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Hydrogen-bond stabilized columnar discotic benzenetrisamides with pendant triphenylene groups

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Experimental Section

Measurements

^{1}H-NMR (300 MHz and 400 MHz) and ^{13}C-NMR (75 MHz and 100 MHz) spectra were obtained with a Bruker spectrometer, using $CDCl_3$ as a solvent. Melting points, thermal phase transition temperatures and optical investigation of the liquid crystalline phases were determined on samples between ordinary glass slides using an Olympus BH-2 polarization microscope equipped with a Mettler FP82HT hot stage, which was controlled by a Mettler FP80HT central processor. Differential scanning calorimetry (DSC) thermograms were obtained on a Perkin Elmer DSC-7 system using 2-5 mg samples in 30 µl sample pans and a scan rate of 10 °C min^{-1}. ΔH is calculated in kJ mol^{-1}.

Temperature dependent X-ray curves were measured on a Philips (Panalytical) X'pert Pro MRD machine equipped with an Anton Paar camera for temperature control. For the measurements in the small angle region, the sample was spread in the isotropic phase on a thin glass slide (about 15 µm thick), which was placed on a temperature-regulated flat copper sample stage.

The accurate masses were obtained using a Finnigan MAT 95 mass spectrometer operating in the 70 eV EI mode at a resolution 5500. Matrix-assisted laser desorption/ionization time-of-flight mass spectra (Maldi-Tof MS) were obtained on an Ultraflex spectrometer using 2,5-dihydroxybenzoic acid (DHB; Sigma-Aldrich) as a matrix.

Infrared spectra (FTIR) were obtained using a Bruker Vector 22 spectrometer. Samples for the temperature-dependent studies were cast from CH_2Cl_2 solution onto a KBr window. The KBr window was first heated to about 10 °C above the isotropisation temperature in order to remove residual water and solvents. The spectra were recorded as a function of decreasing temperature.

Circular dichroism studies were performed on aggregates formed in hexane solutions, at room temperature, on a Jasco J-715 polarimeter with a cell with a 0.1 cm path length. A scan rate was used of 50 nm min^{-1} and 10 scans were averaged.

Charge carriers are created in the materials by high energy radiation (3 MeV) from a van de Graaf accelerator and the mobile charges are detected by monitoring adsorbed microwave power. The electron pulse lengths were varied from 2 to 20 ns, and the maximum beam current is 4 A. The samples were put in a cavity of 6 x 3 x 2 mm^3 in a polyimide block. This block was introduced in a gold plated copper cell, which gives a negligible conductivity signal on irradiation.

Synthesis

All solvents were PA quality. All reactions were carried out under a nitrogen or argon atmosphere. Dry CH_2Cl_2 was freshly distilled from CaH_2. All starting materials were obtained from Sigma-Aldrich and used as received. Compounds **1, 2-Bu, 2-Hex, 3-Hex** and **T-4-Hex** have been reported previously.[1] 2-(3-Bromopropyl)isoindoline-1,3-dione was also prepared according to literature. [2]

(S)-2-(2-Methylbutoxy)phenol, **2-MeBu**

A mixture of 35.0 g catechol (0.32 mol), 5.00 g (*S*)-(+)-1-bromo-2-methylbutane (33.1 mmol) and 3.50 g Cs_2CO_3 was refluxed in 200 ml 2-butanone, under nitrogen, for 72 h. The reaction mixture was cooled and solids were removed by filtration over Hyflo. The filtrate was concentrated under *vacuum* and purified by column chromatography on siliga gel with dichloromethane / petroleum ether (40/60) as eluent in a (1:1) ratio to give 2.52 g (42 %) of **2-MeBu** as a pale yellow oil.

^{1}H-NMR: δ 6.97-6.86 (4H, m, ArH), 5.70 (1H, s, OH), 3.97-3.83 (2H, m, $OC\mathit{H_2}CH$, prochiral Hs), 1.96 (1H, m, CH chiral), 1.63-1.56 (1H, m, $CHC\mathit{H_2}CH_3$, prochiral H), 1.38-1.31 (1H, m, $CHC\mathit{H_2}CH_3$, prochiral H), 1.07 (3H, d, J = 6.78 Hz, $CHC\mathit{H_3}$), 1.00 (3H, t, J = 7.53 Hz, $CH_2C\mathit{H_3}$).

^{13}C-NMR: δ 146.11 (1-ArC-OH), 145.86 (2-Ar*C*-OCH_2), 121.30 (6-ArC-H), 120.10 (3-ArC-H), 114.47 (5-ArC-H), 111.64 (4-ArC-H), 73.65-73.39 (OCH_2), 34.94-34.71 (CH chiral), 26.18-25.94 ($\mathit{C}H_2CH_3$), 16.58-16.33 ($CH\mathit{C}H_3$), 11.31 ($CH_2\mathit{C}H_3$).

