Synthesis of Extended Triphenylenes by Palladium-Catalyzed [2+2+2] Cycloaddition of Triphenylenes

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**General methods:** All reactions were carried out under argon using oven-dried glassware. Solvents were dried by distillation from a drying agent: THF from Na/benzophenone; toluene and benzene from Na; CH$_3$CN and CH$_2$Cl$_2$ from CaH$_2$. TMSCl, $i$-Pr$_2$NEt, $i$-Pr$_2$NH, TMEDA and $t$-BuNH$_2$ were distilled from CaH$_2$ prior to use. 2-Trimethylsilylphenyl triflate (1),$^{[1]}$ 1,1'-2',1''-terphenyl-4'-ol (3,4-diphenylphenol, 8) and Pd(PPh$_3$)$_4$[3] were prepared following published procedures. Commercial reagents were purchased from ABCR GmbH, Aldrich Chemical Co., or Strem Chemicals Inc., and were used without further purification, except that resorcinol monoacetate (10) was purified by column chromatography before use. $n$-BuLi and Bu$_4$NF (TBAF) were used in solution in hexane (2.40 M) and THF (1 M), respectively. TLC was performed on Merck silica gel 60 F$_{254}$; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). $^1$H and $^{13}$C NMR spectra were recorded at 250.13 and 62.83 MHz (Bruker DPX-250 instrument) or 300 and 75 MHz (Varian Mercury-300 instrument), respectively. High- or low-temperature NMR spectra were recorded on either a Bruker AMX-500 or a Varian Inova-750 instrument. Low-resolution electron impact mass spectra (EI-LRMS) were determined at 70 eV on a HP-5988A instrument. High-resolution mass spectra (HRMS) and FAB (positive FAB in 3-nitrobenzyl alcohol) were obtained on a Micromass Autospec spectrometer. MALDI-TOF spectra were determined on a Bruker Autoflex instrument. IR spectra were recorded on a Mattson Cygnus 100 spectrophotometer. Melting points were measured on a Gallenkamp instrument. UV/Vis spectra were obtained on a Varian Cary 100 Bio or a Jasco V-530 spectrophotometers.

**Synthesis of aryne precursor 7a**

5'-Bromo-1,1'-2',1''-terphenyl-4'-ol (2-bromo-4,5-diphenylphenol): A solution of Br$_2$ (160 µL, 3.12 mmol) in toluene (1.6 mL) was added dropwise to a solution of $t$-BuNH$_2$ (110 µL, 1.05 mmol) in toluene (8.0 mL) at -20°C. After addition was complete, the mixture was stirred at room temperature for 10 min. Then, a solution of 1,1'-2',1''-terphenyl-4'-ol$^{[2]}$ (3,4-diphenylphenol, 8, 640 mg, 2.60 mmol) in toluene (2.0 mL) was added dropwise at -78°C, and the resulting mixture was stirred overnight at room temperature. Then, H$_2$O (10 mL) was added, the phases were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue was...
purified by column chromatography (SiO₂; 2:3 CH₂Cl₂/hexane), affording 5'-bromo-1,1':2',1''-terphenyl-4'-ol (682 mg, 81%) as a white solid: m.p. 88-90°C; ¹H NMR (250 MHz, CDCl₃): δ = 7.75 (s, 1H), 7.49-7.27 (m, 11H), 5.75 (s, 1H) ppm; ¹³C NMR (62.8 MHz, CDCl₃): δ = 151.2 (C), 141.6 (C), 140.0 (C), 139.7 (C), 134.5 (C), 133.5 (CH), 129.6 (2CH), 129.5 (2CH), 127.9 (4CH), 126.8 (CH), 126.5 (CH), 117.7 (CH), 109.0 (C) ppm; MS (EI), m/z (%): 326 (73), 324 (77); HRMS (EI) for C₁₈H₁₃⁷⁹BrO, calcd: 324.0150, found: 324.0143; HRMS (EI) for C₁₈H₁₃⁸₁BrO, calcd: 326.0129, found: 326.0133.

