Polycatenar bows with single carbon atom elbow Andreja Lesac,^{*a} Bertrand Donnio,^{*b} Daniel Guillon^b

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SUPPLEMENTARY INFORMATION

Synthesis, spectroscopic and thermal characterization of compounds 6-8

Experimental

General

All the solvents were *puriss p.a.* quality. All the other reagents were used as purchase from Aldrich. ¹H- (300 MHz) and ¹³C- (75.5 MHz) NMR spectra were recorded on Bruker AV 300 instrument in CDCl₃ with SiMe₄ as internal standard unless stated otherwise. Infrared spectra were recorded on Bomem MB 102 spectrophotometer; absorption maxima are given in cm⁻¹. Phase transition temperatures and textures were determined using an Olympus BX51 polarizing microscope equipped with a Linkam TH600 hot stage and PR600 temperature controller. Enthalpies of transition were measured by differential scanning calorimetry with a TA Instruments DSC-Q1000 instrument operated at a scanning rates of 2-to-10°C min⁻¹ on heating and on cooling. The apparatus was calibrated with indium (156.6°C; 28.4J.g⁻¹) and gallium (29.8°C) as the standards. The XRD patterns were obtained with the following experimental set-up. A linear monochromatic Cu-K α_1 beam ($\lambda = 1.5405$ Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator and a Debye-Scherrer-like geometry was used. The crude powder was filled in Lindemann capillaries of 1 mm diameter and 10 µm wall-thickness. The diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 60 Å can be measured, and the sample temperature controlled to within ± 0.05 °C from 20 to 200 °C.

Synthesis

Alkoxybenzoic acids **1a** and **1c** were prepared by *O*-alkylation of methyl 4-hydroxybenzoate followed by hydrolysis under basic conditions while **1b** by *O*-alkylation of 4-

hydroxybenzaldehyde followed by oxidation using Jones reagent. After crystalization from 96% ethanol acids **1a-c** were obtained in 93%, 75% and 92% overall yield respectively.

General procedure for the preparation of 4-(Alkoxybenzoyloxy)benzaldehydes 2a-c

Aldehydes **2a-c** were prepared by direct esterification of **1a-c** with 4-hydroxybenzaldehyde employing standard dicyclohexylcarbodiimide and 4-(*N*,*N*-dimethylamino)pyridine method in dichloromethane.

4-(4-Dodecyloxybenzoyloxy)benzaldehyde 2a. Yield, 89%; PT (°C): Cr 66 SmA 73 N 75 I; ¹H-NMR (CDCl₃) δ : 0.88 (t, *J* = 6.5 Hz, 3H), 1.18-1.48 (m, 18 H), 1.78-1.87 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H Ar), 7.40 (d, *J* = 8.7 Hz, 2H Ar), 7.96 (d, *J* = 8.4 Hz, 2H Ar), 8.14(d, *J* = 8.7 Hz, 2H Ar), 10.02 (s, 1H); ¹³C-NMR (CDCl₃) δ : 14.0, 22.5, 25.9, 29.0, 29.2, 29.4, 29.46, 29.50, 29.52, 31.8, 68.3, 114.4, 120.8, 122.5, 131.1, 132.3, 133.8, 155.8, 163.8, 164.1, 190.8.

4-(3,4-Didodecyloxybenzoyloxy)benzaldehyde 2b. Yield, 86%; mp 86-87 °C; ¹H-NMR (CDCl₃) δ: 0.88-0.92 (m, 6H), 1.29-1.56 (m, 36H), 1.82-1.94 (m, 4H), 4.07-4.13 (m, 4H), 6.96 (d, *J*=8.4 Hz, 1H Ar), 7.42 (d, *J*=8.4 Hz, 2H Ar), 7.67 (d, *J*=1.8 Hz, 1H Ar), 7.84 (dd, *J*₁=1.8 Hz, *J*₂=8.4 Hz, 1H Ar), 7.99 (d, *J*=8.4 Hz, 2H Ar), 10.04 (s, 1H); ¹³C-NMR (CDCl₃) δ: 14.11, 22.70, 25.97, 26.01, 29.04, 29.17, 29.38, 29.41, 29.63, 29.67, 29.70, 31.94, 69.11, 69.46, 112.02, 114.69, 120.85, 122.69, 124.61, 131.25, 133.92, 148.79, 154.25, 156.00, 164.40, 191.01.

