_{in} = number of dendrons forming the inner layer, and μ_{out} = number of dendrons forming the outer layer. The complexity of their intra- and inter- molecular processes that drive the self-assembly into bilayer phases is demonstrated by the lack of any apparent correlation in between the size of supramolecular assemblies upon the transition from hexagonal to cubic phases, as demonstrated by the large variation of x from the equation $a_{cub} = (2+x) a_{hex}$ from $x = 0.44$ to $x = 1.69$, (Figure 2). Excluding the case of $x = 1.69$ for **(4-3,4Et)12G1-CO₂CH₃**, that undergoes a transition from non-hollow singly-segregated polyhedral columns to doubly-segregated polyhedral vesicles, (Figure 9), x varies in a narrower range from 0.44 for **(4-3,4Pr)12G1-CO₂CH₃** up to 0.63 for **(4Bp-3,4Pr)12G1-CO₂CH₃**, whenever the supramolecular assemblies undergo transitions in between doubly-segregated phases. Therefore, it is possible to expect some degree of correlation between the number of dendrons

forming the bilayer assemblies, upon the transition from bilayer columns to bilayer vesicles, as shown in Figure 14b.



Supporting Figure SF11. Geometric representation used in the calculation of the number of dendrons forming the outer and inner layers for the bilayer assemblies with large μ (a) and small μ (b). a - lattice parameter, λ - length of the dendron, α and α' are the two indicated angles, and δ - aliphatic region thickness.

Equation SE1 provides only the sum of μ_{in} and μ_{out} ; therefore at least one additional structural parameter is needed. Figure SF11 illustrates the two proposed methodologies to evaluate the number of dendrons forming the inner and outer layers, respectively. Method A, illustrated geometrically in Figure SF11a, assumes that the length of the building block in the self-assembled state is known. This value, noted by λ , is estimated from proposed molecular model conformations, (Figure SF4, Table ST3). Method B, shown in Figure SF11b, assumes that the thickness δ of the aliphatic region can be estimated from molecular models and that the density of the inner and outer aliphatic regions is the same.

Using the geometric representation from Figure SF11a we obtain:

$$\mu = \mu_{in} + \mu_{out} \quad (SE2.1)$$

$$\mu_{out} = 360^\circ/\alpha \quad (SE2.2)$$

The total number of dendrons within the stratum is equal with the cluster cross-section area divided by the area occupied by one dendron:

$$\mu = (\pi a^2/4)/(\lambda^2 \alpha' /2) \quad (SE3)$$

Furthermore, the geometric representation shown in Figure SF11a provides the correlation of α with α' :

$$(a/2) \sin(\alpha/2) = \lambda \sin(\alpha'/2) \quad (SE4)$$

Finally, the last four equations form a system that is resolved in the variables α , α' , μ_{in} and μ_{out} .

An alternative approach, (*method B* in Figure SF11b), is to assume that the density of the outer aliphatic region is equal with the inner one:

$$\rho_{\text{aliphatic}} \sim (\text{number of dendrons})/(\text{volume}) \Rightarrow$$

$$\mu_{\text{out}}/[(a/2)^2 - (a/2 - \delta)^2] = \mu_{\text{in}}/(\delta + r)^2 \quad (\text{SE5})$$

As illustrated in Figure SF11b, the addition of the length r to the radii of the inner layer is required to compensate for the steric constraints imposed by the packing of the inner confined aliphatic region as is estimated by the equation:

$$r = (3.5/2) \text{ \AA} / \sin[360^\circ/(2\mu_{\text{in}})] \quad (\text{SE6})$$

Equations (SE5, SE6) and (SE2.1) form a system that is resolved in the unknown variables r , μ_{in} and μ_{out} . This is a non-linear system of equations that cannot be solved analytically. Equations (SE5, SE6) were estimated in Table ST3 after two numerical iterations, being evaluated once for $r = 0 \text{ \AA}$ and the resulting $\mu_{\text{in-u}}$ was used to evaluate the final iteration. The two methodologies A and B provided values within close range for μ_{in} and μ_{out} , respectively. As expected from the proposed parameters shown in Figure SF11, method B tends to consistently provide larger values of μ_{out} than method A whenever μ is large. The range of the values provided by the two methods, listed in Table ST3, was used in the interpretation of the electron density reconstructions and in the proposed molecular models. Both methods suggested an increase of μ_{in} upon transitions from bilayer columns to vesicles, as expected from the comparison of a_{hex} with a_{cub} (Table ST3).

