Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Expanded *all*-Phenylene Molecular Spoked Wheels: Cutouts of Graphenylene-3

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1 General Information

1.1 Materials and equipment

Commercially available reagents were used without further purification, unless stated otherwise. All oxygen- and moisture-sensitive reactions were carried out using standard Schlenk techniques under argon. Dry solvents (THF, dichloromethane) were obtained from an M. Braun SPS 800 Solvent Drying System under argon atmosphere. Piperidine and pyridine were distilled under argon over CaH_2. Solvents used for workup and purification were either distilled (dichloromethane (DCM), cyclohexane (Cy), ethyl acetate (EA)) or obtained from commercial suppliers of “p.a.” quality (methanol, chloroform) or HPLC-grade (tetrahydrofurane (THF)).

Thin layer chromatography was performed on silica gel coated aluminium plates (Macherey-Nagel, Alugram SIL G/UV254, 0.25 mm coating with fluorescence indicator). For the detection of the substances UV light of the wavelengths $\lambda = 254$ nm and $\lambda = 366$ nm was used. Column chromatography was performed with glass columns with glass frits filled with 40 – 63 µm silica gel from Merck as a stationary phase. The eluents are given in the specific descriptions.

^1H- and ^{13}C-NMR spectra were recorded on a Bruker Avance I 400 MHz, Bruker Avance I 500 MHz, Bruker Avance III HD 500 MHz Prodigy or Bruker Avance III HD 700 MHz Cryo. Chemical shifts are given in parts per million (ppm) referenced to residual ^1H- or ^{13}C-signals in deuterated solvents. All NMR spectra were recorded at room temperature (RT).

EI-MS spectra were measured on a Thermo Finnigan MAT 95 XL. MALDI-MS spectra were recorded on an ultrafleXtreme TOF/TOF spectrometer by Bruker Daltronik. DCTB or dithranol were used as matrix materials.

Analytical gel permeation chromatography (GPC) was performed in THF at 35 °C on an Agilent Technologies system at a flow rate of 1 mL/min using an IsoPump G1310A, ALS G1329A autosampler, PSS columns (set of 4 columns 8 mm x 300 mm, polystyrene, porosity of 10^2, 10^3, 10^5 and 10^6 Å, with precolumn, Polymer Standards Service GmbH), a VWD G1314B and a RID G1362A detector. Calibration was done with polystyrene standards by Polymer Standard Service GmbH.

Recycling gel permeation chromatography (recGPC) was performed in THF at 35 °C on a Shimadzu system at a flow rate of 5 mL/min using a LC-20 AD pump, DGU-20 A3 degasser, SIL-20 A HAT autosampler, CTO-20 A oven, FRC-10 A fraction collector, FCV-20 AH2 switching valve, PSS columns (set of 3 columns 20 mm x 300 mm, polystyrene, preparative PSS SDV linear S with precolumn 20 mm x 50 mm, preparative PSS SDV) and a SPD-20A UV-detector ($\lambda_1 = 254$ nm and $\lambda_2 = 366$ nm).

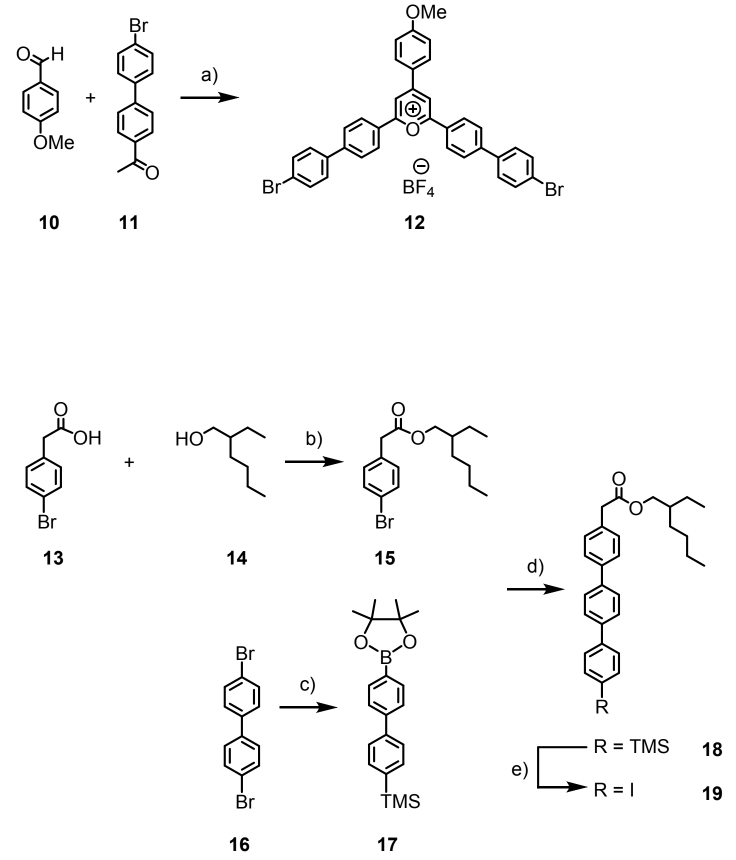
UV/vis spectra were recorded on a Perkin Elmer Lambda 18 spectrometer, fluorescence spectra were measured on a Perkin Elmer LS-50 B luminescence spectrometer. For both methods 10 mm quartz cuvettes by Hellma Analytics were used.

Scanning tunneling microscopy (STM) was performed under ambient conditions (RT) at the solution/solid interface, using octanoic acid (OA) as a solvent and highly oriented pyrolytic graphite (HOPG) as substrate. In a typical experiment, 0.2 µL of a 1 x 10^{-6} M solution of the compound of interest was dropped onto a freshly cleaved HOPG substrate at elevated temperature (110 °C to 120 °C), kept at this temperature for 20 s, and allowed to cool to RT before the STM measurements were performed with the tip immersed into the solution. Bias voltages between -2.1 V and -0.9 V and tunneling current set points in the range of 12 pA to 22 pA were applied to image the supramolecular adlayers shown here. The experimental setup consists of an Agilent 5500 scanning probe microscope that is placed on a Halcyonics actively isolated microscopy workstation. It is acoustically shielded with a home-built box. Scissors cut Pt/Ir (80/20) tips were used and further modified after approach by applying short voltage pulses until the desired resolution was achieved. HOPG was obtained from TipsNano (*via* Anfatec) in ZYB-SS quality. All image sizes given according to internal scanner calibration. Data processing, also for image calibration, was performed using the SPIP 5 (Image Metrology) software package. Molecular modelling was performed using Spartan ’16 and ’18.

Time-resolved and steady-state PL spectra were measured in dilute toluene solution, at RT. Polarization planes of the incident and emitted light were selected using polarization filters. For steady-state PL spectroscopy, a FluoroMax spectrometer was used, and for time-resolved spectroscopy a combination of a Coherent Chamaeleon Ultra II frequency-doubled titanium-sapphire laser (80 MHz repetition rate, 120 fs pulse length, at 340 nm) and a Hamamatsu picosecond streak camera system were used.

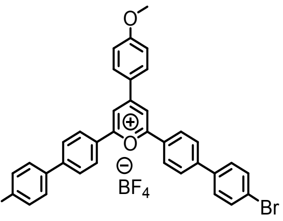
2 Synthesis

2.1 Synthesis of starting materials for the Zimmermann-Fischer condensation



Scheme S1: Synthesis of the starting materials for the Fischer-Zimmermann condensation: a) BF_3• OEt_2, 1,2-dichloroethane, 80 °C, 4 h, 44 %; b) *p*-toluene sulfonic acid (PTSA), 70 °C, 18 h, 95 %; c) 1. THF, *n*-BuLi, -78 °C, 30 min; 2. trimethylsilyl chloride (TMS-Cl), 30 min, -78 °C→RT, 1 h; 3. *n*-BuLi, -78 °C, 30 min; 4. 2-iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, -78 °C→RT, 18 h, 60 %; d) K_2CO_3, toluene, H_2O, $PdCl_2(PPh_3)_2$, PPh_3, 80 °C, 2 d, 56 %; e) ICl, DCM, 0 °C, 1.5 h, 99 %; f) LiOH, THF, H_2O, 60 °C, 1 d, 84 %; g) NaOMe, MeOH, 73 °C, 1 h, 100 %.

12[S1]



Under an Ar atmosphere, BF_3 • OEt_2 (10.2 mL, 68.1 mmol) was added to **10** (4.48 g, 32.9 mmol) and **11** (18.1 g, 65.9 mmol), the mixture was diluted with 1,2-dichloroethane (15 mL) and stirred at 80 °C for 4 h. The mixture was diluted with DCM (5 mL) and poured into EA (200 mL). The precipitate was filtered off, washed with EA, redissolved in DCM (10 mL) and precipitated from EA (200 mL). The precipitate was filtered off and dried under vacuum to yield **12** (10.7 g, 14.6 mmol, 44 %) as a dark red solid.

Formula: $C_{36}H_{25}BBr_2F_4O_2$

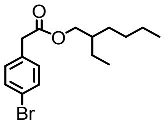
Mol weight: 736.21 g/mol.

^{1}H NMR (400 MHz, DMSO-*d$_6$*, RT): δ [ppm] = 9.06 (s, 2H), 8.72 (d, *J* = 8.8 Hz, 2H), 8.62 (d, *J* = 8.3 Hz, 4H), 8.08 (d, *J* = 8.5 Hz, 4H), 7.84 (d, *J* = 8.6 Hz, 4H), 7.75 (d, *J* = 8.6 Hz, 4H), 7.31 (d, *J* = 8.9 Hz, 2H), 4.00 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d$_6$*, RT): δ [ppm] = 168.19, 165.90, 163.12, 144.44, 137.29, 133.07, 132.12, 129.23, 129.20, 128.46, 127.65, 124.41, 122.72, 115.61, 113.17, 56.26.