4-(3,4,5-Tridodecyloxybenzoyloxy)benzaldehyde 2c. Yield, 80%; mp 48-48 °C; ¹H-NMR (CDCl₃) δ: 0.88-0.92 (m, 9H), 1.29-1.56 (m, 54H), 1.74-1.90 (m, 6H), 4.05-4.11 (m, 6H), 7.41 (d, *J*=8.7 Hz, 2H Ar), 7.41 (s, 2H Ar), 7.99 (d, *J*=8.7 Hz, 2H Ar), 10.05 (s, 1H); ¹³C-NMR (CDCl₃) δ: 14.11, 22.69, 22.70, 26.06, 26.09, 29.30, 29.37, 29.39, 29.58, 29.64, 29.66, 29.70, 29.73, 29.76, 30.36, 31.93, 31.98, 69.32, 73.68, 108.70, 122.64, 123.22, 131.31, 134.06, 143.45, 153.05, 155.89, 164.41, 190.94

General procedure for the preparation of 4-(Alkoxybenzoyloxy)benzoic acids 3a-c

An oxidation was carried out by titrating a vigorously stirred solution of the appropriate aldehyde **2a-c** in acetone at r.t. with the Jones reagent until the colour of the mixture remained orange. After stirring overnight at r.t. the solvent was removed under reduced pressure and the residue was poured into H₂O (100 ml) and extracted with CH_2Cl_2 (3 x 20 ml). The combined organic extracts were washed with H₂O, dried over Na₂SO₄, filtered and concentrated under vacuum. The crude products were purified by crystallisation.

4-(4-Dodecyloxybenzoyloxy)benzoic acid 3a. Crystallised from the mixture ethyl acetate/*n*-hexane (2:1). Yield, 92%; PT (°C): Cr 121 SmC 209 N 216 I; ¹H-NMR (CDCl₃) δ: 0.92 (t, *J*=6.8 Hz, 3H), 1.27-1.52 (m, 18H), 1.77-1.87 (m, 2H), 4.05 (t, *J*=6.5 Hz, 2H), 6.98 (d, *J*=8.8 Hz, 2H Ar), 7.34 (d, *J*=8.4 Hz, 2H Ar), 8.15 (d, *J*=8.8 Hz, 2H Ar), 8.2(d, *J*=8.4 Hz, 2H, Ar); ¹³C-NMR (CDCl₃) δ: 14.10, 22.70, 25,99 29.07, 29.40, 29.57, 29.60, 29.65, 29.71, 31.91, 68.40, 114.42, 121.12, 122.08, 126.63, 131.89, 132.41, 155.63, 163.82, 164.30, 171.11.

4-(3,4-Didodecyloxybenzoyloxy)benzoic acid 3b. Crystallised from the mixture acetone/CH₃CN (2:1). Yield, 91%; mp 165-166 °C; ¹H-NMR (CDCl₃) δ: 0.87-0.92 (m, 6H), 1.22-1.54 (m, 36H), 1.83-1.93 (m, 4H), 4.07-4.13 (m, 4H), 6.96 (d, *J*=8.4 Hz, 1H Ar), 7.35(d, *J*=8.4 Hz, 2H Ar), 7.68 (s, 1 H Ar), 7.84 (d, *J*=8.4 Hz, 1H Ar), 8.22(d, *J*=8.4 Hz, 2H Ar); ¹³C-NMR (CDCl₃) δ: 14.11, 22.70, 25.98, 26.02, 29.04, 29.17, 29.37, 29.41, 29.62, 29.63, 29.67, 29.70, 31.93, 69.11, 69.43, 111.97, 114.65, 120.98, 122.06, 124.58, 126.67, 131.93, 148.77, 154.14, 155.64, 164.49, 171.20

