

Saddle-shaped tetraphenylenes with peripheral gallic esters displaying columnar mesophases

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Supporting Information

Analytical data of tetraphenylenes **2a–f**, **2g–l**.

3,6,7,10,11,14,15-Heptakis[(3,4,5-pentyloxybenzoyl)oxy]tetraphenylen-2-yl 3,4,5-tri-pentyloxybenzoate (2a)

233 mg (28 %) of a colorless solid. ¹H NMR (500 MHz, CDCl₃): δ = 0.89–0.93 (m, 72H), 1.32–1.49 (m, 96H), 1.71–1.78 (m, 48H), 3.82–3.86 (m, 32H), 3.99 (t, *J* = 6.5 Hz, 16H), 7.26 (s, 16H), 7.39 (s, 8H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 14.0, 14.1, 22.4, 22.5, 28.2, 28.2, 29.0, 30.0, 69.0, 73.4, 108.3, 123.0, 124.5, 138.1, 142.0, 143.0, 152.9, 163.8 ppm. FT-IR (ATR): ν = 2954 (m), 2930 (s), 2870 (m), 2167 (w), 1966 (w), 1740 (s), 1585 (m), 1499 (w),

1467 (w), 1429 (m), 1389 (w), 1333 (vs), 1291 (w), 1240 (w), 1187 (vs), 1109 (vs), 1046 (w), 978 (m), 944 (w), 925 (w), 886 (w), 815 (w), 747 (m), 696 (w), 579 (w) cm^{-1} . UV-vis (*n*-hexane): λ_{max} ($\lg \epsilon_{\text{max}}$) = 276 (5.12), 216 (5.51) nm. $\text{C}_{200}\text{H}_{288}\text{O}_{40}$ (3332.4) calcd. C 72.08, H 8.71; found: C 71.90, H 8.73.

3,6,7,10,11,14,15-Heptakis[(3,4,5-hexyloxybenzoyl)oxy]tetraphenylene-2-yl 3,4,5-tri-hexyloxybenzoate (2b)

660 mg (72 %) of a colorless solid. ^1H NMR (500 MHz, CDCl_3): δ = 0.87–0.91 (m, 72H), 1.30–1.48 (m, 144H), 1.70–1.77 (m, 48H), 3.82–3.86 (m, 32H), 3.99 (t, J = 6.6 Hz, 16H), 7.25 (s, 16H), 7.39 (s, 8H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 14.0, 14.1, 22.6, 22.7, 25.7, 25.8, 29.2, 30.3, 31.6, 31.7, 69.0, 73.5, 108.3, 123.0, 124.5, 138.1, 142.0, 143.0, 152.9, 163.8 ppm. FT-IR (ATR): ν = 2953 (m), 2927 (s), 2858 (m), 2165 (w), 1966 (w), 1741 (s), 1585 (m), 1499 (w), 1467 (w), 1429 (m), 1390 (w), 1333 (vs), 1291 (w), 1240 (w), 1187 (vs), 1110 (vs), 983 (w), 919 (w), 891 (w), 860 (w), 747 (s), 591 (w) cm^{-1} . UV-vis (*n*-hexane): λ_{max} ($\lg \epsilon_{\text{max}}$) = 276 (5.09), 216 (5.50) nm. $\text{C}_{224}\text{H}_{336}\text{O}_{40}$ (3669.0 g/mol) calcd. C 73.33, H 9.23; found: C 73.08, H 9.15.

3,6,7,10,11,14,15-Heptakis[(3,4,5-heptyloxybenzoyl)oxy]tetraphenylene-2-yl 3,4,5-tri-heptyloxybenzoate (2c)