MS (ESI+), *m/z* (%): 649.0 (100) $[M-BF_4]^+$. Calculated exact mass: 734.03 Da.

15



13 (10.8 g, 50.2 mmol), **14** (50.0 mL, 320 mmol) and PTSA (8.65 g, 50.2 mmol) were stirred at 70 °C for 18 h. The resulting mixture was purified without any further treatment by column chromatography (Cy:DCM = 1:1, R_f = 0.66) to give **15** (15.7 g, 47.9 mmol, 95 %) as a colorless oil.

Formula: $C_{16}H_{23}BrO_2$,

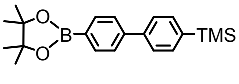
Mol weight: 327.26 g/mol.

^{1}H NMR (400 MHz, CDCl$_3$, RT): δ [ppm] = 7.44 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.00 (d, *J* = 5.8 Hz, 2H), 3.57 (s, 2H), 1.57 – 1.51 (m, 2H), 1.34 – 1.22 (m, 7H), 0.89 – 0.83 (m, 6H).

^{13}C NMR (101 MHz, CDCl$_3$, RT): δ [ppm] = 171.33, 133.31, 131.75, 131.14, 121.21, 67.59, 41.08, 38.87, 30.52, 29.00, 23.92, 23.10, 14.17, 11.12.

MS (EI, 70 eV), *m/z* (%): 326.0 (12) $[M]^{+\bullet}$, 215.9 (84) $[M-C_8H_{17}]^+$, 169.0 (100) $[M-CO_2-C_8H_{17}]^+$. Calculated exact mass: 326.09 Da.

17[S2]



Under an Ar atmosphere, **16** (15.0 g, 48.1 mmol) in THF (250 mL) was cooled to -78 °C and stirred. *n*-BuLi (2 M, 25.2 mL, 50.5 mmol) was slowly added and the mixture was further stirred for 20 min. TMS-Cl (6.10 mL, 48.1 mmol) was added and the mixture was stirred at -78 °C for 20 min and then at RT for 1 h. Subsequently, the mixture was cooled to -78 °C, *n*-BuLi (2 M, 24.05 mL, 48.1 mmol) was slowly added and the mixture further stirred for 20 min. 2-Iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9.60 mL, 47.1 mmol) was added, and the mixture was stirred at RT for 18 h. Water and dichloromethane were added, the organic phase was washed with water and brine, and dried over

$MgSO_4$. After evaporation of the solvent the crude product was purified by column chromatography (Cy:EtOAc = 20:1, R_f = 0.50) to yield **17** (10.2 g, 28.9 mmol, 60 %) as a colorless solid.

Formula: $C_{21}H_{29}BO_2Si$

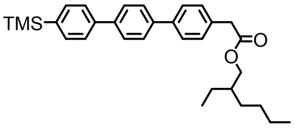
Mol weight: 352.36 g/mol.

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ [ppm] = 7.89 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.61 (m, 6H), 1.37 (s, 12H), 0.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, RT): δ [ppm] = 143.95, 141.51, 139.80, 135.39, 133.96, 126.68, 126.59, 83.96, 27.07, 25.03, 0.95.

MS (EI, 70 eV), *m/z* (%): 352.2 (44) $[M]^{+\bullet}$, 337.1 (100) $[M-CH_3]^+$, 237.1 (20) $[M-CH_3-C_6H_{12}O$. Calculated exact mass: 352.20 Da.

18



Under an Ar atmosphere **15** (10.4 g, 31.8 mmol) **17** (10.2 g, 28.9 mmol) and K_2CO_3 (5.99 g, 43.4 mmol) were dissolved in toluene (30 mL) and water (3 mL). The mixture was purged with Ar for 10 min, and $PdCl_2(PPh_3)_2$ (0.406 g, 0.578 mmol) and PPh_3 (0.455 g, 1.74 mmol) were added. The mixture was stirred at 80 °C for 2 d. Water, aqueous HCl (1 M) and DCM were added. The organic phase was washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (Cy:DCM = 1:1, R_f = 0.38) to yield **18** (7.65 g, 16.2 mmol, 56 %) as a colorless oil.

Formula: $C_{31}H_{40}O_2Si$

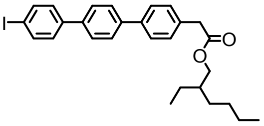
Mol weight: 472.74 g/mol.

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ [ppm] = 7.67 – 7.63 (m, 8H), 7.60 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.38 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 4.04 (d, $^3J_{HH}$ = 5.8 Hz, 2H), 3.68 (s, 2H), 1.59 – 1.55 (m, 2H), 1.36 – 1.23 (m, 7H), 0.89 – 0.84 (m, 6H), 0.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, RT): δ [ppm] = 171.87, 141.19, 140.20, 139.94, 139.61, 139.51, 134.01, 133.51, 129.89, 127.64, 127.54, 127.29, 126.50, 67.50, 41.38, 38.90, 30.53, 29.02, 23.95, 23.11, 14.19, 11.15, -0.93.

MS (MALDI-TOF pos, DCTB), *m/z*: 472.2 $[M]^{+\bullet}$, 457.1 $[M-CH_3]^+$, 345.0 $[M-C_8H_{17}-CH_3]^+$, 315.0 $[M-C_8H_{17}-CO_2]^+$. Calculated exact mass: 472.28 Da.

19



Under an Ar atmosphere, **18** (6.65 g, 16.2 mmol) was dissolved in DCM (50 mL). The solution was cooled to 0 °C and iodomonochloride (17.8 mL, 17.8 mmol, 1 M in DCM) was slowly added and the mixture stirred at 0 °C for 1 h. Then, a 10 % aqueous solution of $NaHSO_3$ was added, and the aqueous layer was extracted with DCM. The organic phase was washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (Cy:DCM = 1:1, $R_f = 0.50$) to yield **19** (8.53 g, 16.2 mmol, 99 %) as a colorless solid.

Formula: $C_{28}H_{31}IO_2$

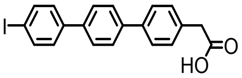
Mol weight: 526.46 g/mol.

^{1}H NMR (400 Hz, $CDCl_3$, RT): δ [ppm] = 7.78 (d, J = 8.5 Hz, 2H), 7.67 – 7.58 (m, 6H), 7.37 (d, J = 8.5 Hz, 4H), 4.03 (d, J = 5.9 Hz, 2H), 3.67 (s, 2H), 1.59 – 1.56 (m, 2H), 1.37 – 1.23 (m, 7H), 0.87 (t, J = 8.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, RT): δ [ppm] = 171.84, 140.34, 140.33, 139.41, 139.05, 138.05, 133.68, 129.94, 129.00, 127.67, 127.38, 127.29, 93.22, 67.52, 41.36, 38.90, 30.53, 29.02, 23.95, 23.11, 14.19, 11.16.

MS (EI, 70 eV), m/z (%): 526.0 (100) $[M]^{+\bullet}$, 413.9 (12) $[M-C_8H_{17}]^+$, 400.2 (42) $[M-I]^+$, 369.0 (38) $[M-C_8H_{17}-CO_2]^+$. Calculated exact mass: 526.14 Da.

20



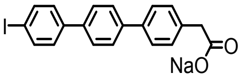
19 (8.18 g, 15.6 mmol) was dissolved in THF (80 mL), LiOH (5.58 g, 233 mmol) in water (60 mL) was added, and the mixture was stirred at 60 °C for 1 d. After cooling to RT, conc. aqueous HCl was added, and the solid was filtered off and washed with THF to yield **20** (5.40 g, 13.0 mmol, 84 %) as a colorless solid. Due to the limited solubility, no NMR spectra were recorded.

Formula: $C_{20}H_{15}IO_2$

Mol weight: 414.24 g/mol.

MS (EI, 70 eV), m/z (%): 414.0 (1000) $[M]^{+\bullet}$, 369.0 (40) $[M-I]^+$, 242.1 (20) $[M-I-CO_2]^+$. Calculated exact mass: 414.01 Da.