4-(3,4,5-Tridodecyloxybenzoyloxy)benzoic acid 3c. Crystallised from the wet acetone (80%). Yield, 89%; mp 88-89 °C; ¹H-NMR (CDCl₃) δ: 0.88-0.92 (m, 9H), 1.29-1.56 (m, 54H), 1.74-1.90 (m, 6H), 4.05- 4.12 (m, 6H), 7.35 (d, *J*=8.5 Hz, 2H Ar), 7.43 (s, 2H Ar), 8.22 (d, *J*=8.7 Hz, 2H Ar); ¹³C-NMR (CDCl₃) δ: 14.02, 22.6, 22.61, 25.97, 25.99, 29.20, 29.28, 29.30, 29.48, 29.54, 29.57, 29.61, 29.64, 29.65, 29.67, 30.26, 31.83, 31.86, 69.22, 73.53, 108.57, 121.94, 123.21, 126.70, 131.82, 143.23, 152.93, 155.39, 164.36, 170.97.

General procedure for the preparation of 6a-c and 7a-c

To the mixture of appropriate acid **3a-c** (2 mmol), DCC (2 mmol) and DMAP (1 mmol) in CH_2Cl_2 (50 mL), 4,4'-dihydroxybenzophenone (1 mmol) or bis(4-hydroxyphenyl)methane (1 mmol) dissolved in a minimum amount of THF was added. After stirring at r.t. under Ar for 5 h. the reaction mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silka gel using the mixture of sovents $CH_2Cl_2/MeOH$ (100:1) for **6a-c** and $CH_2Cl_2/MeOH$ (200:1) for **7a-c**.

4,4'Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]benzophenone 6a. Yield, 74%; PT (°C): Cr1 11.7 Cr2 109 Cr3 171 SmC 195 N 196 I; ¹H-NMR (CDCl₃) δ: 0.90 (t, *J*=6.8 Hz, 6H), 1.22-1.55 (m, 36H), 1.80-1.89 (m, 4H), 4.06 (t, *J*=6.5 Hz, 4H), 7.01 (d, *J*=8.8 Hz, 4H Ar), 7.40 (d, *J*=8.6 Hz, 4H), 7.42 (d, *J*=8.6 Hz, 4H), 7.96 (d, *J*=8.8 Hz, 4H Ar), 8.18 (d, *J*=8.8 Hz, 4H Ar), 8.32 (d, *J*=8.8 Hz, 4H, Ar); ¹³C-NMR (CDCl₃) δ: 14.12, 22.7, 26, 29.08, 29.35, 29.55, 29.63, 29.65, 31.92, 68.41, 114.44, 120.88, 121.8, 122.24, 122.32, 126.4, 131.7, 131.93, 132.44, 132.53, 135.10, 154.22, 155.66, 163.9, 164.00, 164.30, 194.40; IR (KBr): 3110, 2920, 2850, 1733, 1646, 1604, 1287, 1160, 1079, 762. Elemental analysis. Found: C, 75.89; H, 7.22. Calc. for C₆₅H₇₄O₁₁: C, 75.70; H 7.23%.

4,4'Bis[4-(3,4-didodecyloxybenzoyloxy)benzoyloxy]benzophenone 6b. Yield, 68%; PT (°C): Cr1 79.5 Cr2 97 Cr3 113 (Col_hP_A 115) Col_h 121 I; ¹H-NMR (CDCl₃) & 0.88-0.92 (m, 12H), 1.22-1.54 (m, 72H), 1.83-1.93 (m, 8H), 4.08-4.14 (m, 8H), 6.97 (d, *J*=8.5 Hz, 2H Ar), 7.41 (d, *J*=8.5 Hz, 8H Ar), 7.69 (d, *J*=1.9 Hz, 2H Ar), 7.85 (dd, *J*₁=8.5 Hz, *J*₂=1.9 Hz, 2H Ar), 7.97 (d, *J*=8.6 Hz, 4H Ar), 8.32 (d, *J*=8.6 Hz, 4H, Ar); ¹³C-NMR (CDCl₃) & 14.03, 22.62, 25.89, 25.94, 28.96, 29.09, 29.29, 29.30, 29.33, 29.54, 29.55, 29.58, 29.62, 31.85, 69.02, 69.32, 111.88, 114.56, 120.80, 121.72, 122.19, 124.52, 126.33, 131.62, 131.85, 135.03, 148.68, 154.11, 154.14, 155.61, 163.93, 164.35, 194.32; IR (KBr): 3077, 2920, 2850, 1733, 1665, 1599, 1269, 1160, 1063, 754. Elemental analysis. Found: C, 76.20; H, 8.77. Calc. for $C_{89}H_{122}O_{13}$: C, 76.36; H, 8.78%.