MS $[M]^{+\bullet}$: calculated for $C_{11}H_{16}O_2$: 180.1150 amu; found $[M]^{+\bullet}$ 180.1148 amu.

2-[3-(3,6,7,10,11-Pentakishexyloxytriphenylen-2-yloxy)propyl]isoindole-1,3-dione,

2-(3-Bromopropyl)isoindoline-1,3-dione[2] (5.00 g, 18 mmol), 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-ol **3-Hex**[1] (5.70 g, 7.70 mmol) and 3.00 g K_2CO_3 in 2-butanone (50 ml) were stirred at reflux for 20 h. After the solvent was evaporated under vacuum, 100 ml water was added and the crude product extracted with dichloromethane (3 x 50 ml). The organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvent was evaporated under vacuum and the product recrystallized from acetonitrile, when 7.00 g (7.50 mmol, 97 %) of pure product was obtained; m.p. 88 °C.

^{1}H-NMR: δ 7.92-7.68 (10H, m, ArH), 4.31-4.17 (12H, m, OCH_2), 4.02 (2H, t, J = 6.00 Hz, CH_2N), 2.35-1.25 (m, 42H, CH_2), 0.95 (15H, m, CH_3).

^{13}C-NMR: δ 166.53 (C=O), 147.39-146.63 (ArC-O triphenylene), 132.08 (C-H phthalimide), 130.35 (C-C phthalimide), 122.35-121.55 (ArC-C triphenylene), 121.33 (C-H phthalimide), 107.15-105.19 (ArC-H triphenylene), 67.91-67.68 ($OC\mathit{H_2}(CH_2)_4$), 66.02 ($\mathit{O}CH_2CH_2CH_2N$), 33.67 ($N\mathit{C}H_2CH_2CH_2O$), 29.84-20.81 ($OCH_2(\mathit{C}H_2)_4CH_3$), 12.20 ($CH_3$).

MS $[M]^{+\bullet}$: calculated for $C_{59}H_{81}NO_8$: 931.5962 amu; found $[M]^{+\bullet}$ 931.5973 amu.

2-Hydroxy-6,7,10,11-tetrakishexyloxy-3-(butyloxy)triphenylene, **3-Bu**

A mixture of 1.20 g (7.20 mmol) of **2-Bu** and 5.30 g (9.74 mmol) of **1** was dissolved in 20 ml freshly distilled dichloromethane. Under anhydrous conditions, 5.00 g of $FeCl_3$ was then carefully added. The reaction mixture was stirred for 30 min. under nitrogen at room temperature. The triphenylene compound crystallized after addition of 150 ml cold methanol. The reaction mixture was further cooled to -35 °C and the precipitate was filtered off. The crystals were washed several times with cold methanol. The crude product was purified by column chromatography over silica gel with dichloromethane / petroleum ether 40-60, in a (1:1) ratio as eluent. After recrystallization from acetonitrile, 1.30 g (1.80 mmol, 25 %) of **3-Bu** as white crystals, was obtained; m.p. 103 °C.

^{1}H-NMR: δ 7.89-7.71 (6H, m, ArH), 5.82 (1H, s, OH), 4.23 (2H, t, J = 6.00 Hz, OCH_2), 4.18-4.11 (8H, m, OCH_2), 1.91-1.82 (10H, m, $OCH_2C\mathit{H_2}$), 1.57-1.28 (26H, m, CH_2), 1.01 (3H, t, J = 6.00 Hz, CH_3), 0.89 (12H, bt, J = 7.14 Hz, CH_3).

^{13}C-NMR: δ 149.18-148.78, 145.84-145.28 (ArC-O), 123.96-122.98 (ArC-C), 106.67-104.35 (ArC-H), 69.97-68.79 (OCH_2), 31.69-19.36 (CH_2), 14.05, 13.92 (CH_3).

MS $[M]^{+\bullet}$: calculated for $C_{46}H_{68}O_6$: 716.5016 amu; found $[M]^{+\bullet}$ 716.5007 amu.

2-Hydroxy-6,7,10,11-tetrakishexyloxy-3-(2-methylbutoxy)triphenylene, **3-MeBu**

A mixture of **2-MeBu** (1.20 g, 6.67 mmol) and **1** (4.99 g, 9.02 mmol) was dissolved in 20 ml freshly distilled dichloromethane. Under anhydrous conditions, 7.00 g of $FeCl_3$ was then carefully added. The reaction mixture was stirred, under nitrogen, for 30 minutes at room temperature. The triphenylene compound crystallized after addition of 150 ml cold methanol. The mixture was further cooled to –35 °C and the precipitate filtered off. The crystals were washed several times with cold methanol. The crude product was purified by column chromatography over silica gel with dichloromethane / petroleum ether 40-60, in a (1:1) ratio as eluent. After recrystallization from acetonitrile, 1.30 g (1.78 mmol, 27 %) of **3-MeBu** was obtained; m. p. 94 ºC.