3-Bromo-2-triphenylenol (9): A solution of 5'-bromo-1,1':2',1''-terphenyl-4'-ol (449 mg, 1.38 mmol) in CS₂ (60 mL) was added to a suspension of AlCl₃ (4.57 g, 34.5 mmol) and CuCl₂ (4.27 g, 31.7 mmol) in CS₂ (400 mL) at room temperature. The mixture was stirred at room temperature for 5 h and then poured on 10% aqueous HCl solution (200 mL). The phases were separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂, hexane was added, and the resulting precipitate was filtered, affording 9 (380 mg, 85%) as a white solid: m.p. 135-140°C; ¹H NMR (250 MHz, CDCl₃): δ = 8.71 (s, 1H), 8.63-8.50 (m, 2H), 8.19 (s, 1H), 7.70-7.60 (m, 4H), 5.75 (s, 1H) ppm; ¹³C NMR (62.8 MHz, CDCl₃): δ = 151.1 (C), 131.2 (C), 130.1 (C), 129.0 (C), 128.8 (C), 128.7 (C), 127.7 (CH), 127.4 (CH), 127.3 (CH), 127.1 (CH), 126.9 (CH), 123.4 (CH), 123.3 (2 CH), 122.7 (CH), 114.8 (C), 111.4 (C), 109.0 (CH) ppm; MS (EI), m/z (%): 324 (93), 322 (90); HRMS (EI) for C₁₈H₁₁⁷⁹BrO, calcd: 321.9993, found: 321.9989; HRMS (EI) for C₁₈H₁₁⁸¹BrO, calcd: 323.9973, found: 323.9970; UV/Vis (CH₂Cl₂), λ_max (ε): 351 (5600), 335 (6000), 290 (sh, 14800), 264 (44000), 256 (sh, 33200 mol⁻¹ dm³ cm⁻¹) nm.

3-(Trimethylsilyl)triphenylenyl 2-trifluoromethanesulfonate (7a): A solution of 3-bromo-2-triphenylenol (9, 205 mg, 0.64 mmol) and HMDS (140 µL, 0.66 mmol) in THF (2.0 mL) was refluxed for 1 h. The solvent was evaporated under reduced pressure, and the residue was subjected to vacuum to remove excess NH₃ and unreacted HMDS. ¹H NMR of the crude residue showed quantitative formation of the corresponding silyl ether. This crude product was dissolved in THF (4.0 mL), and the solution was cooled to -100°C (external temperature). n-BuLi (270 µL, 2.59 M, 0.70 mmol) was added dropwise and the reaction mixture was stirred for 30 min while the temperature reached -80°C. The mixture was again cooled to -100°C, Tf₂O (130 µL, 0.77 mmol) was added
dropwise and stirring was kept up for 30 min while the temperature returned to -80°C. Then, saturated aqueous NaHCO₃ (2 mL) was added at low temperature, the phases were separated, and the aqueous layer was extracted with Et₂O. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂; 1:2 CH₂Cl₂/hexane), affording 7a (182 mg, 64%) as a white solid: m.p. 133-135°C; ¹H NMR (250 MHz, CDCl₃): δ = 8.81 (s, 1H), 8.68-8.60 (m, 3H), 8.56 (s, 1H), 8.49 (d, J = 9.4 Hz, 1H), 7.74-7.69 (m, 4H), 0.53 (s, 9H) ppm; ¹³C NMR (62.8 MHz, CDCl₃): δ = 154.3 (C), 132.3 (C), 131.9 (CH), 131.1 (C), 130.4 (C), 129.9 (C), 128.7 (C), 128.5 (C), 128.4 (CH), 128.3 (C), 127.8 (CH), 127.6 (2 CH), 127.2 (CH), 123.5 (CH), 123.4 (CH), 123.3 (CH), 118.6 (q, J = 321 Hz, CF₃), 113.4 (CH), -0.6 (TMS) ppm; MS (EI), m/z (%): 448 (83), 433 (65); HRMS (EI) for C₂₂H₁₉F₃O₃SSi, calcld: 448.0776, found: 448.0774; IR (KBr): 1212, 1144, 921, 840, 752 cm⁻¹; UV/Vis (CH₂Cl₂), λ max (ε): 308 (11900), 287 (22700), 262 (69200), 255 (sh, 49000 mol⁻¹ dm³ cm⁻¹) nm.