662 mg (65 %) of a colorless solid. ^1H NMR (500 MHz, CDCl_3): δ = 0.86–0.90 (m, 72H), 1.26–1.48 (m, 192H), 1.71–1.77 (m, 48H), 3.81–3.86 (m, 32H), 3.99 (t, J = 6.6 Hz, 16H), 7.25 (s, 16H), 7.40 (s, 8H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 14.1, 14.1, 22.6, 22.7, 20.0, 26.1, 29.1, 29.2, 29.3, 30.4, 31.8, 31.9, 69.0, 73.5, 108.3, 123.0, 124.5, 138.1, 142.0, 143.0, 152.9, 163.8 ppm. FT-IR (ATR): ν = 2953 (m), 2924 (s), 2855 (m), 2166 (w), 1966 (w), 1742 (s), 1585 (m), 1499 (w), 1467 (w), 1429 (m), 1390 (w), 1333 (vs), 1291 (w), 1272 (w), 1187 (vs), 1111 (vs), 986 (w), 934 (w), 861 (w), 817 (w), 747 (m), 639 (m), 619 (m)

cm⁻¹. UV-vis (*n*-hexane): λ_{max} (lg ϵ_{max}) = 276 (5.13), 216 (5.53) nm. C₂₄₉H₃₈₈O₄₀ (4075.8) calcd. C 74.36, H 9.72; C 74.26, H 9.57.

3,6,7,10,11,14,15-Heptakis[(3,4,5-octyloxybenzoyl)oxy]tetraphenylene-2-yl 3,4,5-tri-octyloxybenzoate (2d)

304 mg (28 %) of a colorless solid. ¹H-NMR (500 MHz, CDCl₃): δ = 0.86–0.89 (m, 72H), 1.27–1.48 (m, 240H), 1.71–1.76 (m, 48H), 3.81–3.85 (m, 32H), 3.98 (t, *J* = 6.6 Hz, 16H), 7.25 (s, 16H), 7.40 (s, 8H) ppm. ¹³C-NMR (125 MHz, CDCl₃): δ = 14.1, 22.7, 22.7, 26.1, 26.1, 29.3, 29.4, 29.4, 29.5, 30.4, 31.9, 31.9, 69.0, 73.5, 108.3, 123.0, 124.5, 138.1, 142.0, 143.0, 152.9, 163.8 ppm. FT-IR (ATR): ν = 2922 (vs), 2854 (s), 1742 (s), 1585 (m), 1499 (w), 1467 (w), 1430 (m), 1390 (w), 1334 (s), 1291 (w), 1274 (w), 1192 (vs), 1113 (vs), 986 (w), 946 (w), 890 (w), 748 (w), 632 (s), 530 (s) cm⁻¹. UV-vis (*n*-hexane): λ_{max} (lg ϵ_{max}) = 277 (5.11), 216 (5.49) nm. C₂₇₀H₄₂₈O₄₀ (4342.3) calcd. C 75.17, H 10.00; found: C 75.36, H 9.88.

3,6,7,10,11,14,15-Heptakis[(3,4,5-nonyloxybenzoyl)oxy]tetraphenylene-2-yl 3,4,5-tri-nonyloxybenzoate (2e)

807 mg (69 %) of a colorless solid. ¹H-NMR (500 MHz, CDCl₃): δ = 0.85–0.89 (m, 72H), 1.27–1.47 (m, 288H), 1.71–1.76 (m, 48H), 3.80–3.85 (m, 32H), 3.98 (t, *J* = 6.5 Hz, 16H), 7.26 (s, 16H), 7.39 (s, 8H) ppm. ¹³C-NMR (125 MHz, CDCl₃): δ = 14.1, 22.7, 22.7, 26.1, 26.1, 29.3, 29.4, 29.4, 29.5, 30.4, 31.9, 31.9, 69.0, 73.5, 108.3, 123.0, 124.5, 138.1, 142.0, 143.0, 152.9, 163.8 ppm. FT-IR (ATR): ν = 2921 (s), 2853 (s), 1744 (m), 1586 (m), 1500 (w), 1467 (w), 1431 (m), 1390 (w), 1336 (s), 1292 (w), 1272 (w), 1194 (m), 1115 (m), 985 (w), 891 (w), 748 (w), 632 (vs), 536 (vs) cm⁻¹. UV-vis (*n*-hexane): λ_{max} (lg ϵ_{max}) = 276 (5.11), 216 (5.51) nm. C₂₉₆H₄₈₀O₄₀ (4679.0) calcd. C 75.98, H 10.34; found: C 76.15, H 10.30.