^{1}H-NMR: δ 7.98-7.78 (6H, m, ArH), 5.90 (1H, s, OH), 4.25 (8H, t, J = 6.00 Hz, OCH_2), 4.20-4.10 (2H, m, $OC\mathit{H_2}CH$), 2.10-1.91 (1H, m, CH chiral), 1.74-1.27 (34H, m, CH_2), 1.16 (3H, d, J = 6.00 Hz, $C\mathit{H_3}CH$), 1.06 (3H, t, J = 6.00 Hz, $CH_2C\mathit{H_3}$), 0.95 (12H, bt, J = 6.00 Hz, CH_3).
^{13}C-NMR: δ 149.19-145.29 (ArC-O), 123.77-122.99 (ArC-C), 107.82-104.33 (ArC-H), 73.79 (O*C*H$_2$CH), 70.05-69.16 ($OCH_2\mathit{C}H_2$), 34.83 (CH chiral), 31.69-22.66 (CH_2), 16.78 (*C*HCH$_3$), 14.05 (CH_3), 11.45 ($CHCH_2\mathit{C}H_3$).
MS $[M]^{+\bullet}$: calculated for $C_{47}H_{70}O_6$: 730.5172 amu; found $[M]^{+\bullet}$ 730.5165 amu.

2-(4-Bromobutyloxy)-6,7,10,11-tetrakishexyloxy-3-(butyloxy)triphenylene

A mixture of **3-Bu** (1.30 g, 1.80 mmol), 1.90 g of 1,4-dibromobutane (8.70 mmol) and 2.00 g of K_2CO_3 was refluxed in 60 ml of 2-butanone for 20 h. After cooling the reaction mixture to room temperature the solvent was evaporated, 50 ml of dichloromethane was added and K_2CO_3 removed by filtration. The filtrate was concentrated and the redidue recrystallized from acetonitrile, yielding 1.30 g (1.60 mmol, 90 %) of the bromobutoxy derivative as white crystals Cr-56 °C-Col$_h$-70 °C-I.
^{1}H NMR: δ 7.86-7.85 (6H, asymmetric singlet, ArH), 4.31-4.23 (12H, m, OCH_2), 3.62 (2H, t, J = 6.00 Hz, CH_2Br), 2.22-2.11 (4H, m, $C\mathit{H_2}C\mathit{H_2}CH_2Br$), 2.01-1.91 (10H, m, CH_2), 1.67-1.37 (26H, m, CH_2), 1.07 (3H, t, J = 7.53 Hz, CH_3), 0.95 (12H, bt, J = 6.96 Hz, CH_3).
^{13}C NMR: δ 149.10-148.56 (ArC-O), 123.91-123.48 (ArC-C), 107.63-106.92 (ArC-H), 69.79-69.74 (OCH_2), 69.15 (OCH_2), 68.81 (OCH_2), 33.70 (CH_2Br), 31.69-19.43 (CH_2), 14.05-13.99 (CH_3).
MS $[M]^{+\bullet}$: calculated for $C_{50}H_{75}BrO_6$: 850.4747 amu; found $[M]^{+\bullet}$ 850.4729 amu.

2-(4-Bromobutyloxy)-6,7,10,11-tetrakishexyloxy-3-(2-methylbutoxy)triphenylene

A mixture of 1.10 g (1.50 mmol) of **3-MeBu**, 1.62 g (7.50 mmol) of 1,4-dibromobutane and 2.00 g of K_2CO_3 was refluxed in 60 ml of 2-butanone for 20 h. After cooling the reaction mixture to room temperature the solvent was evaporated, 50 ml of dichloromethane was added and K_2CO_3 removed by filtration. The filtrate was concentrated and the redidue recrystallized from acetonitrile, yielding 0.76 g (0.88 mmol, 59 %) of the bromobutoxy derivative. Cr - 51 °C - Col$_h$ - 70 °C - I.
^{1}H NMR: δ 7.86-7.83 (6H, m, ArH), 4.31-4.23 (10H, m, OCH_2), 4.11-4.03 (2H, m, $OC\mathit{H_2}CH$), 3.61 (2H, t, J = 6.00 Hz, CH_2Br), 2.23-1.36 (39H, m, CH_2 + chiral CH), 1.16-1.14 (3H, d, J = 6.60 Hz, $C\mathit{H_3}CH$), 1.05 (3H, t, J = 7.53 Hz, $C\mathit{H_3}CH_2CH$), 0.95 (12H, t, J = 7.14 Hz, CH_3).
^{13}C NMR: δ 149.20-148.60 (ArC-O), 123.92-123.41 (ArC-C), 107.69-106.79 (ArC-H), 74.24 (O*C*H$_2$CH) 69.90-68.78 (O*C*H$_2$CH$_2$), 34.99 (CH chiral), 33.71 (CH_2Br), 31.69-22.66 (CH_2), 16.80 (*C*H$_3$CH), 14.05 (CH_3), 11.50 (*C*H$_3$CH$_2$CH).
MS $[M]^{+\bullet}$: calculated for $C_{51}H_{77}BrO_6$: 864.4904 amu; found $[M]^{+\bullet}$ 864.4891 amu.