Synthesis of aryne precursor 7b

4-Bromo-3-hydroxyphenyl acetate: i-Pr₂NH (410 µL, 2.95 mmol) was added to a solution of resorcinol monoacetate (10, 4.49 g, 29.54 mmol) in CH₂Cl₂ (210 mL). NBS (6.05 g, 33.97 mmol) was added in one portion at -100°C, and the resulting mixture was stirred for 14 h while the temperature reached 20°C. Then, 10% aqueous HCl (150 mL) was added, the phases were separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure, and the resulting residue was purified by column chromatography (SiO₂; 1:1 to 3:1 CH₂Cl₂/hexane), affording 4-bromo-3-hydroxyphenyl acetate (3.60 g, 53%) as a yellowish oil: ¹H NMR (250 MHz, CDCl₃): δ = 7.45 (d, J = 8.7 Hz, 1H), 6.79 (d, J = 2.6 Hz, 1H), 6.62 (dd, J = 8.7, 2.6 Hz, 1H), 5.61 (br s, 1H), 2.29 (s, 3H) ppm; ¹³C NMR (62.8 MHz, CDCl₃): δ = 169.5 (C), 153.0 (C), 150.7 (C), 132.3 (CH), 114.9 (CH), 109.8 (CH), 106.9 (C), 21.0 (CH₃) ppm; MS (EI), m/z (%): 232 (11), 230 (11); HRMS (EI) for C₈H₇BrO₃, calcld: 229.9579, found: 229.9584; HRMS (EI) for C₈H₇BrO₃, calcld: 231.9558, found: 231.9565.

5-Acetoxy-2-bromophenyl trifluoromethanesulfonate (11): Tf₂O (2.25 mL, 13.42 mmol) was added dropwise to a solution of 4-bromo-3-hydroxyphenyl acetate (1.35 g, 5.84 mmol) and i-Pr₂NEt (1.17 mL, 6.71 mmol) in CH₂Cl₂ (11 mL) at 0°C, and this reaction mixture was stirred at room temperature for 80 min. Then, cold 5% aqueous
NaHCO₃ (10 mL) was slowly added and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. And the resulting residue was purified by column chromatography (SiO₂: 1:1 CH₂Cl₂/hexane), affording 11 (1.95 g, 92%) as a yellowish oil: ¹H NMR (250 MHz, CDCl₃): δ = 7.68 (d, J = 8.8 Hz, 1H), 7.20 (d, J = 2.5 Hz, 1H), 7.08 (dd, J = 8.8, 2.5 Hz, 1H), 2.32 (s, 3H) ppm; ¹³C NMR (62.8 MHz, CDCl₃): δ = 168.4 (C), 150.3 (C), 146.8 (C), 134.2 (CH), 122.9 (CH), 118.6 (q, J = 321 Hz, CF₃), 117.0 (CH), 112.5 (C), 21.0 (CH₃) ppm; MS (EI), m/z (%): 364 (12), 362 (9); HRMS (EI) for C₉H₆⁷⁹BrF₃O₅S, calcd: 361.9071, found: 361.9084; HRMS (EI) for C₉H₆⁸¹BrF₃O₅S, calcd: 363.9051, found: 363.9059.

4-Bromo-1,2-bis(hexyloxy)benzene:⁵ SiO₂ (9.00 g) and NBS (3.36 g, 18.86 mmol) were added to a solution of 1,2-bis(hexyloxy)benzene (4.99 g, 17.92 mmol) in CH₂Cl₂ (180 mL). After vigorous stirring at room temperature for 8 h, this mixture was filtered to remove SiO₂, concentrated under reduced pressure to approx. 50 mL, and washed with saturated aqueous Na₂S₂O₅ (50 mL). The aqueous layer was extracted with CH₂Cl₂ and the combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography (SiO₂: 1:1 CH₂Cl₂/hexane), affording 4-bromo-1,2-bis(hexyloxy)benzene (6.39 g, 100%) as a colourless oil: ¹H NMR (250 MHz, CDCl₃): δ = 6.99 (d, J = 9.0 Hz, 1H), 6.97 (s, 1H), 6.73 (d, J = 9.0 Hz, 1H), 3.98-3.92 (m, 4H), 1.84-1.74 (m, 4H), 1.48-1.27 (m, 12H), 0.93-0.87 (m, 6H); MS (EI), m/z (%): 358 (18), 356 (18).