21

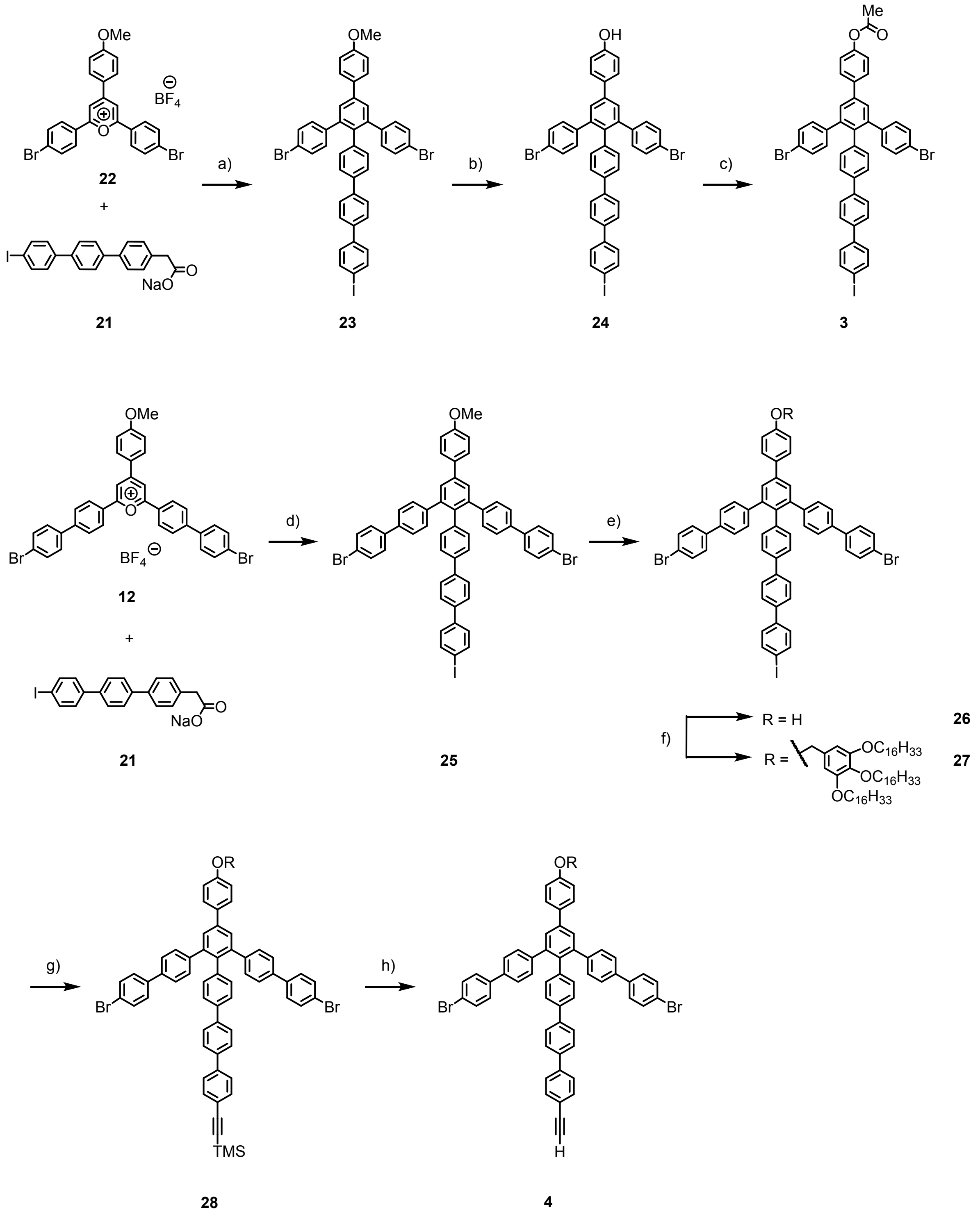


20 (5.40 g, 13.0 mmol) was suspended in MeOH (40 mL), and a solution of NaOMe in MeOH (30 %; 2.35 g, 13.0 mmol) was added. The mixture was heated to reflux for 1 h. Then the solvent was evaporated to yield **21** (5.67 g, 16.0 mmol, 100 %) as a colorless solid. Due to the limited solubility, no analytical characterization was performed.

Formula: $C_{20}H_{14}INaO_2$

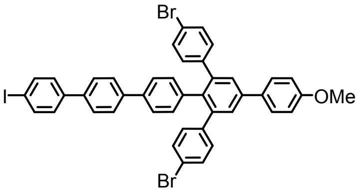
Mol weight: 436.22 g/mol.

2.2 Synthesis of the precursors for the unsymmetrically substituted acetylene



Scheme S2: Synthesis of the precursors for the unsymmetrically substituted acetylene. a) Benzoic anhydride, 150 °C, 4 h, 50 %; b) BBr_3, DCM, -78°C→RT, 18 h, 72 %; c) pyridine, acetic anhydride, RT, 18 h, 99 %; d) benzoic anhydride, 150 °C, 4.5 h; e) BBr_3, DCM, RT, 2 d, 21 % (over 2 steps d) and e)); f) 3,4,5-tris-(hexadecyloxy)benzyl chloride, Cs_2CO_3, DMF, 110 °C, 2 d; 98 %; g) TMS-acetylene, $PdCl_2(PPh_3)_2$, CuI, PPh_3, THF, piperidine, RT, 18 h, 95 %; h) K_2CO_3, MeOH, THF, RT, 18 h, 96 %.

23



Under an Ar atmosphere, **21** (0.888 mg, 2.04 mmol), **22** (1.19 g, 2.04 mmol**),** prepared according to Ref. S3, and benzoic anhydride (5.10 g, 22.5 mmol) were heated to 70 °C for 10 min and then to 150 °C for 4 h. From time to time, sublimed benzoic anhydride was transferred from the cooler back to the solution by melting with a heat gun. Without further workup, the product was purified by column chromatography (Cy:DCM = 1:1, R_f = 0.87) to yield **23** (0.855 g; 1.01 mmol; 50 %) as a colorless solid.

Formula: $C_{43}H_{29}Br_2IO$

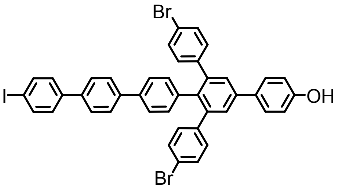
Mol weight: 848.42 g/mol

^{1}H NMR (500 MHz, $CDCl_3$, RT): δ [ppm] = 7.77 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.57 (m, 8H), 7.36 (d, *J* = 8.5 Hz, 4H), 7.32 (d, *J* = 8.5 Hz, 4H), 7.05 – 6.99 (m, 6H), 6.91 (d, *J* = 8.3 Hz, 2H), 3.87 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, RT): δ [ppm] = 159.71, 141.53, 140.86, 140.34, 140.33, 139.80, 139.08, 138.12, 138.09, 138.04, 136.92, 132.63, 132.22, 131.67, 131.07, 128.98, 128.33, 128.19, 127.42, 127.35, 126.15, 120.95, 114.55, 93.20, 55.55.

MS (MALDI-TOF pos, DCTB), *m/z*: 846.0 $[M]^+$. Calculated exact mass: 845.96 Da.

24



Under an Ar atmosphere, **23** (0.855 g, 1.01 mmol) in DCM (100 mL) was cooled to -78 °C, and a solution of BBr_3 in DCM (3.03 mL, 3.03 mmol, 1 M in DCM) was slowly added. The mixture was allowed to warm to RT and stirred for 18 h. Water was added, and the aqueous phase extracted with DCM. The organic phase was washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent the crude product was purified by column chromatography (DCM, R_f = 0.45) to yield **24** (0.606 g, 0.73 mmol, 72 %) as a cream colored solid.

Formula: $C_{42}H_{27}Br_2IO$

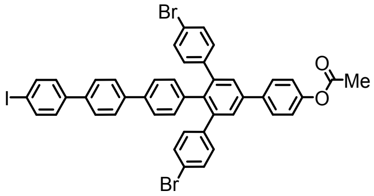
Mol weight: 834.39 g/mol.

^{1}H NMR (500 MHz, CDCl$_3$, RT): δ [ppm] = 7.77 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.60 (d, $_{\mathrm{H}}$ = 4.0 Hz, 4H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.39 – 7.34 (m, 4H), 7.32 (d, *J* = 8.4 Hz, 4H), 7.03 (d, *J* = 8.4 Hz, 4H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H).

^{13}C NMR (126 MHz, CDCl$_3$, RT): δ [ppm] = 155.64, 141.54, 140.83, 140.33, 140.25, 139.79, 139.08, 138.10, 138.04, 136.99, 132.93, 132.21, 131.66, 131.62, 131.13, 131.08, 128.98, 128.58, 128.18, 127.42, 127.35, 126.16, 120.96, 115.98, 93.21.

MS (MALDI-TOF pos, DCTB), *m/z*: 832.0 [M]$^+$. Calculated exact mass: 831.95 Da.

3



24 (0.600 g, 0.71 mmol) was dissolved in pyridine (50 mL), acetic anhydride (1.00 mL, 10.1 mmol) was slowly added and the mixture was stirred at RT for 18h. Water was added, and the aqueous layer was extracted with DCM. The organic phase was washed with water and brine and dried over MgSO$_4$. After evaporation of the solvent the crude product was purified by column chromatography (DCM, R_f = 0.86) to yield **3** (0.622 g, 0.71 mmol, 99 %) as a cream colored solid.

Formula: $C_{44}H_{29}Br_2IO_2$

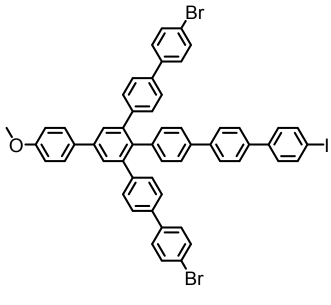
Mol weight: 876.43 g/mol.

^{1}H NMR (500 MHz, CDCl$_3$, RT): δ [ppm] = 7.78 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.65 – 7.58 (m, 6H), 7.37 – 7.34 (m, 4H), 7.32 (d, *J* = 8.5 Hz, 4H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 4H), 6.92 (d, *J* = 8.3 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, RT): δ [ppm] = 169.66, 150.62, 141.63, 140.65, 140.31, 139.89, 139.75, 139.11, 138.19, 138.04, 137.95, 137.63, 132.16, 131.64, 131.12, 128.98, 128.59, 128.34, 127.43, 127.35, 126.19, 122.24, 121.05, 93.22, 21.33.

MS (MALDI-TOF pos, DCTB), *m/z*: 874.0 [M]$^+$. Calculated exact mass: 873.96 Da.

25



Under an Ar atmosphere, **12** (8.44 g, 11.5 mmol), **21** (5.00 g, 11.5 mmol), and benzoic anhydride (27.5 g, 121.6 mmol) were heated to 60 °C for 30 min and then to 150 °C for 4.5 h. From time to time, sublimed benzoic anhydride was transferred from the cooler back to the solution by melting it with a heat gun. Without further workup the product was purified by column chromatography (Cy:DCM = 1:1, R_f = 0.82). Precipitated product was extracted from the silica gel with DCM. In total, **25** (7.55 g) was obtained as a cream colored solid that contains some impurities.