2-(5-Bromopentyloxy)-3,6,7,10,11-pentakishexyloxytriphenylene

A mixture of 2.38 g (3.19 mmol) of 2-hydroxy-3,6,7,10,11-pentakishexyloxytriphenylene **3-Hex**, 2.50 g of 1,5-dibromopentane (10.9 mmol) and 5.00 g of K_2CO_3 was refluxed in 60 ml of 2-butanone for 20 h. After cooling the reaction mixture to room temperature the solvent was evaporated, 50 ml of dichloromethane was added and K_2CO_3 removed by filtration. The filtrate was concentrated and the redidue recrystallized from acetonitrile, yielding 2.22 g (2.48 mmol; 78 %) of the bromopentyloxy derivative as colorless crystals. M.p. 69 °C.

^{1}H-NMR: δ 7.86 (6H, s, ArH), 4.45-4.24 (12H, m, OCH_2), 3.44 (2H, t, J = 6.80 Hz, CH_2Br), 2.08-1.28 (46H, m, CH_2), 0.96 (15H, t, J = 6.80 Hz, CH_3).

^{13}C-NMR: δ 148.91 (ArC-O), 123.53 (ArC-C), 107.21 (ArC-H), 69.63 (OCH_2), 40.68 (CH_2Br), 31.90-22.65 (CH_2), 14.12-14.05 (CH_3).

MS $[M]^{+\bullet}$: calculated for $C_{53}H_{81}BrO_6$: 892.5217 amu; found: $[M]^{+\bullet}$ 892.5204 amu.

2-(6-Bromohexyloxy)-3,6,7,10,11-pentakishexyloxytriphenylene

A mixture of 1.77 g (2.37 mmol) of 2-hydroxy-3,6,7,10,11-pentakishexyloxytriphenylene **3-Hex**, 5.70 g of 1,6-dibromohexane (23 mmol) and 5.00 g of Cs_2CO_3 was refluxed in acetonitrile, under nitrogen, for 5 h. After filtration of the salts and removal of the solvent, the product was recrystallized from acetonitrile, yielding 1.52 g (1.67 mmol; 71 %) of the bromohexyloxy derivative as colorless crystals. M.p. 62 °C.

^{1}H-NMR: δ 7.85 (6H, s, ArH), 4.25 (12H, t, J = 6.00 Hz, OCH_2), 3.47 (2H, t, J = 6.00 Hz, CH_2Br), 2.19-1.91 (12H, m, CH_2CH_2O), 1.75-1.09 (36H, m, CH_2), 0.93 (15H, bt, J = 6.00 Hz, CH_3).

^{13}C-NMR: δ 149.01 (ArC-O), 123.59 (ArC-C), 107.40 (ArC-H), 69.73 (OCH_2), 33.76 (CH_2Br), 32.74-22.66 (CH_2), 14.05 (CH_3).

MS $[M]^{+\bullet}$: calculated for $C_{54}H_{83}BrO_6$: 906.5373 amu; found: $[M]^{+\bullet}$ 906.5388 amu.

2-(4-Azidobutyloxy)-6,7,10,11-tetrakishexyloxy-3-(butyloxy)triphenylene

A mixture of 1.30 g (1.80 mmol) of 2-(4-bromobutyloxy)-6,7,10,11-tetrakishexyloxy-3-(butyloxy)triphenylene and 0.51 g (7.90 mmol) of sodium azide was refluxed in 50 ml ethanol for 10 h. After adding dichloromethane, the excess of sodium azide was filtrated off and the crude product was purified by column chromatography over silica gel eluting with dichloromethane / petroleum ether 40/60 in a (2:1) ratio. After recrystallization from acetonitrile, 0.74 g (0.91 mmol; 58 %) of the azido derivative was obtained as white crystals,. Cr - 60 °C - Col_h - 84 °C - I.

^{1}H NMR: δ 7.77 (6H, s, ArH), 4.21-4.14 (12H, m, OCH_2), 3.38 (2H, t, J = 6.00 Hz, CH_2N_3), 1.93-1.82 (14H, m, CH_2), 1.46-1.32 (26H, m, CH_2), 0.98 (3H, t, J = 6.00 Hz, CH_3), 0.89-0.84 (12H, m, CH_3).

^{13}C NMR: δ 149.10-148.65 (ArC-O), 123.90-123.48 (ArC-C), 107.61-106.93 (ArC-H), 69.79-69.14 (OCH_2), 69.08 (OCH_2), 51.31 (CH_2N_3), 31.69-19.41 (CH_2), 14.05-13.97 (CH_3).