3,4-Bis(hexyloxy)-1-phenylboronic acid (13):⁶ n-BuLi (8.20 mL, 2.40 M, 19.71 mmol) was added dropwise to a solution of 4-bromo-1,2-bis(hexyloxy)benzene (6.39 g, 17.90 mmol) in THF (90 mL), and the mixture was stirred at -80°C for 1 h. Then, B(OMe)₃ (10.14 mL, 90.50 mmol) was added and the mixture was allowed to reach room temperature while stirring overnight, after which a further 10% aqueous HCl (100 mL) was added and stirring was kept up for 30 min. The phases were separated and the aqueous layer was extracted with AcOEt. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to obtain a pale yellow solid, which was washed with hexane (100 mL) and filtered, affording a mixture of the boronic acid 13 and the corresponding boroxine, the cyclic anhydride trimer [(ArBO)₃]. Heating this mixture at 50°C under reduced pressure for 18 h completed the...
dehydration of the boronic acid, affording the boroxine derived from 13 (3.98 g, 73 %) as a white solid: 

\[ \delta = 7.82 (d, J = 8.1 \text{ Hz}, 3H), 7.70 (s, 3H), 7.00 (d, J = 8.1 \text{ Hz}, 3H), 4.17-4.07 (m, 12H), 1.91-1.83 (m, 12H), 1.55-1.37 (m, 36H), 0.96-0.93 (m, 18H). \]

**3,3''4,4''-Tetrakis(hexyloxy)-1,1':2',1''-terphenyl-4'-ol (14):** An aqueous Na\textsubscript{2}CO\textsubscript{3} solution (2%, 200 mL) was added to a mixture of triflate 11 (3.51 g, 9.67 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (1.12 g, 0.97 mmol) and the boroxine derived from boronic acid 13 (11.5 g, 12.57 mmol) in THF (65 mL). After stirring at 85°C for 48 h, this mixture was cooled to room temperature and the phases were separated. The aqueous phase was acidified to pH 1 by careful addition of 10% aqueous HCl solution, and was then extracted with Et\textsubscript{2}O. The combined organic layers were dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under reduced pressure. The resulting crude was dissolved in THF (150 mL), a mixture of saturated NaHCO\textsubscript{3} and MeOH (1:1, 150 mL) was added, and this mixture was stirred at 85°C for 12 h, after which the phases were separated and the aqueous layer was carefully acidified to pH 1 with 10% aqueous HCl and extracted with AcOEt. The combined organic layers were dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO\textsubscript{2}; 1:4 AcOEt/hexane), affording 14 (5.31 g, 85%): 

\[ \delta = 7.17 (m, 1H), 6.75 (d, J = 8.4 \text{ Hz}, 1H), 6.73 (s, 1H), 6.68-6.57 (m, 4H), 6.50 (s, 1H), 6.48 (s, 1H), 5.80 (br s, 1H), 3.86 (t, J = 6.7 \text{ Hz}, 4H), 3.63-3.56 (m, 4H), 1.73-1.63 (m, 4H), 1.56-1.48 (m, 4H), 1.39-1.16 (m, 24H), 0.83-0.78 (m, 12H) \text{ ppm}; \]

\[ ^{13}\text{C NMR (62.8 MHz, CDCl}_3\text{): } \delta = 155.0 (C), 148.1 (2C), 147.6 (C), 147.4 (C), 141.4 (C), 134.3 (2C), 132.6 (C), 131.5 (CH), 121.9 (2CH), 117.0 (CH), 116.0 (CH), 115.7 (CH), 114.1 (CH), 113.2 (2CH), 69.3 (CH\textsubscript{2}), 69.2 (CH\textsubscript{2}), 69.0 (2CH\textsubscript{2}), 31.6 (2CH\textsubscript{2}), 31.5 (2CH\textsubscript{2}), 29.22 (CH\textsubscript{2}), 29.20 (CH\textsubscript{2}), 29.0 (CH\textsubscript{2}), 28.9 (CH\textsubscript{2}), 25.7 (2CH\textsubscript{2}), 25.6 (2CH\textsubscript{2}), 22.6 (4CH\textsubscript{2}), 14.0 (4CH\textsubscript{3}) \text{ ppm}; MS (EI), m/z (%): 646 (100); HRMS (EI) for C\textsubscript{42}H\textsubscript{62}O\textsubscript{5}, calcld: 646.4597, found: 646.4592. \]