Formula: $C_{55}H_{37}Br_2IO$

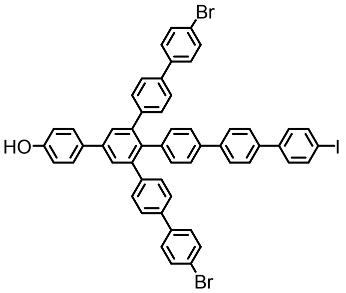
Mol weight: 1000.61 g/mol.

^{1}H NMR (500 MHz, $CDCl_3$, RT): δ [ppm] = 7.76 (d, *J* = 8.5 Hz, 2H), 7.71 (s, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.63 – 7.49 (m, 8H), 7.46 – 7.38 (m, 8H), 7.36 – 7.32 (m, 4H), 7.27 – 7.25 (m, 4H), 7.03 – 7.00 (m, 4H), 3.88 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, RT): δ [ppm] = 159.63, 142.11, 141.51, 140.27, 140.22, 139.94, 139.69, 138.94, 138. 72, 138.03, 137.97, 137.79, 137.11, 132.90, 132.39, 131.96, 130.66, 128.92, 128.68, 128.36, 128.26, 127.34, 127.28, 126.33, 125.98, 121.61, 114.52, 93.19, 55.55.

MS (MALDI-TOF pos, DCTB), *m/z*: 998.0 $[M]^+$. Calculated exact mass: 998.03 Da.

26



Under an Ar atmosphere, slightly impure **25** (7.55 g, about 7.55 mmol) in DCM (100 mL) was cooled to -78 °C and a solution of BBr_3 in DCM (22.6 mL, 22.6 mmol, 1 M in DCM) was slowly added. The mixture was warmed to RT and stirred for 2 d, while it turned dark green. Water was added, the mixture stirred for 15 min, and the aqueous phase was extracted with DCM. The organic phase was washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (DCM, R_f = 0.57) to yield **26** (2.43 g, 2.46 mmol, 21 % over 2 steps) as a cream colored solid.

Formula: $C_{54}H_{35}Br_2IO$

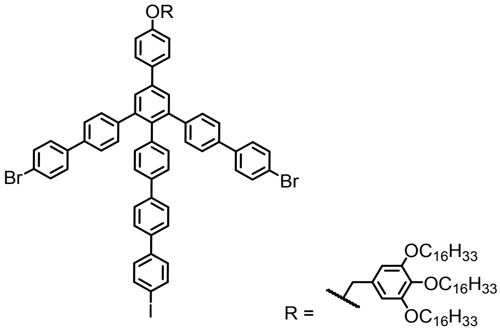
Mol weight: 986.59 g/mol.

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ [ppm] = 7.76 (d, *J* = 8.5 Hz, 2H), 7.69 (s, 2H), 7.64 – 7.49 (m, 10H), 7.45 – 7.38 (m, 8H), 7.37 – 7.32 (m, 4H), 7.26 – 7.24 (m, 4H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, RT): δ [ppm] = 155.55, 142.12, 141.47, 140.26, 140.13, 139.93, 139.68, 138.95, 138.69, 138.03, 137.98, 137.80, 137.17, 133.20, 132.38, 131.96, 130.65, 128.92, 128.68, 128.61, 128.25, 127.34, 127.28, 126.34, 125.99, 121.62, 115.96, 93.20.

MS (MALDI-TOF pos, DCTB), *m/z*: 984.0 $[M]^+$. Calculated exact mass: 984.01 Da.

27



Under an Ar atmosphere, **26** (500 mg, 0.51 mmol), 3,4,5-tris-(hexadecyloxy)benzyl chloride (1.29 g, 1.52 mmol) and Cs_2CO_3 (496 mg, 1.52 mmol) in DMF (50 mL) were stirred at 110 °C for 2 d. The solvent was removed under reduced pressure and the residue dissolved in DCM and 10 % aqueous HCl. The aqueous layer was extracted with DCM. The organic phase was washed with water, 10 % aqueous HCl and brine and dried over $MgSO_4$. After evaporation of the solvent the crude product was purified by column chromatography (Cy:DCM = 1:1, R_f = 0.77) to yield **27** (0.894 g, 0.50 mmol, 98 %) as a colorless solid.

Formula: $C_{109}H_{137}Br_2IO_4$

Mol weight: 1798.00 g/mol.

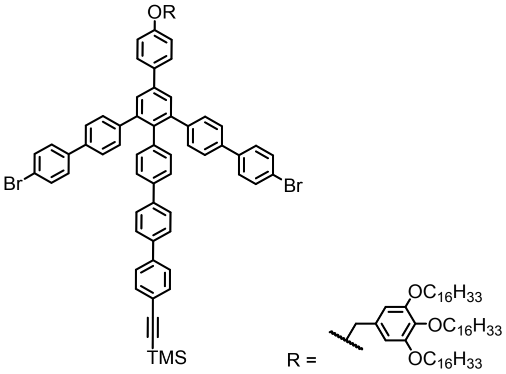
^{1}H NMR (500 MHz, $CDCl_3$, RT): δ [ppm] = 7.76 (d, *J* = 8.4 Hz, 2H), 7.71 (s, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 4H), 7.44 – 7.40 (m, 8H), 7.36 – 7.33 (m, 4H), 7.26 (d, *J* = 8.3 Hz, 4H), 7.09 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 6.65 (s, 2H), 5.01 (s, 2H), 4.01 – 3.95 (m, 6H), 1.83 – 1.72 (m, 6H), 1.51 – 1.44 (m, 6H), 1.36 – 1.26 (m, 72H), 0.90 – 0.87 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, RT): δ [ppm] = 158.88, 153.49, 142.13, 141.49, 140.26, 140.15, 139.94, 139.68, 138.95, 138.70, 138.21, 138.04, 137.98, 137.81, 137.16, 133.15, 132.39, 131.96, 131.86, 130.65, 128.92, 128.67, 128.42, 128.36, 128.25, 127.34, 127.28, 126.33, 125.99, 121.62, 115.45, 106.37, 93.20, 73.61, 70.73, 69.33, 32.09, 30.52, 29.92, 29.90, 29.88, 29.84, 29.83, 29.82, 29.80, 29.60, 29.59, 29.54, 29.53, 26.31, 26.28, 22.85, 14.28.

MS (MALDI-TOF pos, DCTB), *m/z*: 1798.2 $[M]^+$, 1821.3 $[M+Na]^+$. Calculated exact mass: 1794.79 Da.

GPC (PS-calibration) M_p = 2.25 x 10^3 g mol^{-1}.

28



Under an Ar atmosphere, **27** (956 mg, 0.53 mmol) in THF (20 mL) and piperidine (40 mL) was purged with Ar for 30 min. $PdCl_2(PPh_3)_2$ (7.5 mg, 10.6 µmol), PPh_3 (8.4 mg, 31.9 µmol) and CuI (3.0 mg, 16.0 µmol) were added. Trimethylsilyl acetylene (57.4 mg, 585 µmol) was added, and the solution was stirred at RT for 18 h. The solution was acidified with 10 % aqueous HCl, and the organic layer was separated. The aqueous layer was extracted with DCM. The organic phase was washed with water and brine, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (Cy:DCM = 1:1, R_f = 0.70) to yield **28** (0.890 g, 0.50 mmol, 95 %) as a colorless solid.

Formula: $C_{114}H_{146}Br_2O_4Si$

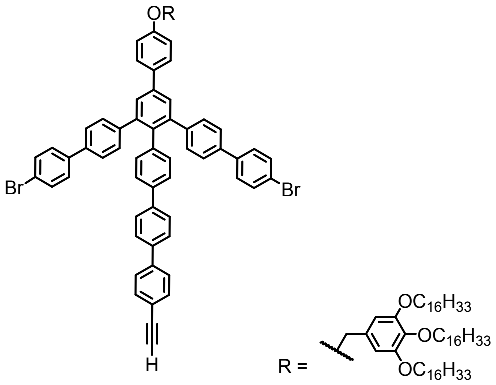
Mol weight: 1768.31 g/mol.

^{1}H NMR (500 MHz, CD_2Cl_2, RT): δ [ppm] = 7.70 (d, *J* = 9.3 Hz, 4H), 7.62 (s, 4H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 4H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.48 – 7.43 (m, 8H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 4H), 7.09 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.66 (s, 2H), 5.02 (s, 2H), 3.98 (t, *J* = 6.5 Hz, 4H), 3.92 (t, *J* = 6.6 Hz, 2H), 1.83 – 1.75 (m, 4H), 1.75 – 1.68 (m, 2H), 1.51 – 1.44 (m, 6H), 1.38 – 1.21 (m, 72H), 0.90 – 0.83 (m, 9H), 0.26 (s, 9H).

^{13}C NMR (126 MHz, CD_2Cl_2, RT): δ [ppm] = 159.34, 153.86, 142.63, 142.08, 141.02, 140.39, 140.20, 140.06, 139.42, 139.34, 138.32, 138.29, 137.64, 133.46, 132.85, 132.52, 132.36, 131.13, 129.07, 128.70, 128.55, 127.73, 127.64, 127.21, 126.64, 126.27, 122.66, 121.92, 115.85, 106.48, 95.54, 73.91, 71.03, 69.62, 32.52, 30.94, 30.35, 30.34, 30.32, 30.30, 30.27, 30.25, 30.24, 30.21, 30.02, 29.96, 29.95, 27.50, 26.72, 23.28, 14.46.