MS $[M]^{+\bullet}$: calculated for $C_{50}H_{75}N_3O_6$: 813.5656 amu; found $[M]^{+\bullet}$ 813.5643 amu.

2-(4-Azidobutyloxy)-6,7,10,11-tetrakishexyloxy-3-(2-methylbutoxy)triphenylene

Using the same procedure, a mixture of 0.76 g (0.88 mmol) of 2-(4-bromobutyloxy)-6,7,10,11-tetrakishexyloxy-3-(2-methylbutoxy)triphenylene and 0.29 g (4.40 mmol) of sodium azide yielded 0.70 g (0.85 mmol, 97 %) of the azido derivative. Cr - 46 ºC - Col_h - 64 ºC - I.

^{1}H NMR: δ 7.86-7.84 (6H, m, ArH), 4.30-4.23 (10H, m, OCH_2CH_2), 4.12, 4.03 (2H, 2 x dd, J = 6.00 Hz, J = 3.00 Hz, OCH_2CH), 3.47 (2H, t, J = 6.60 Hz, CH_2N_3), 2.05-1.91 (7H, m, 3 x CH_2 + CH chiral), 1.63-1.36 (32H, m, CH_2), 1.15 (3H, d, J = 6.00 Hz, CH_3CH), 1.05 (3H, t, J = 6.00 Hz, CH_3CH_2CH), 0.98-0.93 (12H, m, CH_3).

^{13}C NMR: δ 149.20-148.60 (ArC-O), 123.78-123.40 (ArC-C), 107.67-106.79 (ArC-H), 74.22 (OCH_2CH), 69.90-69.07 (OCH_2CH_2), 51.31 (CH_2N_3), 34.98 (CH chiral), 31.69-22.66 (CH_2), 16.80 (CH_3CH), 14.05 (CH_3), 11.48 (CH_3CH_2CH).

MS $[M]^{+\bullet}$: calculated for $C_{51}H_{77}N_3O_6$: 827.5812 amu; found $[M]^{+\bullet}$ 827.5808 amu.

2-(5-Azidopentyloxy)-3,6,7,10,11-pentakishexyloxytriphenylene

A mixture of 1.94 g (2.17 mmol) of 2-(5-bromopentyloxy)-3,6,7,10,11-pentakis-hexyloxytriphenylene and 1.64 g (25 mmol) of sodium azide in ethanol was refluxed for 10 h. After the reaction was complete the solvent was evaporated. After addition of 20 ml of water, the reaction mixture was extracted with 2 x 20 ml of CH_2Cl_2; the organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated under *vacuum*. After recrystallization from acetonitrile, 1.96 g (2.29 mmol; 95 %) of compound the azido derivative was obtained as white crystals. M.p. 63°C.

^{1}H-NMR: δ 7.86 (6H, s, ArH), 4.26 (12H, t, J = 6.40 Hz, OCH_2), 3.38 (2H, t, J = 6.40 Hz, CH_2N_3), 2.13-1.28 (46H, m, CH_2), 0.96 (15H, t, J = 6.80 Hz, CH_3).

^{13}C-NMR: δ 149.00 (ArC-O), 123.56 (ArC-C), 107.39 (ArC-H), 69.74 (OCH_2), 51.42 (CH_2N_3), 31.69-22.66 (CH_2), 14.05 (CH_3).

MS $[M]^{+\bullet}$: calculated for $C_{53}H_{81}N_3O_6$: 855.6125 amu; found $[M]^{+\bullet}$ 855.6119 amu.

2-(6-Azidohexyloxy)-3,6,7,10,11-pentakishexyloxytriphenylene

A solution of 1.52 g (1.67 mmol) of 2-(6-bromohexyloxy)-3,6,7,10,11-pentakishexyloxy-triphenylene and 1.23 g (19.0 mmol) of sodium azide in ethanol was refluxed for 15 h. After the reaction was complete the solvent was evaporated. After addition of 20 ml of water the reaction mixture was extracted with 2 x 20 ml of CH_2Cl_2; the organic layer was dried on anhydrous sodium sulfate and the solvent was evaporated under vacuum. After recrystallization from acetonitrile, a quantitative amount of the azido derivative was obtained as white crystals. M.p. 57 °C.

^{1}H-NMR: δ 7.85 (6H, s, ArH), 4.25 (12H, t, J = 6.00 Hz, OCH_2), 3.33 (2H, t, J = 6.96 Hz, CH_2N_3), 2.00-1.91 (12H, m, $OCH_2C\mathit{H_2}$), 1.68-1.41 (36H, m, CH_2), 0.95 (15H, bt, J = 6.96 Hz, CH_3).

^{13}C-NMR: δ 149.04-148.85 (ArC-O), 123.73-123.59 (ArC-C), 107.40-107.26 (ArC-H), 69.73-69.48 (OCH_2), 51.41 (CH_2N_3), 31.69-22.66 (CH_2), 14.05 (CH_3).