4,4'Bis[4-(3,4,5-tridodecyloxybenzoyloxy)benzoyloxy]benzophenone 6c. Yield, 63%; PT (°C): G 45 Cr1 69 Cr2 75 Col_h 78 I; ¹H-NMR (CDCl₃) δ: 0.88-0.92 (m, 18H) 1.22-1.57 (m, 108H), 1.75-1.91 (m, 12H), 4.06-4.12 (m, 12H), 7.41 (d, *J*=8.7 Hz, 4H Ar), 7.42 (d, *J*=8.7 Hz, 4H Ar), 7.45 (s, 4H Ar), 7.97 (d, *J*=8.7 Hz, 4H Ar), 8.33 (d, *J*=8.6 Hz, 4H Ar); ¹³C-NMR (CDCl₃) δ: 14.12, 22.69, 22.71, 26.07, 26.10, 29.30, 29.37, 29.41, 29.57, 29.64, 29.67, 29.7, 29.75, 29.76, 30.36, 31.93, 31.95, 69.33, 73.64, 108.70, 121.79, 122.28, 123.22, 126.57, 131.72, 131.96, 135.13, 143.41, 153.06, 154.21, 155.59, 163.99, 164.45, 194.44; IR (KBr): 3090, 2920, 2850, 1733, 1655, 1600, 1270, 1160, 1062, 756. Elemental analysis. Found: C, 76.86; H, 9.65. Calc. for C₁₁₃H₁₇₀O₁₅: C, 76.74; H, 9.69%.

Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxyphenyl]methane 7a. Yield, 60%; PT (°C): G 104 Cr1 124 Cr2 131 Col_r 168.5 I; ¹H-NMR (CDCl₃) δ : 0.91 (t, *J*=6.5 Hz, 6H), 1.22-1.54 (m, 36H), 1.81-1.90 (m, 4H), 4.05-4.10 (m, 6H), 7.01 (d, *J*=9.0 Hz, 4H Ar), 7.19 (d, *J*=8.3 Hz, 4H), 7.29 (d, *J*=8.3 Hz, 4H), 7.39 (d, *J*=8.6 Hz, 4H Ar), 8.18 (d, *J*=9.0 Hz, 4H Ar), 8.30 (d, *J*=8.6 Hz, 4H, Ar); ¹³C-NMR (CDCl₃) δ : 14.14, 22.70, 25.99, 29.09, 29.37, 29.57, 29.60, 29.65, 29.67, 31.93, 40.37, 68.39, 114.42, 120.98, 121.70, 122.08, 126.97, 129.99, 131.80, 132.43, 138.47, 149.31, 155.35, 163.83, 164.33, 164.56; IR (KBr): 3081, 2922, 2852, 1732, 1605, 1272, 1161, 1066, 761; Elemental analysis. Found: C, 76.92; H, 7.48. Calc. for C₆₅H₇₆O₁₀: C, 76.74; H, 7.53%.