MS (MALDI-TOF pos, DCTB), *m/z*: 1791.9 [M+Na]$^+$, 1766.9 [M]$^+$. Calculated exact mass: 1764.94 Da.

4



Under an Ar atmosphere, **28** (890 mg, 0.50 mmol) and K_2CO_3 (695 mg, 5.03 mmol) were stirred in THF (60 mL) and MeOH (30 mL) at RT for 18 h. Water was added, and the aqueous layer was extracted with DCM. The organic phase was washed with water and brine, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (Cy:DCM = 1:1, $R_f = 0.68$) to yield **4** (0.821 g, 0.48 mmol, 96 %) as a colorless solid

Formula: $C_{111}H_{138}Br_2O_4$

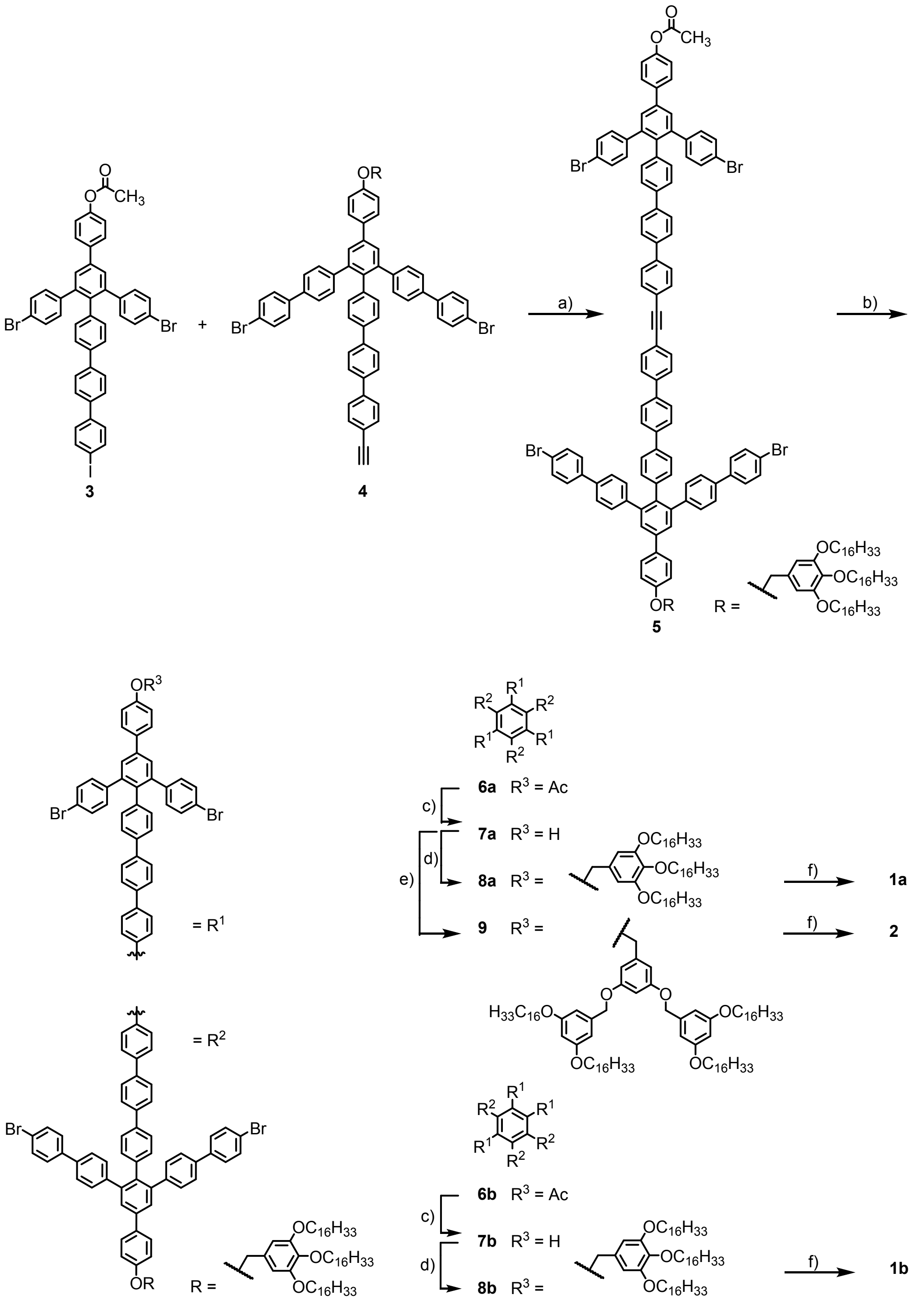
Mol weight: 1696.13 g/mol.

^{1}H NMR (500 MHz, CD_2Cl_2, RT): δ [ppm] = 7.72 – 7.67 (m, 4H), 7.63 (s, 4H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 4H), 7.46 (d, *J* = 8.7 Hz, 4H), 7.45 (d, *J* = 8.5 Hz, 4H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 4H), 7.09 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.66 (s, 2H), 5.02 (s, 2H), 3.98 (t, *J* = 6.5 Hz, 4H), 3.92 (t, *J* = 6.6 Hz, 2H), 3.19 (s, 1H), 1.83 – 1.76 (m, 4H), 1.75 – 1.68 (m, 2H), 1.51 – 1.44 (m, 6H), 1.39 – 1.21 (m, 72H), 0.92 – 0.84 (m, 9H).

^{13}C NMR (126 MHz, CD_2Cl_2, RT): δ [ppm] = 159.33, 153.85, 142.62, 142.07, 141.42, 140.39, 140.28, 140.05, 139.35, 138.29, 138.28, 137.62, 133.45, 133.09, 132.86, 132.51, 132.36, 131.12, 129.06, 128.70, 128.54, 127.78, 127.66, 127.30, 126.64, 126.28, 121.92, 121.54, 115.84, 106.46, 83.89, 78.31, 73.91, 71.02, 69.60, 32.51, 30.94, 30.65, 30.34, 30.32, 30.30, 30.26, 30.25, 30.21, 30.02, 29.96, 29.95, 27.50, 26.71, 23.28, 14.46.

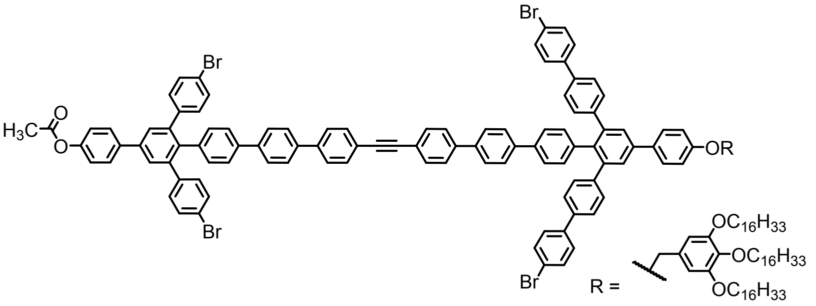
MS (MALDI-TOF pos, DCTB), *m/z*: 2508.2 $[M+C_{55}H_{103}O_3]^+$, 1719.0 $[M+Na]^+$, 1695.0 $[M]^+$. Calculated exact mass: 1692.90 Da.

2.3 Synthesis of the spoked wheels



Scheme S3: Synthesis of the spoked wheels: a) $PdCl_2(PPh_3)_2$, CuI, PPh_3, THF, Et_3N, RT, 18 h; 82 %; b) $Co_2(CO)_8$, toluene, 135 °C, 18 h, 55 % (**6a** and **6b**); c) NaOH, THF, H_2O, 45 °C, 18 h, 96 % (29 % **7a** and 67 % **7b**); d) 3,4,5-tris(hexadecyloxy)benzyl chloride, K_2CO_3, DMF, toluene, 95 °C, 18 h, **8a**: 54 %, **8b**: 90 %; e) 3,5-bis[3,5-bis(hexadecyloxy)benzyloxy]benzyl chloride, Cs_2CO_3, DMF, toluene, 95 °C, 18 h, 79 %; f) $Ni(COD)_2$, 2,2-bipyridine, THF, COD, 120 °C (μW), 12 min, **1a**: 17 %, **1b**: 7 %, **2**: 33%.

5



Under an Ar atmosphere, **3** (467 mg, 532 µmol) and **4** (821 mg, 484 µmol) in THF (40 mL) and Et_3N (40 mL) were purged with Ar for 30 min. $PdCl_2(PPh_3)_2$ (6.8 mg, 9.68 µmol), PPh_3 (7.6 mg, 29.0 µmol) and CuI (2.8 mg, 14.5 µmol) were added. The solution was stirred at RT for 18 h. The solution was acidified with 10 % aqueous HCl and the organic layer separated. The aqueous layer was extracted with DCM. The organic phase was washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by filtering a DCM solution through a short silica gel column (DCM), and subsequent recGPC separation to yield **5** (970 mg, 397 µmol, 82 %) as a colorless solid.

Formula: $C_{155}H_{166}Br_4O_6$

Mol weight: 2444.64 g/mol.

^{1}H NMR (500 MHz, CD_2Cl_2, RT): δ [ppm] = 7.75 – 7.61 (m, 24H), 7.54 (d, $^3J_{HH}$ = 8.6 Hz, 4H), 7.47 (d, $^3J_{HH}$ = 8.6 Hz, 4H), 7.45 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 7.43 – 7.39 (m, 4H), 7.35 (d, $^3J_{HH}$ = 8.5 Hz, 4H), 7.29 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 7.21 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.12 – 7.04 (m, 8H), 6.97 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 6.66 (s, 2H), 5.02 (s, 2H), 3.98 (t, $^3J_{HH}$ = 6.5 Hz, 4H), 3.93 (t, $^3J_{HH}$ = 6.6 Hz, 2H), 2.31 (s, 3H), 1.83 – 1.76 (m, 4H), 1.76 – 1.69 (m, 2H), 1.51 – 1.44 (m, 6H), 1.40 – 1.21 (m, 72H), 0.93 – 0.84 (m, 9H).