**5'-Bromo-3,3''4,4''-tetrakis(hexyloxy)-1,1':2',1''-terphenyl-4'-ol:** SiO\textsubscript{2} (4.08 g) and NBS (1.73 g, 9.72 mmol) were each added in one portion to a solution of 14 (5.27 g, 8.16 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (140 mL), and this mixture was vigorously stirred at room temperature for 6 h, after which it was filtered and washed with saturated aqueous Na\textsubscript{2}S\textsubscript{2}O\textsubscript{5} (100 mL). The aqueous layer was extracted with CH\textsubscript{2}Cl\textsubscript{2} and the combined organic layers were dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under
reduced pressure. The residue was purified by column chromatography (SiO\textsubscript{2}; 2:1 CH\textsubscript{2}Cl\textsubscript{2}/hexane), affording 5'-bromo-3,3''4,4''-tetrakis(hexyloxy)-1,1':2',1''-terphenyl-4'-ol (3.77 g, 64%): \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}): δ = 7.50 (s, 1H), 7.06 (s, 1H), 6.76-6.60 (m, 4H), 6.56 (d, J = 8.8 Hz, 2H), 5.66 (s, 1H), 3.94 (t, J = 6.5 Hz, 4H), 3.72-3.66 (m, 4H), 1.85-1.74 (m, 4H), 1.69-1.60 (m, 4H), 1.48-1.26 (m, 24H), 0.93-0.88 (m, 12H) ppm; \textsuperscript{13}C NMR (62.8 MHz, CDCl\textsubscript{3}): δ = 151.2 (C), 148.3 (C), 148.1 (2C), 147.9 (C), 141.4 (C), 134.4 (C), 133.3 (CH), 133.1 (C), 132.9 (C), 121.8 (CH), 121.7 (CH), 117.5 (CH), 115.8 (CH), 115.5 (CH), 113.3 (CH), 113.1 (C), 108.5 (C), 69.15 (2CH\textsubscript{2}), 69.06 (2CH\textsubscript{2}), 31.6 (4CH\textsubscript{2}), 29.2 (2CH\textsubscript{2}), 29.0 (2CH\textsubscript{2}), 25.7 (4CH\textsubscript{2}), 22.6 (4CH\textsubscript{2}), 14.0 (4CH\textsubscript{3}) ppm; MS (EI), m/z (%): 726 (100), 724 (90); HRMS (EI) for C\textsubscript{42}H\textsubscript{61}\textsubscript{79}BrO\textsubscript{5}, calcd: 724.3702, found: 724.3684; HRMS (EI) for C\textsubscript{42}H\textsubscript{61}\textsubscript{81}BrO\textsubscript{5}, calcd: 726.3682, found: 726.3667.