3,6,7,10,11,14,15-Heptakis[(3,4,5-decyloxybenzoyl)oxy]tetraphenylene-2-yl 3,4,5-tri-decyloxybenzoate (2f)

727 mg (58 %) of a colorless solid. ^1H NMR (500 MHz, CDCl_3): δ = 0.85–0.89 (m, 72H), 1.26–1.48 (m, 336H), 1.70–1.76 (m, 48H), 3.80–3.85 (m, 32H), 3.98 (t, J = 6.5 Hz, 16H), 7.25 (s, 16H), 7.40 (s, 8H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 14.1, 22.7, 22.7, 26.1, 26.1, 29.3, 29.4, 29.4, 29.5, 29.6, 29.6, 29.7, 29.7, 29.7, 29.8, 30.4, 31.9, 31.9, 69.0, 73.5, 108.3, 123.0, 124.5, 138.1, 142.0, 143.0, 152.9, 163.8 ppm. FT-IR (ATR): ν = 2953 (m), 2920 (vs), 2852 (s), 1743 (m), 1586 (m), 1500 (w), 1467 (w), 1431 (m), 1390 (w), 1336 (s), 1116 (m), 983 (w), 924 (w), 890 (w), 748 (w), 632 (vs), 531 (vs) cm^{-1} . UV-vis (*n*-hexane): λ_{max} ($\lg \epsilon_{\text{max}}$) = 277 (5.16), 216 (5.57) nm. $\text{C}_{320}\text{H}_{528}\text{O}_{40}$ (5015.6) calcd. C 76.63, H 10.61; found: C 76.53, H 10.53.

3,6,7,10,11,14,15-Heptakis[(3,4,5-undecyloxybenzoyl)oxy]tetraphenylene-2-yl 3,4,5-tri-undecyloxybenzoate (2g)

910 mg (68 %) of a colorless solid. ^1H NMR (500 MHz, CDCl_3): δ = 0.85–0.89 (m, 72H), 1.26–1.46 (m, 384H), 1.72–1.74 (m, 48H), 3.81–3.83 (m, 32H), 3.98 (t, J = 6.5 Hz, 16H), 7.24 (s, 16H), 7.39 (s, 8H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 14.1, 22.7, 22.7, 26.1, 26.1, 29.4, 29.4, 29.5, 29.6, 29.7, 29.7, 29.8, 30.4, 32.0, 32.0, 69.0, 73.5, 108.3, 123.0, 124.5, 138.1, 142.0, 143.0, 152.9, 163.8 ppm. FT-IR (ATR): ν = 2921 (vs), 2852 (s), 1744 (m), 1586 (m), 1500 (w), 1467 (w), 1431 (w), 1390 (w), 1336 (m), 1292 (w), 1242 (w), 1193 (m), 1117 (m), 986 (w), 891 (w), 749 (w), 632 (vs), 537 (vs) cm^{-1} . UV-vis (*n*-Hexan): λ_{max} ($\lg \epsilon_{\text{max}}$) = 276 (5.10), 216 (5.49) nm. $\text{C}_{344}\text{H}_{576}\text{O}_{40}$ (5352.2) calcd. C 77.20, H 10.85; found: C 77.29, H 10.77.

3,6,7,10,11,14,15-Heptakis[(3,4,5-tridecyloxybenzoyl)oxy]tetraphenylene-2-yl 3,4,5-tridecyloxybenzoate (2i)

979 mg (65 %) of a colorless solid. ^1H NMR (500 MHz, CDCl_3): δ = 0.86–0.89 (m, 72H), 1.25–1.49 (m, 480H), 1.71–1.74 (m, 48H), 3.82–3.83 (m, 32H), 3.98 (t, J = 6.5 Hz, 16H), 7.24 (s, 16H), 7.39 (s, 8H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 14.1, 22.7, 26.1, 26.2, 29.4, 29.4, 29.6, 29.7, 29.7, 29.8, 30.4, 32.0, 69.0, 73.5, 108.3, 123.0, 124.5, 138.1, 142.0, 143.0, 152.9, 163.8 ppm. FT-IR (ATR): ν = 2920 (vs), 2852 (vs), 1744 (m), 1586 (m), 1500 (w), 1487 (w), 1431 (m), 1391 (w), 1336 (m), 1292 (w), 1242 (w), 1194 (m), 1117 (m), 986 (w), 891 (w), 749 (w), 720 (w), 632 (vs) cm^{-1} . UV-vis (*n*-hexane): λ_{max} ($\lg \epsilon_{\text{max}}$) = 274 (5.16), 213 (5.70) nm. $\text{C}_{392}\text{H}_{672}\text{O}_{40}$ (6025.5) calcd. C 78.14, H 11.24; found: C 78.23, H 11.19.