Supporting Table ST3. Calculation of the Number of Dendrons Forming the Inner Layer, μ_{in} , and Outer Layer, μ_{out} , of the Hybrid Dendritic Esters Self-Assembled into Doubly-Segregated Aliphatic-Aromatic Supramolecular Structures

Compound	Phase ^a	$a/2$ ^b (Å) $a/4$ ^c (Å)	μ ^d	λ , δ ^e (Å)	α ^f (°)	α' ^g (°)	$\mu_{\text{in-A}}$ ^h	$\mu_{\text{out-A}}$ ⁱ	$\mu_{\text{in-u}}$ ^j	r ^k (Å)	$\mu_{\text{in-B}}$ ^l	$\mu_{\text{out-B}}$ ^m
(4Bp-3,4Pr)12G1-CO ₂ CH ₃	<i>h</i>	42.0	21	29, 14	24.61	35.96	6.4	14.6	3.50	2.24	4.5	16.5
	<i>c</i>	55.4	33	29, 14	20.52	39.78	15.5	17.5	4.17	2.56	5.6	27.4
(4Bp-3,4Et)12G1-CO ₂ CH ₃	<i>h</i>	40.8	20	27.8, 14	26.11	38.68	6.2	13.8	3.43	2.21	4.3	15.7
	<i>c</i>	52.4	30	27.8, 14	22.24	42.63	13.8	16.2	4.01	2.48	5.3	24.7
(6Np-3,4Pr)12G1-CO ₂ CH ₃	<i>h</i> ⁿ	34.2	14	27.2, 14	32.08	40.65	2.8	11.2	2.87	1.97	3.5	10.5
	<i>c</i>	43.8	21	27.2, 14	27.19	44.51	7.8	13.2	3.36	2.17	4.3	16.7
(6Np-3,4Et)12G1-CO ₂ CH ₃	<i>h</i> ⁿ	33.0	13	26.1, 14	34.68	44.27	2.6	10.4	2.76	1.93	3.4	9.6
	<i>c</i>	42.8	20	26.1, 14	28.95	48.40	7.6	12.4	3.27	2.14	4.1	15.9
(4-3,4Pr)12G1-CO ₂ CH ₃	<i>h</i> ⁿ	31.9	12	25, 14	37.76	48.69	2.5	9.5	2.63	1.88	3.2	8.8
	<i>c</i>	39.0	17	25, 14	32.34	51.47	5.9	11.1	3.05	2.04	3.8	13.2
(4-3,4Et)12G1-CO ₂ CH ₃	<i>c</i>	39.9	19	23.8, 14	30.98	53.12	7.4	11.6	3.33	2.16	4.2	14.8
(4Bp-3,4Et)dm8*G1-CO ₂ CH ₃	<i>c</i>	43.5	22	25, 11	27.84	49.43	9.1	12.9	2.78	1.94	3.7	18.3
(4Bp-3,4)Et6G1-CO ₂ CH ₃	<i>c</i>	34.8	16	23, 9	33.38	51.51	4.8	11.2	2.07	1.75	2.8	13.2
(6Np-3,4)dm8*G1-CO ₂ CH ₃	<i>h</i>	33.4	12	24, 11	40.84	58.10	3.2	8.8	1.98	1.75	2.5	9.5

^a Lattice notation: *h*- columnar hexagonal and *c*- $Pm\bar{3}n$ cubic. ^{b,c} Cluster radii calculated for hexagonal phase from $a/2$ and for cubic phases from $a/4$, where a is the lattice dimension listed in Table 1. ^d Number of dendrons per cluster cross-section listed in Table 1. ^e Dendron length λ , used in *method A*, and average aliphatic region δ thickness, used in *method B*, calculated from molecular model with mixed trans-gauche conformation for the alkyl chains assuming no cluster-to-cluster interdigitation. ^{f,g} Angles defined in Figure SF11 calculated using *method A* from eq SE3, SE4: $\alpha' = \pi(a/2)^2/(\lambda^2\mu/2)$ and $\alpha = 2\sin^{-1}[\lambda(a/2)\sin(\alpha'/2)]$. ^{h,i} Number of dendrons forming the inner and outer layer, respectively, calculated using *method A* from eq SE2: $\mu_{\text{out-A}} = 360^\circ/\alpha$ and $\mu_{\text{in-A}} = \mu - \mu_{\text{out-A}}$. ^j Number of dendrons, (un-corrected; first iteration of the non-linear system of equations SE5, SE6), forming the inner layer calculated using *method B* with $r = 0$ in eq SE5: $\mu_{\text{in-u}} = \mu/(a/\delta)$. ^k Correction factor r calculated from $r = (3.5 \text{ \AA} / 2) / \sin[360^\circ/(2\mu_{\text{in-u}})]$, as shown in Figure SF11b. ^{l,m} Number of dendrons forming the inner and outer layer, respectively, calculated using *method B* with non-zero correction factor r in eq SE5: $\mu_{\text{in-B}} = \mu/[1+(a\delta-\delta^2)/(\delta-r)^2]$ and $\mu_{\text{out-B}} = \mu - \mu_{\text{in-B}}$. ⁿ Bi-layer assignment is not definitive; these hexagonal phases have relatively small D_{col} .