3-Bromo-6,7,10,11-tetrakis(hexyloxy)-2-triphenylenol (15): A solution of 5'-bromo-3,3'',4,4''-tetrakis(hexyloxy)-1,1':2',1''-terphenyl-4'-ol (1.71 g, 2.37 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (200 mL) was added to a suspension of anhydrous FeCl\textsubscript{3} (1.14 g, 7.10 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (80 mL). This mixture was vigorously stirred at room temperature for 25 min, MeOH (150 mL) was added, and stirring was kept up for a further 60 min. The solvent was removed under reduced pressure and the crude was purified by column chromatography (SiO\textsubscript{2}; 2:1 CH\textsubscript{2}Cl\textsubscript{2}/hexane), affording a yellowish solid. This solid was washed with MeOH (50 mL), obtaining 15 (1.64 g, 96%) as a white solid: m.p. 127-129°C. \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}): δ = 8.49 (s, 1H), 8.00 (s, 1H), 7.80 (s, 1H), 7.76 (s, 2H), 7.74 (s, 1H), 5.71 (s, 1H), 4.25-4.15 (m, 8H), 2.00-1.87 (m, 8H), 1.58-1.56 (m, 8H), 1.40-1.29 (m, 16H), 0.96-0.86 (m, 12H) ppm; \textsuperscript{13}C NMR (62.8 MHz, CDCl\textsubscript{3}): δ = 150.1 (C), 149.8 (C), 149.2 (C), 149.1 (C), 149.0 (C), 130.3 (C), 126.5 (CH), 124.42 (C), 124.39 (C), 123.3 (C), 122.5 (2C), 110.1 (C), 108.5 (CH), 107.1 (CH), 106.8 (CH), 106.6 (CH), 106.2 (CH), 69.7 (CH\textsubscript{2}), 69.5 (CH\textsubscript{2}), 69.3 (CH\textsubscript{2}), 69.2 (CH\textsubscript{2}), 31.7 (4CH\textsubscript{2}), 29.7 (CH\textsubscript{2}), 29.32 (2CH\textsubscript{2}), 29.26 (CH\textsubscript{2}), 25.8 (4CH\textsubscript{2}), 22.6 (4CH\textsubscript{2}), 14.0 (4CH\textsubscript{3}) ppm; MS (EI), m/z (%): 726 (100), 724 (90); HRMS (EI) for C\textsubscript{42}H\textsubscript{61}\textsuperscript{79}BrO\textsubscript{5}, calcd: 722.3546, found: 722.3516; HRMS (EI) for C\textsubscript{42}H\textsubscript{61}\textsuperscript{81}BrO\textsubscript{5}, calcd: 724.3525, found: 724.3519; UV/Vis (CH\textsubscript{2}Cl\textsubscript{2}), λ\textsubscript{max} (ε): 310 (16400), 278 (55800), 270 (sh, 51400 mol\textsuperscript{-1} dm\textsuperscript{3} cm\textsuperscript{-1}) nm.

6,7,10,11-Tetrakis(hexyloxy)-3-(trimethylsilyl)-2-triphenylenol (16): A solution of 15 (0.564 g, 0.78 mmol) and HMDS (0.180 mL, 0.86 mmol) in THF (6 mL) was refluxed for 60 min. The solvent was evaporated under reduced pressure and the residue
was subjected to vacuum to remove excess NH$_3$ and unreacted HMDS. The quantitative formation of the corresponding silyl ether was verified by $^1$H NMR spectroscopy. $n$-BuLi (0.66 mL, 2.36 M, 1.56 mmol) was added dropwise to a solution of the crude silyl ether and TMEDA (59 µL, 0.39 mmol) in THF (7.5 mL) at -100°C, and this mixture was stirred for 70 min while the temperature reached -30°C. TMSCl (0.320 mL, 2.50 mmol) was added, stirring was continued at room temperature for 30 min, aqueous HCl solution (5%, 4 mL) was added, and after a further 2 h stirring at room temperature the phases were separated and the aqueous layer was extracted with Et$_2$O. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO$_2$; 1:3 Et$_2$O/hexane), affording 16 (0.452 g, 81%) as a yellow solid: m.p. 68-70°C; $^1$H NMR (250 MHz, CDCl$_3$): δ = 8.50 (s, 1H), 8.02 (s, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.76 (s, 1H), 7.72 (s, 1H), 6.10 (s, 1H), 4.29-4.18 (m, 6H), 3.88 (t, $J$ = 6.1 Hz, 2H), 1.99-1.87 (m, 6H), 1.58-1.52 (m, 8H), 1.44-1.32 (m, 12H), 1.27-1.10 (m, 6H), 0.96-0.86 (m, 9H), 0.81 (t, $J$ = 6.5 Hz, 3H), 0.48 (s, 9H) ppm; $^{13}$C NMR (62.8 MHz, CDCl$_3$): δ = 159.4 (C), 149.3 (C), 149.0 (C), 148.6 (C), 148.5 (C), 131.4 (C), 130.5 (CH), 125.7 (C), 124.6 (C), 124.3 (C), 123.1 (C), 122.8 (C), 122.2 (C), 107.3 (CH), 106.8 (CH), 106.6 (2CH), 106.4 (CH), 69.8 (CH$_2$), 69.6 (CH$_2$), 69.4 (CH$_2$), 69.1 (CH$_2$), 31.64 (2CH$_2$), 31.59 (CH$_2$), 31.51 (CH$_2$), 29.3 (CH$_2$), 29.2 (2CH$_2$), 29.0 (CH$_2$), 25.83 (3CH$_2$), 25.77 (CH$_2$), 22.6 (3CH$_2$), 22.5 (CH$_2$), 14.0 (4CH$_2$), -0.8 (TMS) ppm; MS (FAB$^+$), m/z (%): 716 (100); HRMS (FAB$^+$) for C$_{45}$H$_{68}$O$_5$Si, calcd: 716.4836, found: 716.4820; UV/Vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ (ε): 310 (9200), 279 (259000), 271 (sh, 23000 mol$^{-1}$ dm$^3$ cm$^{-1}$) nm.