Bis[4-(3,4-didodecyloxybenzoyloxy)benzoyloxyphenyl]methane 7b. Yield, 64%; PT (°C): Cr1 71 Cr2 122 I; ¹H-NMR (CDCl₃) δ: 0.88-0.92 (m, 12H), 1.29-1.58 (m, 72H), 1.83-1.94 (m, 8H), 4.07-4.14 (m, 10H), 6.96 (d, *J*=8.4 Hz, 2H Ar), 7.19 (d, *J*=8.0 Hz, 4H Ar), 7.29 (d, *J*=8.0 Hz, 4H Ar), 7.38 (d, *J*=8.4 Hz, 4H Ar), 7.69 (s, 2H Ar), 7.86 (d, *J*=8.4 Hz, 2H Ar), 8.30

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(d, J=8.4 Hz, 4H Ar); ¹³C-NMR (CDCl₃) & 14.13, 22.70, 25.98, 26.02, 29.04, 29.17, 29.38, 29.39, 29.42, 29.63, 29.64, 29.67, 29.71, 31.94, 40.71, 69.11, 69.40, 111.96, 114.64, 120.98, 121.70, 122.11, 124.57, 126.98, 129.99, 131.80, 138.47, 148.76, 149.30, 154.14, 155.14, 164.47, 164.57; IR (KBr): 3077, 2920, 2848, 1735, 1600, 1269, 1161, 756. Elemental analysis. Found: C, 76.89; H, 9.08. Calc. for C₈₉H₁₂₄O₁₂: C, 77.13; H, 9.02%.

Bis[4-(3,4,5-tridodecyloxybenzoyloxy)benzoyloxyphenyl]methane 7c. Yield, 53%; PT (°C): G 17.5 Cr1 45 Cr2 50 Cr3 64 Col_h 68 I; ¹H-NMR (CDCl₃) & 0.88-0.92 (m, 18H) 1.29-1.56 (m, 108H), 1.74-1.91 (m, 12H), 4.05-4.12 (m, 14H), 7.19 (d, *J*=8.5 Hz, 4H Ar), 7.29 (d, *J*=8.5 Hz, 4H Ar), 7.37 (d, *J*=8.7 Hz, 4H Ar), 7.45 (s, 4H Ar), 8.31 (d, *J*=8.7 Hz, 4H Ar); ¹³C-NMR (CDCl₃) & 14.12, 22.69, 22.71, 26.07, 26.09, 29.31, 29.37, 29.40, 29.57, 29.64, 29.67, 29.71, 29.74, 29.75, 29.76, 30.36, 31.93, 40.72, 69.32, 73.63, 108.68, 121.69, 122.10, 123.32, 127.13, 129.99, 131.83, 138.49, 143.35, 149.29, 153.04, 155.28, 164.49, 164.53; IR (KBr): 3070, 2919, 2848, 1732, 1595, 1274, 1162, 750. Elemental analysis. Found: C, 77.59; H, 9.95. Calc. for C₁₁₃H₁₇₂O₁₄: C, 77.35; H, 9.88%.

General procedure for the preparation of diphenylmethanols 8a-c

Solution of NaBH₄ (0.1 mmol) in 85% *i*-PrOH was added dropwise to the solution of appropriate ketone **6a-c** in THF (20 mL) at r.t. After stirring at r.t. overnight, a few drops of formic acid were added. The reaction mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silika gel using the mixture of sovents $CH_2Cl_2/DIPE$ (25:1) as eluent.

Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxyphenyl]methanol 8a. Yield, 65%; PT (°C): Cr1 129 Col_r 164 I; ¹H-NMR (CDCl₃) & 0.90 (t, *J*=6.6 Hz, 6H), 1.29-1.55 (m, 36H), 1.81-1.90 (m, 4H), 2.37 (d, *J*=3.6 Hz, 1H), 4.07 (t, *J*=6.6 Hz, 4H), 5.95 (d, *J*=3.6 Hz, 1H), 7.00 (d, *J*=9.0 Hz, 4H Ar), 7.24 (d, *J*=8.6 Hz, 4H), 7.39 (d, *J*=9.0 Hz, 4H), 7.49 (d, *J*=8.6 Hz, 4H Ar), 8.17 (d, *J*=9.0 Hz, 4H Ar), 8.29 (d, *J*=8.6 Hz, 4H, Ar); ¹³C-NMR (CDCl₃) & 14.12, 22.70, 25.99, 29.10, 29.36, 29.56, 29.60, 29.64, 29.66, 31.93, 68.41, 75.31, 114.43, 120.97, 121.81, 122.11, 126.85, 127.84, 131.83, 132.43, 141.23, 150.36, 155.43, 163.85, 164.34, 164.46; IR (KBr): 3518, 3077, 2919, 2852, 1732, 1605, 1275, 1198, 1165, 1074, 761. Elemental analysis. Found: C, 75.24; H, 7.50. Calc. for $C_{65}H_{76}O_{11}$: C, 75.55; H, 7.41%.