Supporting Table ST4. Calculation of the Average Electron Density Based on the Fitted Parameters ^a

Dendron	Phase	D _{aliphatic} (Å)	D _{aromatic} (Å)	D _{aliphatic-in} (Å)	D _{core} (Å)	N _{aliphatic} (e ⁻)	N _{aromatic} (e ⁻)	ρ _{aliphatic} (e ⁻ /Å ³)	ρ _{aromatic} (e ⁻ /Å ³)	ρ _{aliphatic-in} (e ⁻ /Å ³)
(4Bp-3,4)12G1-CO ₂ CH ₃	hollow hexagonal	69.1	48		14.8	194	278	0.29	0.50	
(6Np-3,4)12G1-CO ₂ CH ₃	hollow hexagonal	61.7	42.3		14.1	194	250	0.30	0.50	
(4Bp-3,4Pr)12G1-CO ₂ CH ₃	bilayer hexagonal	84.0	64.0	26.0		194	294	0.27	0.49	0.46
	μ _{in} = 6									
	bilayer hexagonal	84.0	63.1	24.2		194	294	0.28	0.49	0.45
	μ _{in} = 5									
	bilayer hexagonal	84.0	62.2	22.4		194	294	0.28	0.50	0.42
	μ _{in} = 4									
	bilayer hexagonal	84.0	59.2	21.8		194	294	0.27	0.55	0.33
	μ _{in} = 3									
	hollow hexagonal	84.0	56.0		18.0	194	294	0.29	0.60	
	μ _{in} = 0									
	bilayer hollow cubic	110.8	83.1	38.8	16.6	194	294	0.23	0.49	0.36
(4-3,4Pr)12G1-CO ₂ CH ₃	bilayer cubic	78.0	53.0	27.7		194	214	0.21	0.51	0.36
(4-3,4Et)12G1-CO ₂ CH ₃	hexagonal	43.1	28			194	206	0.30	0.45	

^a The fitted parameters are D_{aromatic}, D_{aliphatic-in}, and D_{core} extracted from the fit of the powder XRD, (Supporting Table ST5). Their error of ± 3.5 Å provides an error range of the average electron density of ± 25%.

Supporting Table ST5. The (4Bp-3,4Pr)12G1-CO₂CH₃ hhc-Model Fitted Parameters for the Columnar Hexagonal Phase Performed as a Function of the Number of Dendron in the Core Region ^a

μ _{in}	μ _{out}	A ₁₀ ^{experimental} (a.u.) [A ₁₀ ^{hhc-model} (a.u.)]	A ₁₁ ^{experimental} (a.u.) [A ₁₁ ^{hhc-model} (a.u.)]	A ₂₀ ^{experimental} (a.u.) [A ₂₀ ^{hhc-model} (a.u.)]	A ₂₁ ^{experimental} (a.u.) [A ₂₁ ^{hhc-model} (a.u.)]	A ₃₀ ^{experimental} (a.u.) [A ₃₀ ^{hhc-model} (a.u.)]	R ^b	D _{aromatic} (Å)	D _{aliphatic-in} (Å)	D _{core} (Å)
0	21	28.4 [25.6]	-28.3 [-22.3]	-25.7 [-28.3]	-7.1 [-10.6]	-5.4 [-8.3]	0.175	56	n/a	18
3	18	28.4 [28.6]	-28.3 [-25.4]	-25.7 [-29.9]	-7.1 [-3.7]	-5.4 [-2.3]	0.144	59.2	21.8	n/a
4	17	28.4 [29.3]	-28.3 [-25.9]	-25.7 [-29.9]	-7.1 [-1.3]	-5.4 [-0.5]	0.188	60.1	23.3	n/a
4	17	28.4 [27.6]	-28.3 [-24.7]	-25.7 [-27.4]	7.1 [1.7]	5.4 [0.5]	0.174	62.2	22.4	n/a
5	16	28.4 [27.8]	-28.3 [-25.6]	-25.7 [-27.7]	7.1 [3.8]	5.4 [1.9]	0.122	63.1	24.2	n/a
6	15	28.4 [27.9]	-28.3 [-26.3]	-25.7 [-27.7]	7.1 [6.0]	5.4 [3.2]	0.079	64.0	26.0	n/a

^a The fitted parameters are D_{aromatic}, D_{aliphatic-in}, and D_{core} extracted from the hhc-model fit of the powder XRD. Their error is ± 3.5 Å. ^b The least χ₂-square fit R coefficient illustrates the fit quality (R=0 corresponds to the ideal fit).

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