3,6,7,10,11,14,15-Heptakis[(3,4,5-tetradecyloxybenzoyl)oxy]tetraphenylene-2-yl 3,4,5-tetradecyloxybenzoate (2j)

986 mg (62 %) of a colorless solid. ^1H NMR (500 MHz, CDCl_3): δ = 0.86–0.89 (m, 72H), 1.25–1.49 (m, 528H), 1.70–1.75 (m, 48H), 3.78–3.84 (m, 32H), 3.96 (t, J = 6.5 Hz, 16H), 7.24 (s, 16H), 7.39 (s, 8H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 14.1, 22.7, 26.1, 26.2, 29.4, 29.4, 29.6, 29.7, 29.7, 29.8, 29.8, 29.8, 30.4, 32.0, 69.0, 73.5, 108.3, 123.0, 124.5, 138.1, 142.0, 143.0, 152.9, 163.8 ppm. FT-IR (ATR): ν = 2919 (vs), 2850 (vs), 1743 (m), 1586 (m), 1499 (w), 1467 (w), 1431 (w), 1390 (w), 1335 (s), 1291 (w), 1273 (w), 1241 (w), 1192 (s), 1117 (s), 986 (w), 926 (w), 891 (w), 749 (w), 721 (w), 631 (vs), 539 (vs) cm^{-1} . UV-vis (*n*-hexane): λ_{max} ($\lg \epsilon_{\text{max}}$) = 277 (5.10), 217 (5.46) nm. $\text{C}_{416}\text{H}_{720}\text{O}_{40}$ (6362.1) calcd. C 78.53, H 11.41; found: C 78.32, H 11.33.

3,6,7,10,11,14,15-Heptakis[(3,4,5-pentadecyloxybenzoyl)oxy]tetraphenylene-2-yl 3,4,5-tripentadecyloxybenzoate (2k)

670 mg (40 %) of a colorless solid. ^1H NMR (500 MHz, CDCl_3): δ = 0.86–0.89 (m, 72H), 1.25–1.46 (m, 576H), 1.70–1.75 (m, 48H), 3.80–3.84 (m, 32H), 3.97 (t, J = 6.5 Hz, 16H), 7.24 (s, 16H), 7.39 (s, 8H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 14.1, 22.7, 26.1, 26.2, 29.4, 29.4, 29.6, 29.7, 29.7, 29.8, 29.8, 30.4, 32.0, 69.0, 73.5, 108.3, 123.0, 124.5, 138.1, 142.0, 143.0, 152.9, 163.8 ppm. FT-IR (ATR): ν = 2916 (vs), 2849 (vs), 1966 (w), 1743 (m), 1586 (m), 1499 (w), 1467 (m), 1430 (m), 1389 (w), 1334 (s), 1292 (w), 1240 (w), 1189 (s), 1115 (s), 983 (w), 939 (w), 891 (w), 861 (w), 747 (m), 721 (m), 671 (w), 633 (w), 592 (w) cm^{-1} . UV-vis (*n*-hexane): λ_{max} ($\lg \epsilon_{\text{max}}$) = 276 (5.05), 216 (5.50) nm. $\text{C}_{440}\text{H}_{768}\text{O}_{40}$ (6698.8) calcd. C 78.89, H 11.56; found: C 78.67, H 11.51.

3,6,7,10,11,14,15-Heptakis[(3,4,5-hexadecyloxybenzoyl)oxy]tetraphenylene-2-yl 3,4,5-trihexadecyloxybenzoate (2l)