MS $[M]^{+\bullet}$: calculated for $C_{54}H_{83}N_3O_6$: 869.6282 amu; found $[M]^{+\bullet}$ 869.6289 amu.

3-(3,6,7,10,11-Pentakishexyloxytriphenylen-2-yloxy)propan-1-amine, **4-3-Hex**

A stirred mixture of 2-(3-(3,6,7,10,11-pentakishexyloxytriphenylen-2-yloxy)propyl)-isoindoline-1,3-dione (7.00 g, 7.50 mmol) and hydrazine monohydrate (1.90 g, 38 mmol) was refluxed in 40 ml ethanol. A white precipitate was rapidly produced. This was later decomposed with a large excess of hydrochloric acid at reflux. The newly formed precipitate was then removed by warm filtration. The filtrate was cooled to room temperature and the solvent evaporated. The residue was redissolved in dichloromethane and a new precipitate was obtained. This was again filtered off and the filtrate was again concentrated under vacuum. The crude product was purified by recrystallization from acetonitrile to give 3-(3,6,7,10,11–pentakishexyloxytriphenylen-2-yloxy)propan-1-amine **4-3-Hex** (4.80 g, 6.00 mmol, 80 %).

^{1}H-NMR: δ 7.85-7.78 (6H, m, ArH), 4.43 (2H, t, J = 6.00 Hz, $O\mathit{CH_2}CH_2CH_2NH_2$), 4.24 (10H, t, J = 6.00 Hz, $O\mathit{CH_2}(CH_2)_4CH_3$), 3.74 (2H, t, J = 6.00 Hz, $\mathit{CH_2}NH_2$), 3.40 (2H, bs, NH_2), 2.35 (2H, m, $OCH_2\mathit{CH_2}CH_2NH_2$), 2.29-1.27 (40H, m, $OCH_2(\mathit{CH_2})_4CH_3$), 0.98-0.85 (15H, m, CH_3).

^{13}C-NMR: δ 149.51-147.36 (ArC-O), 125.81-123.44 (ArC-C), 107.82-105.81 (ArC-H), 70.15-68.81 (OCH_2), 59.44 ($N\mathit{C}H_2CH_2CH_2O$), 31.83-22.78 ($OCH_2(\mathit{C}H_2)_4CH_3$), 14.11 ($CH_3$).

MS $[M]^{+\bullet}$: calculated for $C_{51}H_{79}NO_6$: 801.5907 amu; found $[M]^{+\bullet}$ 801.5897 amu.

4-(6,7,10,11-Tetrakishexyloxy-3-butyloxytriphenylen-2-yloxy)butylamine, **4-4-Bu**

A mixture of 0.74 g (0.91 mmol) of 2-(4-azidobutyloxy)-6,7,10,11-tetrakishexyloxy-3-(butyloxy)triphenylene and 0.35 g (9.1 mmol) $LiAlH_4$ in dry THF under nitrogen, at room temperature for 2 h. The excess of $LiAlH_4$ was destroyed by adding a few drops of 1M NaOH and additional $Na_2SO_4 \cdot 10H_2O$. After stirring for 3 h. the salts were filtered off and the crude product was concentrated under vacuum, yielded 0.67 g of **4-4-Bu** (0.85 mmol, 93 %). No further purification was required for the next reaction step.

MS $[M]^{+\bullet}$: calculated for $C_{50}H_{77}NO_6$: 787.5751 amu; found $[M]^{+\bullet}$ 787.5737 amu.

The amino-terminated triphenylene derivatives **4-4-MeBu, 4-5-Hex** and **4-6-Hex** were synthesized using the same procedure by reduction of the corresponding azide derivatives with $LiAlH_4$ in THF.

4-4-MeBu: MS $[M]^{+\bullet}$: calculated for $C_{51}H_{79}NO_6$: 801.5907 amu; found $[M]^{+\bullet}$ 801.5898 amu.

4-5-Hex: MS $[M]^{+\bullet}$: calculated for $C_{53}H_{83}NO_6$: 829.6220 amu; found $[M]^{+\bullet}$ 829.6193 amu;

4-6-Hex: MS $[M]^{+\bullet}$: calculated for $C_{54}H_{85}NO_6$: 843.6377 amu; found $[M]^{+\bullet}$ 843.6323 amu.

Benzene-1,3,5-tricarboxylic acid tris-{[3-(3,6,7,10,11-pentahexyloxy-triphenylen-2-yloxy)-propyl]-amide}, **T-3-Hex**

A mixture of 1.50 g (1.87 mmol) of amine-terminated triphenylene **4-3-Hex** and 0.80 g triethylamine was dissolved in 20 ml freshly distilled dichloromethane and stirred under nitrogen, for 10 minutes, at room temperature. To this a solution of 1,3,5-benzenetricarboxylic acid chloride (0.16 g, 0.60 mmol) in 5.00 ml dichloromethane was added dropwise. After 24 h the reaction mixture was concentrated and the crude product was purified by column chromatography, using silica gel and dichloromethane / methanol as eluent (gradual increase of methanol from 0.5 to 1 %). The product was precipitated from acetonitrile, yielding 70 mg (0.03 mmol, 4.50 %) of **T-3-Hex** as a white powder.