^{13}C NMR (126 MHz, CD_2Cl_2, RT): δ [ppm] = 169.98, 159.34, 153.86, 151.24, 142.63, 142.09, 141.30, 140.90, 140.86, 140.39, 140.19, 140.09, 140.05, 139.58, 139.46, 139.33, 138.62, 138.31, 138.28, 138.20, 137.64, 133.46, 132.87, 132.67, 132.59, 132.51, 132.37, 132.21, 131.43, 131.13, 129.07, 128.92, 128.70, 128.64, 128.55, 127.79, 127.74, 127.66, 127.40, 127.36, 126.65, 126.44, 126.28, 122.77, 121.93, 121.29, 115.85, 106.47, 90.59, 73.91, 71.03, 69.62, 32.53, 32.52, 30.95, 30.36, 30.35, 30.33, 30.31, 30.27, 30.25, 30.24, 30.22, 30.03, 29.97, 29.95, 26.75, 26.72, 23.28, 14.47.

MS (MALDI-TOF pos, DCTB), *m/z*: 3257.9 $[M+C_{55}H_{103}O_3]^+$, 2444.9 $[M]^+$. Calculated exact mass: 2438.94 Da.

GPC (THF, vs. PS): $M_p = 3.95 \times 10^3$ g/mol.

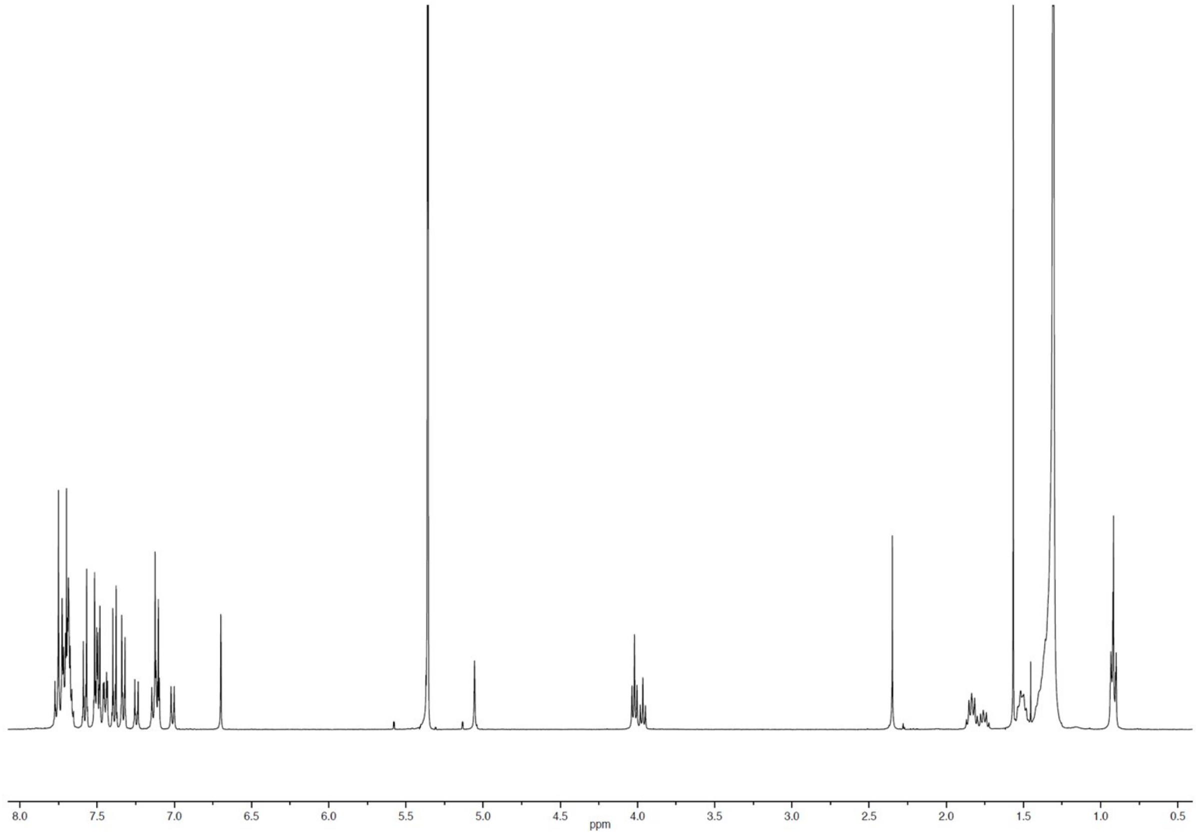
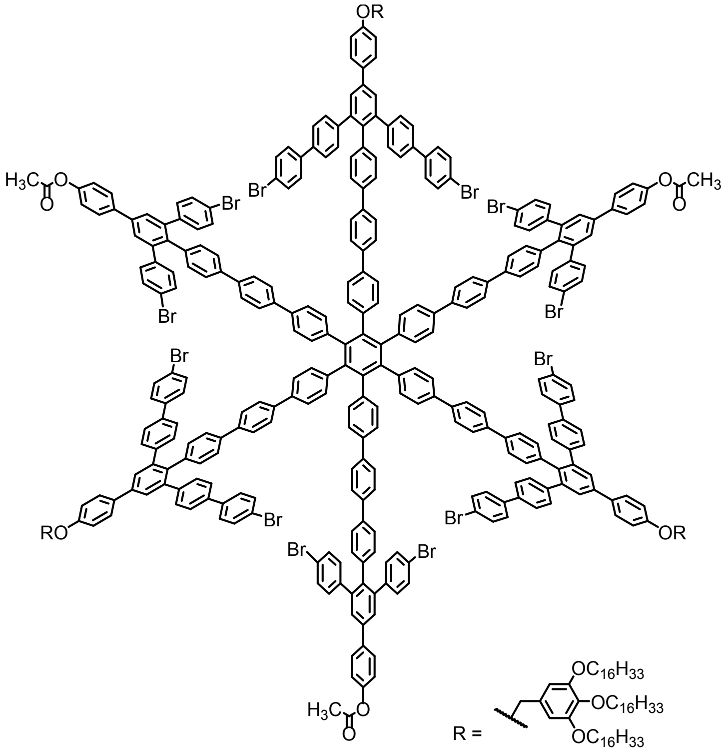
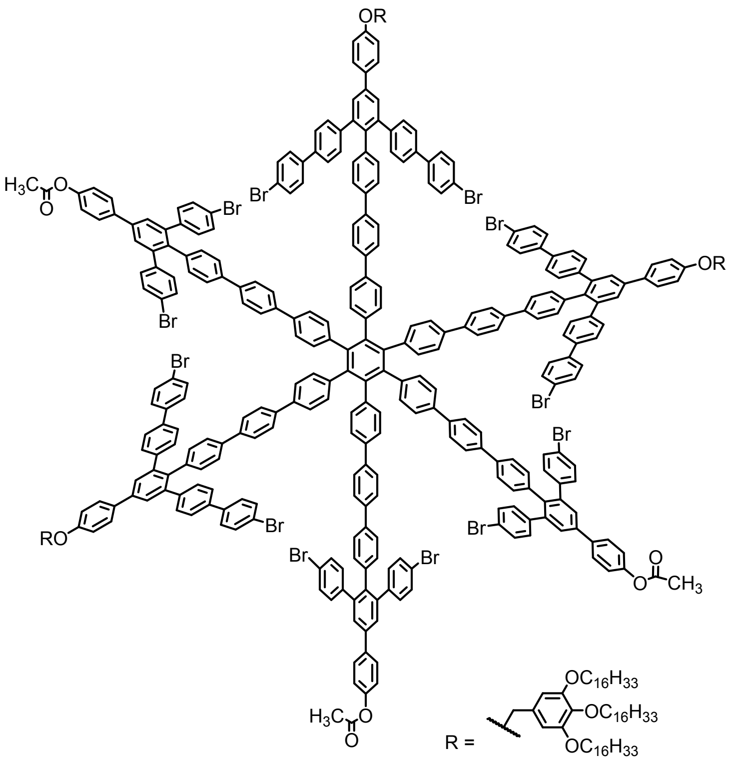


Figure S1: ^{1}H NMR spectrum of **5** (CD_2Cl_2).

6a and 6b



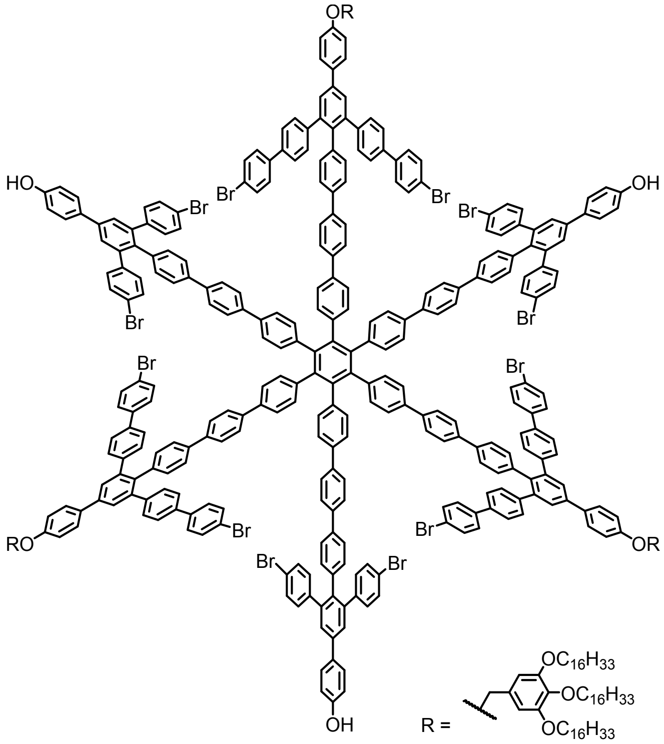


Under an Ar atmosphere, **5** (127 mg, 52.0 µmol) in toluene (10 mL) was purged with Ar at 50 °C for 30 min. $Co_2(CO)_8$ (3.6 mg, 10.4 µmol) was added, and the mixture was heated to reflux for 18 h. The solvent was evaporated under reduced pressure, and the crude product was purified by filtering a DCM solution through a short silica gel column (DCM) and subsequent recGPC separation to yield a mixture of **6a** and **6b** (70.3 mg, 9.59 µmol, 55 %).