862 mg (49 %) of a colorless solid. ^1H NMR (500 MHz, CDCl_3): δ = 0.86–0.89 (m, 72H), 1.25–1.47 (m, 624H), 1.70–1.75 (m, 48H), 3.80–3.84 (m, 32H), 3.97 (t, J = 6.5 Hz, 16H), 7.24 (s, 16H), 7.39 (s, 8H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 14.1, 22.7, 26.1, 26.2, 29.4, 29.4, 29.6, 29.7, 29.7, 29.7, 29.8, 29.8, 30.4, 32.0, 69.0, 73.5, 108.3, 123.0, 124.5, 138.1, 142.0, 143.0, 152.9, 163.8 ppm. FT-IR (ATR): ν = 2916 (vs), 2849 (vs), 1743 (m), 1586 (m), 1499 (w), 1467 (w), 1430 (m), 1389 (w), 1334 (s), 1291 (w), 1240 (w), 1190 (s), 1116 (s), 983 (w), 943 (w), 890 (w), 816 (w), 747 (m), 721 (m), 673 (w), 579 (w), 559 (w) cm^{-1} . UV-vis (*n*-hexane): λ_{max} ($\lg \epsilon_{\text{max}}$) = 276 (5.08), 216 (5.53) nm. $\text{C}_{464}\text{H}_{816}\text{O}_{40}$ (7035.4) calcd. C 79.21, H 11.69; found: C 79.01, H 11.67.

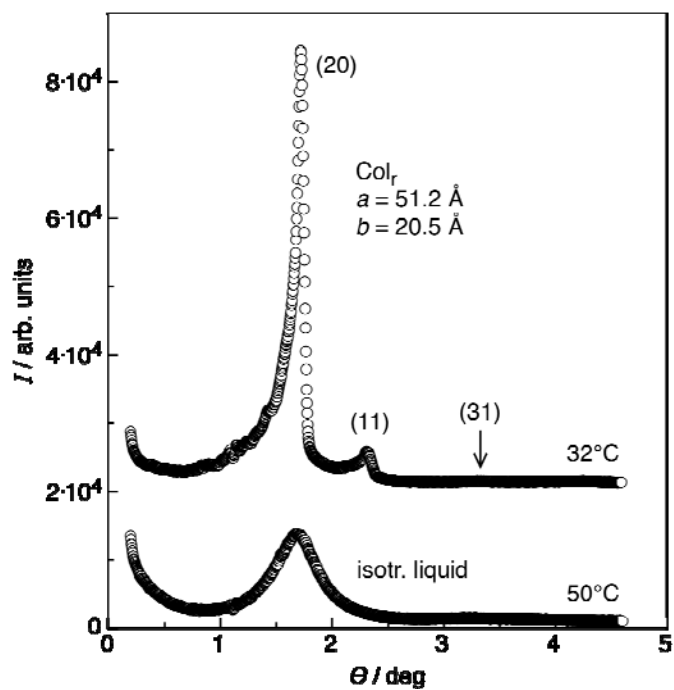


Figure S1: X-ray scattering profile of derivative **2f**.

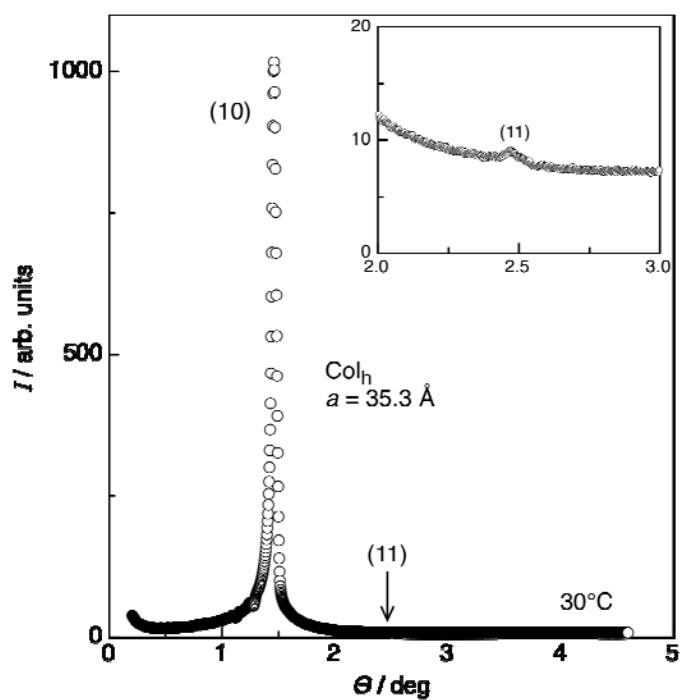


Figure S2: X-ray scattering profile of derivative **2j** at 30 °C.