^1H NMR: δ 8.56 (3H, s, benzene C-H), 7.82-7.77 (12H, m, C-H triphenylene), 7.55 (3H, bt, J = 5.46 Hz, NH), 7.45 (6H, d, J = 5.24 Hz, C-H triphenylene), 4.26-4.19 (18H, m, OCH_2), 4.10 (6H, t, J= 6.00 Hz, OCH_2), 4.04 (6H, bt, J = 6.00 Hz, OCH_2), 3.90 (6H, t, J = 6.00 Hz, OCH_2), 3.82 (6H, q, J = 6.00 Hz, $C\mathit{H_2}NH$), 2.14-1.14 (126H, m, CH_2), 0.98-0.88 (36H, m, CH_3), 0.80 (9H, t, J = 7.17 Hz, CH_3).

^{13}C NMR: δ 165.82 (C=O), 149.12-148.21 (ArC-O triphenylene), 135.68 (Ar*C*-C=O benzene), 128.72 (ArC-H benzene), 123.75-123.21 (ArC-C triphenylene), 107.11-106.23 (ArC-H triphenylene), 69.74-68.75 (OCH_2), 38.75 (CH_2NH), 31.74-22.50 (CH_2), 14.05-13.95 (CH_3). ^1H - ^1H COSY and HETCOR (indicated also in the Results and Discussions part of this manuscript) NMR measurements also confirm the structure of compound **7a**.

MS: MALDI-TOF-MS $[M+H]^{+\bullet}$: calculated for $C_{162}H_{238}N_3O_{21}$: 2561.76 amu; found $[M+H]^{+\bullet}$ 2562.10 amu.

Benzene-1,3,5-tricarboxylic acid tris-{[4-(3-butyloxy-6,7,10,11-tetrahexyloxy-triphenylen-2-yloxy)-butyl]-amide}, **T-4-Bu**

A similar procedure as above described was used for the synthesis of **T-4-Hex**. A mixture of 0.67 g (0.85 mmol) of **4-4-Bu** and 0.07 g (0.26 mmol) of 1,3,5-benzenetricarboxylic acid chloride yielded 117 mg (0.05 mmol, 18 %) of **T-4-Bu** as a white powder.

^{1}H NMR: δ 8.46 (3H, s, C-H benzene), 7.82-7.67 (18H, m, C-H triphenylene), 7.07 (3H, t, J = 5.46 Hz, NH), 4.25-4.05 (36H, m, OCH_2), 3.57 (6H, bq, J = 5.46 Hz, CH_2NH), 1.96-1.41 (120H, m, CH_2), 0.97-0.90 (45H, m, CH_3).

^{13}C NMR: δ 165.75 (C=O), 149.12-148.16 (ArC-O triphenylene), 135.58 (Ar*C*-C=O benzene), 128.19 (ArC-H benzene) 123.74-123.43 (ArC-C triphenylene), 107.42-106.93 (ArC-H triphenylene), 69.82-68.91 (OCH_2), 55.01 (CH_2NH), 31.72-19.26 (CH_2), 14.05-13.88 (CH_3). ^{1}H - ^{1}H COSY and HETCOR NMR measurements also confirm the structure of compound **7b**.

MS: MALDI-TOF-MS $[M+H]^{+\bullet}$: calculated for $C_{159}H_{232}N_3O_{21}$: 2519.71 amu; found $[M+H]^{+\bullet}$ 2519.94 amu.

Benzene-1,3,5-tricarboxylic acid tris-{[4-(3-(2-methyl)butyloxy-6,7,10,11-tetrahexyloxy-triphenylen-2-yloxy)-butyl]-amide}, **T-4-MeBu**

A similar procedure as above described was used for the synthesis of **T-4-MeBu**. A mixture of 0.72 g (0.90 mmol) of amine-terminated triphenylene **4-4-MeBu** and 1,3,5-benzenetricarboxylic acid chloride (64.0 mg, 0.24 mmol) in gave 0.28 g (0.11 mmol, 46 %) of **T-4-MeBu** as a white powder.

^{1}H NMR: δ 8.40 (3H, s, C-H benzene), 7.83-7.74 (18H, m, C-H triphenylene), 6.90 (3H, t, J = 5,60 Hz, NH), 4.26-3.96 (30H, m, OCH_2), 3.97 (6H, dd, J = 6.80 Hz, 3 x OCH_2CH), 3.58 (6H, q, J = 6.00 Hz, 3 x CH_2NH), 1.97-1.28 (117H, m, CH chiral + CH_2), 1.05 (9H, d, J = 6.80 Hz, 3 x CH_3CH), 0.97-0.93 (45H, m, CH_3).