7a and 7b

To the mixture of **6a** and **6b** (84.0 mg, 11.5 µmol) in THF (15 mL) and H_2O (2 mL) was added NaOH powder (45.8 mg, 114 µmol), and the reaction mixture was stirred at 45 °C for 18 h. The solution was acidified with 10 % aqueous HCl, and the organic layer separated. The aqueous layer was extracted with DCM. The organic phase was washed with water and brine, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (DCM, R_f^a = 0.72, R_f^b = 0.35) to yield **7a** (23.8 mg; 3.30 µmol, 29 %) and **7b** (55.7 mg, 7.70 µmol, 67 %), both as colorless solids.

7a



Formula: $C_{459}H_{492}Br_{12}O_{15}$

Mol weight: 7207.82 g/mol

^{1}H NMR (700 MHz, CD_2Cl_2, RT): δ [ppm] = 7.68 – 7.63 (m, 12H), 7.59 – 7.53 (m, 12H), 7.42 (d, J = 8.3 Hz, 12H), 7.36 – 7.13 (m, 96H), 7.12 – 7.08 (m, 12H), 7.06 (d, $^3J_{HH}$ = 9.0 Hz, 6H), 7.00 – 6.97 (m, 12H), 6.94 (d, J = 8.0 Hz, 6H), 6.91 (d, J = 8.6 Hz, 6H), 6.86 (d, J = 7.8 Hz, 6H), 6.65 (s, 6H), 4.99 (s, 6H), 3.97 (t, J = 6.5 Hz, 12H), 3.93 (t, J = 6.6 Hz, 6H), 1.81 – 1.76 (m, 12H), 1.75 – 1.69 (m, 6H), 1.50 – 1.43 (m, 18H), 1.38 – 1.22 (m, 216H), 0.90 – 0.85 (m, 27H).

^{13}C NMR (176 MHz, CD_2Cl_2, RT): δ [ppm] = 159.32, 156.39, 153.85, 145.63, 144.10, 142.57, 142.01, 141.92, 141.42, 141.01, 140.50, 139.86, 138.25, 138.19, 137.68, 137.40, 133.47, 133.06, 132.79, 132.62, 132.55, 132.34, 132.32, 132.18, 131.39, 131.12, 129.00, 128.87, 128.70, 128.46, 127.32, 126.63, 126.28, 125.71, 121.94, 121.22, 116.34, 115.79, 106.46, 73.95, 71.00, 69.61, 67.74, 35.20, 34.96, 32.52, 32.51, 30.93, 30.39, 30.36, 30.35, 30.34, 30.32, 30.30, 30.26, 30.25, 30.24, 30.21, 30.18, 30.02, 29.96, 29.95, 29.86, 29.73, 28.36, 26.74, 26.72, 25.61, 23.28, 22.16, 14.47.

MS (MALDI-TOF pos, DCTB), *m/z*: 7269.8 $[M+K+Na-H]^+$. Calculated exact mass: 7190.79 Da.

GPC (THF, vs. PS): $M_p = 9.73 \times 10^3$ g/mol.

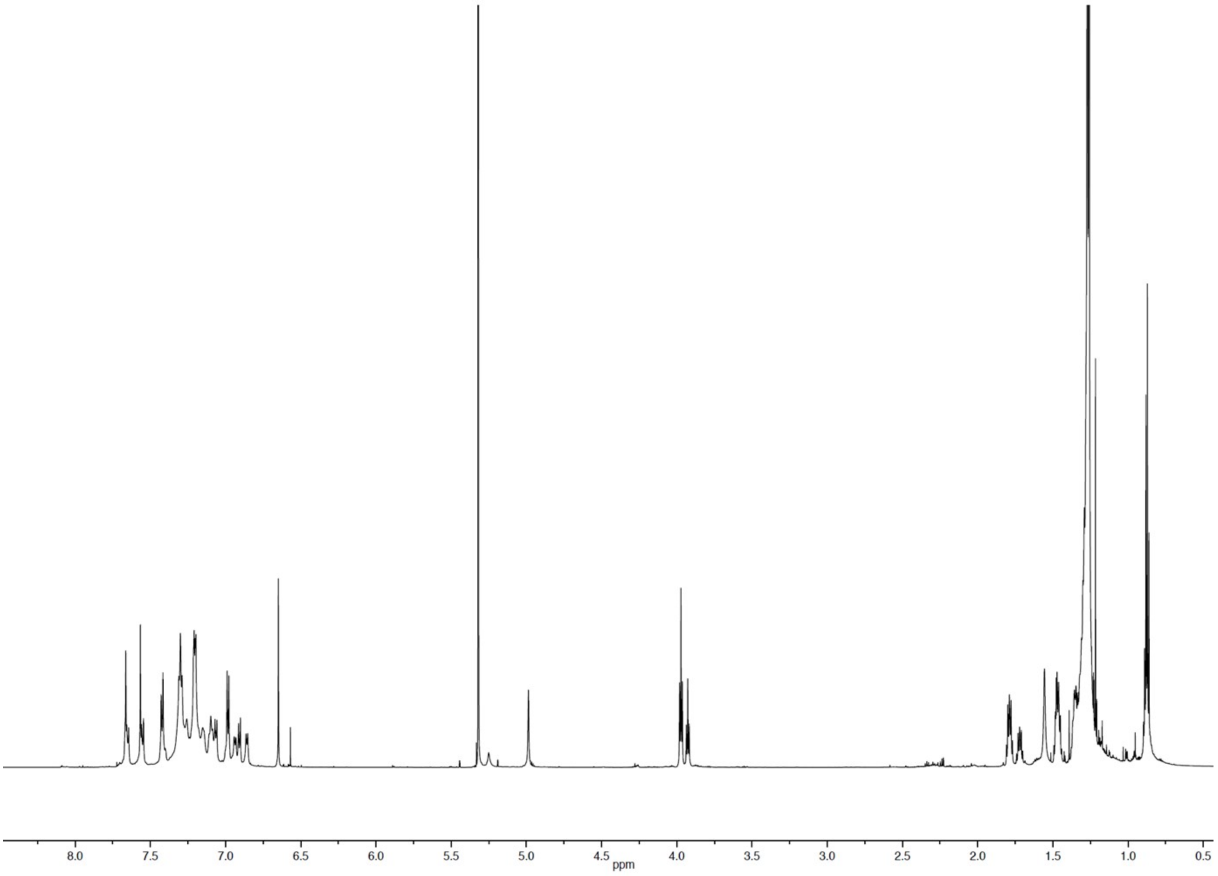
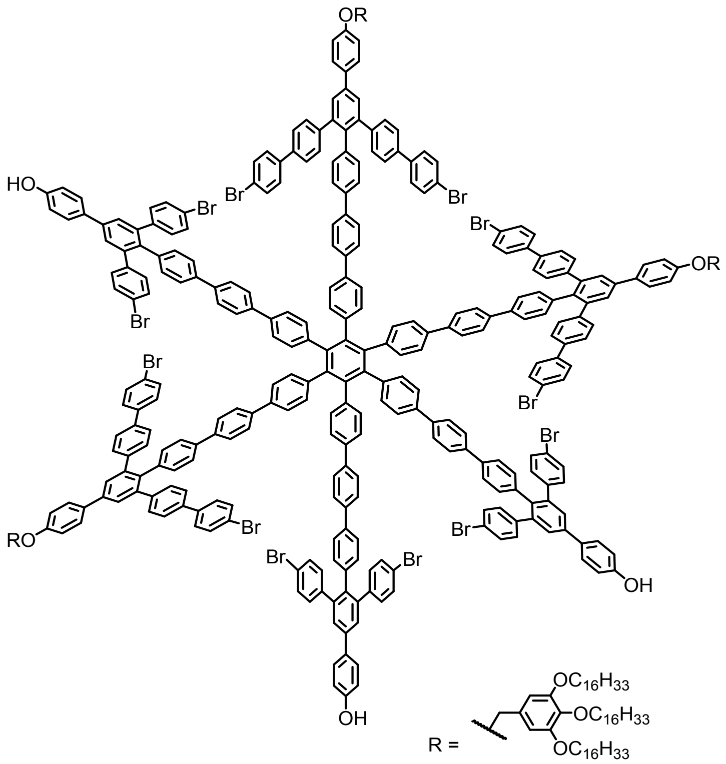


Figure S2: ^{1}H NMR spectrum of **7a** (CD_2Cl_2).