Bis[4-(3,4-didodecyloxybenzoyloxy)benzoyloxyphenyl]methanol 8b. Yield, 66%; PT (°C): Cr1 70 Cr2 139 I; ¹H-NMR (CDCl₃) δ 0.85-0.90 (m, 12H), 1.16-1.54 (m, 72H), 1.81-1.91 (m, 8H), 2.34 (d, *J*=3.6 Hz, 1H), 4.05-4.11 (m, 8H), 5.92 (d, *J*=3.6 Hz, 1H), 6.94 (d, *J*=8.7 Hz, 2H Ar), 7.22 (d, *J*=8.7 Hz, 4H Ar), 7.36 (d, *J*=8.7 Hz, 4H Ar), 7.47 (d, *J*=8.7 Hz, 4H Ar), 7.66 (s, 2H Ar), 7.83 (d, *J*=8.7 Hz, 2H Ar), 8.27 (d, *J*=8.7 Hz, 4H Ar); ¹³C-NMR (CDCl₃) δ : 14.12, 22.70, 25.98, 26.02, 29.04, 29.17, 29.38, 29.39, 29.42, 29.57, 29.62, 29.63, 29.67, 29.71, 31.94, 69.11, 69.40, 75.29, 111.96, 114.64, 120.96, 121.80, 122.14, 124.58, 126.85, 127.84, 131.83, 141.24, 148.76, 150.33, 154.15, 155.45, 164.45, 164.48; IR (KBr): 3510, 3082, 2920, 2852, 1735, 1600, 1271, 1200, 1161, 752. Elemental analysis. Found: C, 76.11; H, 9.09. Calc. for C₈₉H₁₂₄O₁₃: C, 76.25; H, 8.92%.

Bis[4-(3,4,5-tridodecyloxybenzoyloxy)benzoyloxyphenyl]methanol 8c. Yield, 70%; PT (°C): G 41 Cr1 62 Cr2 83 (Col_h 73) I; ¹H-NMR (CDCl₃) & 0.88-0.92 (m, 18H) 1.29-1.56 (m, 108H), 1.75-1.91 (m, 12H), 2.37 (d, *J*=3.6 Hz, 1H), 4.05-4.12 (m, 12H), 5.95 (d, *J*=3.6 Hz, 1H), 7.25 (d, *J*=8.9 Hz, 4H Ar), 7.37 (d, *J*=8.4 Hz, 4H Ar), 7.44 (s, 4H Ar), 7.50 (d, *J*=8.4 Hz, 4H Ar), 8.30 (d, *J*=8.9 Hz, 4H Ar); ¹³C-NMR (CDCl₃) & 14.12, 22.69, 22.71, 26.07, 26.09, 29.30, 29.37, 29.40, 29.58, 29.64, 29.67, 29.70, 29.75, 29.76, 30.36, 31.93, 31.95, 69.32, 73.63, 75.27, 108.68, 121.78, 122.14, 123.29, 126.99, 127.84, 131.85, 141.26, 143.37, 150.31, 153.04, 155.34, 164.48; IR (KBr): 3521, 3070, 2922, 2852, 1737, 1595, 1270, 1191, 1161, 746. Elemental analysis. Found: C, 76.92; H, 9.80. Calc. for C₁₁₃H₁₇₂O₁₅: C, 76.65; H, 9.79%.

Thermal behaviour of the compounds 6-8



Fig S1 TGA thermograms of the dicatenar bows



Fig S2 TGA thermograms of the tetracatenar bows



Fig S3 TGA thermograms of the hexacatenar bows



Fig S4 DSC thermograms of the compounds 6a-6c



Fig S5 DSC thermograms of the compounds 7a-7c



Fig S6 DSC thermograms of the compounds 8a-8c