6,7,10,11-Tetrakis(hexyloxy)-3-(trimethylsilyl)triphenylenyl 2-trifluoromethanesulfonate (7b): Tf$_2$O (0.160 mL, 0.98 mmol) was added dropwise to a solution of compound 16 (0.573 g, 0.80 mmol) and pyridine (0.120 mL, 1.44 mmol) in CH$_2$Cl$_2$ (8 mL) at 0°C, and this mixture was stirred at room temperature for 30 min. Cold 5% aqueous NaHCO$_3$ (10 mL) was added slowly, stirring was continued for 15 min, the phases were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layers were washed with 5% aqueous HCl (10 mL), the phases were separated and the aqueous layer was again extracted with CH$_2$Cl$_2$. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO$_2$; 1:3 Et$_2$O/hexane), affording 7b (0.675 g, 100%) as a yellowish solid: m.p. 80-84°C; $^1$H NMR (250 MHz, CDCl$_3$): δ
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= 8.59 (s, 1H), 8.35 (s, 1H), 7.98 (s, 1H), 7.81 (s, 3H), 4.28-4.21 (m, 8H), 2.02-1.91 (m, 8H), 1.62-1.54 (m, 8H), 1.48-1.39 (m, 16H), 0.94 (t, J = 6.8 Hz, 12H), 0.5 (s, 9H) ppm; 

$^1$H NMR (62.8 MHz, CDCl$_3$): $\delta$ = 153.4 (C), 150.3 (C), 150.0 (C), 149.1 (2C), 131.3 (CH), 131.1 (C), 129.1 (C), 127.3 (C), 124.8 (C), 124.4 (C), 122.4 (C), 122.3 (C), 118.7 (q, J = 320 Hz, CF$_3$), 112.8 (CH), 106.9 (CH), 106.6 (CH), 106.5 (2CH), 69.4 (3CH$_2$), 69.1 (CH$_2$), 31.7 (4CH$_2$), 29.3 (3CH$_2$), 29.2 (CH$_2$), 25.8 (4CH$_2$), 22.6 (4CH$_2$), 14.0 (4CH$_3$), -0.7 (TMS) ppm; MS (FAB$^+$), m/z (%): 848 (100); HRMS (FAB$^+$) for C$_{46}$H$_{67}$F$_3$O$_7$SSi, calcd: 848.4329, found: 848.4293; IR (CsI): 2929, 2858, 1264, 842 cm$^{-1}$; UV/Vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ (ε): 307 (34100), 280 (106600), 271 (sh, 76900 mol$^{-1}$ dm$^3$ cm$^{-1}$) nm.

References

SUPPORTING INFORMATION

[Chemical structure image]

[Diagram of NMR spectra]
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R = -OC₆H₁₃
During $^{13}$C-NMR characterization decomposition of compound 18b in CDCl$_3$ was observed.
Concentration dependence of the $^1$H-NMR spectrum of compound $20b$ in CDCl$_3$. 

20b, $R = -OC_6H_{13}$
$20b$, $R = -\text{OC}_6\text{H}_{13}$
SUPPORTING INFORMATION

22a

 ppm (δ)

5.50 6.00 6.50 7.00 7.50 8.00 8.50 9.00 9.50 10.00 10.50

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ppm (δ) 10.50 10.00 9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50

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S29