^{13}C NMR:δ 165.72 (C=O), 149.13-148.30 (ArC-O triphenylene), 135.49 (Ar*C*-C=O benzene), 128.00 (ArC-H benzene), 123.74-123.36 (ArC-C triphenylene), 107.56-106.46 (ArC-H triphenylene), 74.12 (O*C*H_2CH), 69.87-69.18 (O*C*H_2CH_2), 39.85 (CH_2NH), 34.71 (CH chiral), 31.71-22.66 (CH_2), 16.78 (*C*H_3CH), 14.05 (*C*$H_3CH_2CH_2$), 11.44 (*C*H_3CH_2CH). ^{1}H - ^{1}H COSY and HETCOR NMR measurements also confirm the structure of compound **T-4-MeBu**.

MS: MALDI-TOF-MS $[M+H]^{+\bullet}$: calculated for $C_{162}H_{238}N_3O_{21}$: 2561.76 amu; found $[M+H]^{+\bullet}$ 2561.28 amu.

Benzene-1,3,5-tricarboxylic acid tris-{[5-(3,6,7,10,11-pentahexyloxy-triphenylen-2-yloxy)-pentyl]-amide}, **T-5-Hex**

A similar procedure as above described was used for the synthesis of **T-5-Hex.** A mixture of 0.80 g (0.96 mmol) of amine-terminated triphenylene **4-5-Hex** and 1,3,5-benzenetricarboxylic acid chloride (114 mg, 0.43 mmol) yielding 0.35 g (0.13 mmol, 31 %) of **T-5-Hex** as a white powder.

^{1}H NMR: δ 8.41 (3H, s, C-H benzene), 7.84-7.83 (18H, m, C-H triphenylene), 6.80 (3H, t, J = 5.20 Hz, NH), 4.23-4.19 (36H, m, OCH_2), 3.51-3.47 (6H, q, J = 6.40 Hz, 3 x $C\mathit{H_2}NH$), 2.02-1.27 (138H, m, CH_2), 0.96-0.89 (45H, m, CH_3).

^{13}C NMR: δ 167.92 (C=O), 151.31-150.93 (ArC-O triphenylene), 137.56 (Ar*C*-C=O benzene), 130.28 (ArC-H benzene), 125.97-125.81 (ArC-C triphenylene), 109.64-109.32 (ArC-H triphenylene), 72.04-71.75 (OCH_2), 42.52 (CH_2NH), 33.96-24.92 (CH_2), 16.32 (CH_3). ^{1}H - ^{1}H COSY and HETCOR NMR measurements also confirm the structure of compound **T-5-Hex**.

MS: MALDI-TOF-MS $[M]^{+\bullet}$: calculated for $C_{168}H_{249}N_3O_{21}$: 2644.85 amu; found $[M]^{+\bullet}$ 2644.18 amu.

Benzene-1,3,5-tricarboxylic acid tris-{[6-(3,6,7,10,11-pentahexyloxy-triphenylen-2-yloxy)-hexyl]-amide}, **T-6-Hex**

A similar procedure as above described was used for the synthesis of **T-6-Hex.** A mixture of 1.01 g (1.19 mmol) of amine-terminated triphenylene **4-6-Hex** and 1,3,5-benzenetricarboxylic acid chloride (133 mg, 0.50 mmol) yielded 0.25 g (0.93 x 10^{-1} mmol, 19 %) of **T-6-Hex** as a white powder.

^{1}H NMR: δ 8.34 (3H, s, C-H benzene), 7.85 (18H, s, C-H triphenylene), 6.45 (3H, t, J = 5.64 Hz, NH), 4.24 (36H, t, J = 6.00 Hz, OCH_2), 3.49 (6H, q, J = 6.00 Hz, 3 x $C\mathit{H_2}NH$), 2.00-1.90 (36H, m, $OCH_2C\mathit{H_2}$), 1.70-1.40 (108H, m, CH_2), 0.97-0.90 (45H, m, 15 x CH_3).

^{13}C NMR: δ 165.60 (C=O), 149.02-148.85 (ArC-O triphenylene), 135.26 (Ar*C*-C=O benzene), 127.87 (ArC-H benzene), 123.68-123.59 (ArC-C triphenylene), 107.36-107.26 (ArC-H triphenylene), 69.72-69.49 (OCH_2), 40.24 (CH_2NH), 31.69-22.66 (CH_2), 14.05 (CH_3). ^{1}H - ^{1}H COSY and HETCOR NMR measurements also confirm the structure of compound **T-6-Hex**.

MS: MALDI-TOF-MS $[M+3H]^{+\bullet}$: calculated for $C_{171}H_{258}N_3O_{21}$: 2689.92 amu; found $[M+3H]^{+\bullet}$ 2689.54 amu.

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