7b



Formula: $C_{459}H_{492}Br_{12}O_{15}$

Mol weight: 7207.82 g/mol

^{1}H NMR (700 MHz, CD_2Cl_2, RT): δ [ppm] = 7.69 – 7.64 (m, 12H), 7.58 – 7.53 (m, 12H), 7.43 – 7.37 (m, 12H), 7.35 – 7.04 (m, 114H), 7.01 – 6.89 (m, 24H), 6.88 – 6.82 (m, 6H), 6.66 (s, 6H), 4.99 (s, 6H), 3.98 (t, *J* = 6.5 Hz, 12H), 3.94 (t, *J* = 6.6 Hz, 6H), 1.82 – 1.76 (m, 12H), 1.76 – 1.70 (m, 6H), 1.50 – 1.43 (m, 18H), 1.39 – 1.21 (m, 216H), 0.92 – 0.84 (m, 27H).

^{13}C NMR (176 MHz, CD_2Cl_2, RT): δ [ppm] = 171.15, 159.32, 156.42, 153.86, 142.58, 142.01, 141.92, 141.42, 141.00, 140.51, 140.37, 139.85, 138.39, 138.25, 138.24, 138.18, 137.67, 137.40, 133.47, 133.04, 132.79, 132.62, 132.56, 132.34, 132.33, 132.19, 131.40, 131.12, 129.64, 129.00, 128.98, 128.87, 128.70, 128.48, 127.30, 126.63, 126.33, 125.73, 121.94, 121.24, 116.35, 115.79, 106.47, 91.99, 73.97, 71.01, 69.62, 45.67, 37.99, 35.22, 32.53, 32.52, 31.78, 30.94, 30.37, 30.35, 30.33, 30.31, 30.27, 30.26, 30.25, 30.22, 30.20, 30.19, 30.13, 30.07, 30.03, 29.97, 29.96, 29.87, 29.69, 28.51, 26.75, 26.73, 25.62, 24.71, 23.29, 22.17, 14.48.

MS (MALDI-TOF pos, DCTB), *m/z*: 7270.7 $[M+K+Na-H]^+$. Calculated exact mass: 7190.79 Da.

GPC (THF, vs. PS): $M_p = 10.03 \times 10^3$ g/mol.

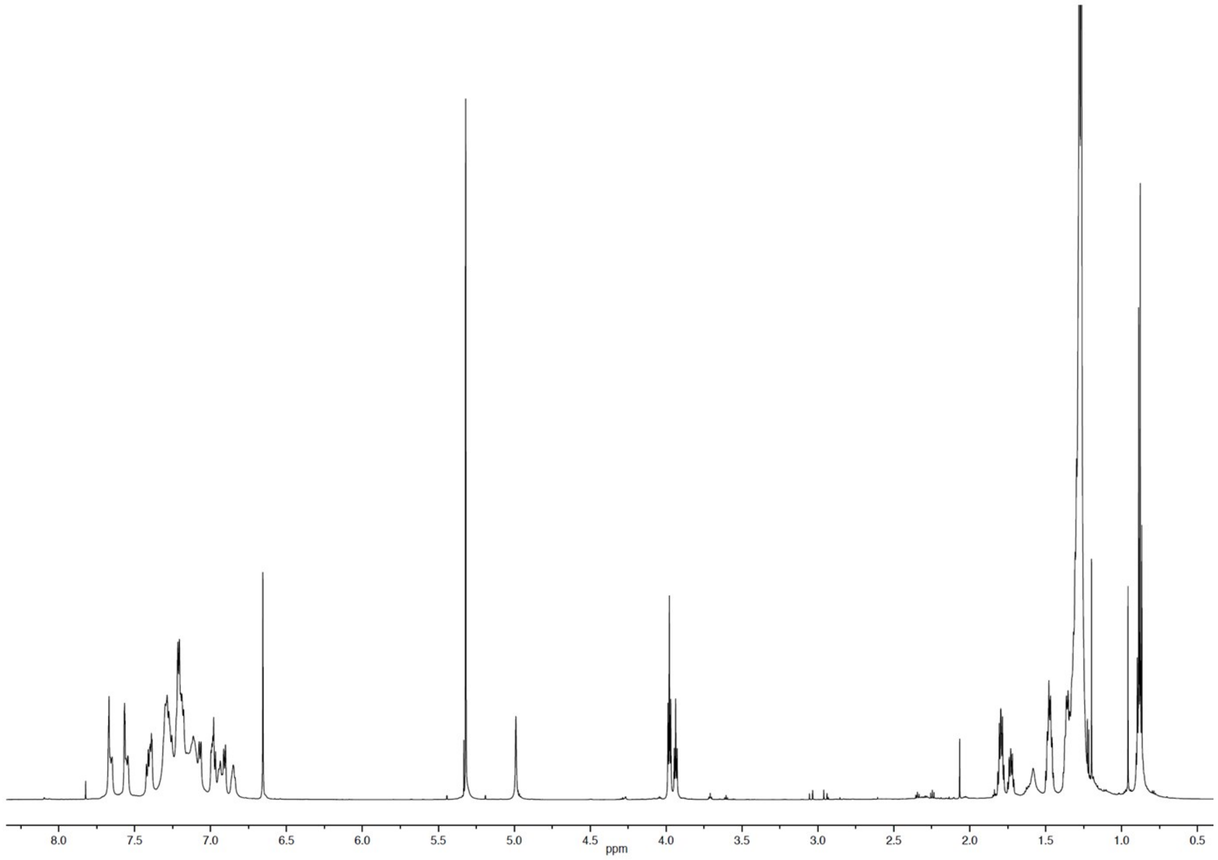
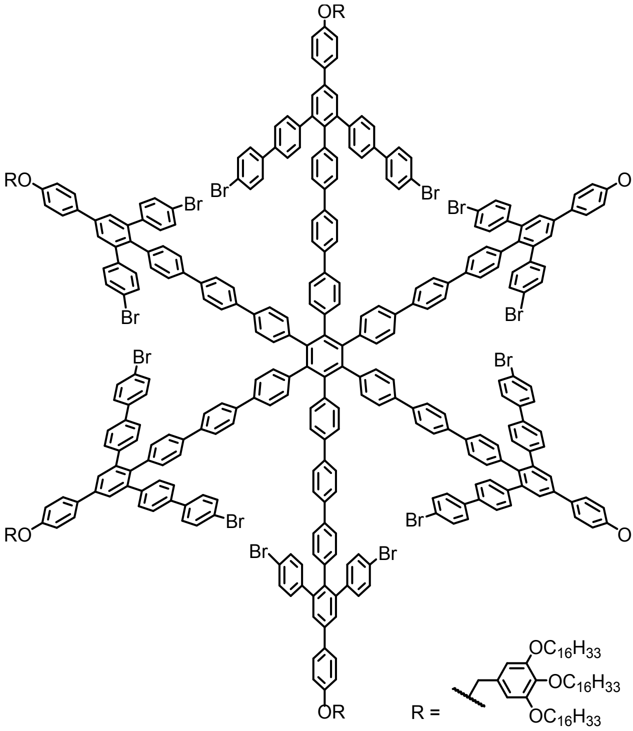


Figure S3: ^{1}H NMR spectrum of **7b** (CD_2Cl_2).

8a



Under an Ar atmosphere, **7a** (23.1 mg, 3.20 µmol), 3,4,5-tris-(hexadecyloxy)benzyl chloride (27.1 mg, 32.0 µmol) and Cs_2CO_3 (10.4 mg, 32.0 µmol) in DMF (10 mL) and toluene (5 mL) were stirred at 95 °C for 18 h. The solvent was removed under reduced pressure, and the residue was dissolved in DCM and acidified with 1 M aqueous HCl. The aqueous layer was extracted with DCM. The organic phase was washed with water, 10 % aqueous HCl and brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by recGPC to yield **8a** (16.7 mg, 1.70 µmol, 54 %) as a colorless solid.

Formula: $C_{624}H_{798}Br_{12}O_{24}$

Mol weight: 9642.07 g/mol

^{1}H NMR (500 MHz, CD_2Cl_2, RT): δ [ppm] = 7.74 – 7.69 (m, 12H), 7.69 – 7.65 (m, 6H), 7.64 (s, 6H), 7.49 (d, *J* = 8.5 Hz, 12H), 7.45 – 7.34 (m, 42H), 7.32 – 7.20 (m, 54H), 7.15 – 7.08 (m, 24H), 7.05 (d, *J* = 8.4 Hz, 12H), 7.01 (d, *J* = 7.8 Hz, 6H), 6.93 (d, *J* = 7.8 Hz, 6H), 6.69 (d, *J* = 1.8 Hz, 12H), 5.03 (s, 12H), 4.01 (t, *J* = 6.5 Hz, 24H), 3.96 (t, *J* = 6.6 Hz, 12H), 1.87 – 1.79 (m, 24H), 1.79 – 1.71 (m, 12H), 1.55 – 1.47 (m, 36H), 1.44 – 1.25 (m, 432H), 0.96 – 0.88 (m, 54H).

^{13}C NMR (126 MHz, CD_2Cl_2, RT): δ [ppm] = 153.85, 142.57, 141.95, 141.43, 139.92, 138.31, 138.20, 132.62, 132.45, 132.34, 132.18, 131.38, 131.11, 129.02, 128.69, 128.66, 128.48, 127.34, 126.62, 126.30, 121.92, 121.21, 115.80, 106.48, 73.90, 71.02, 69.60, 32.53, 32.52, 30.94, 30.36, 30.34, 30.32, 30.30, 30.27, 30.25, 30.24, 30.21, 30.03, 29.97, 29.95, 26.75, 26.72, 23.28, 14.47.

MS (MALDI-TOF pos, DCTB), *m/z*: 9680.3 $[M+K]^+$.9665.3 (100) $[M+Na]^+$. Calculated exact mass: 9623.14 Da.

GPC (THF, vs. PS): M_p = 12.94 x 10^3 g/mol.

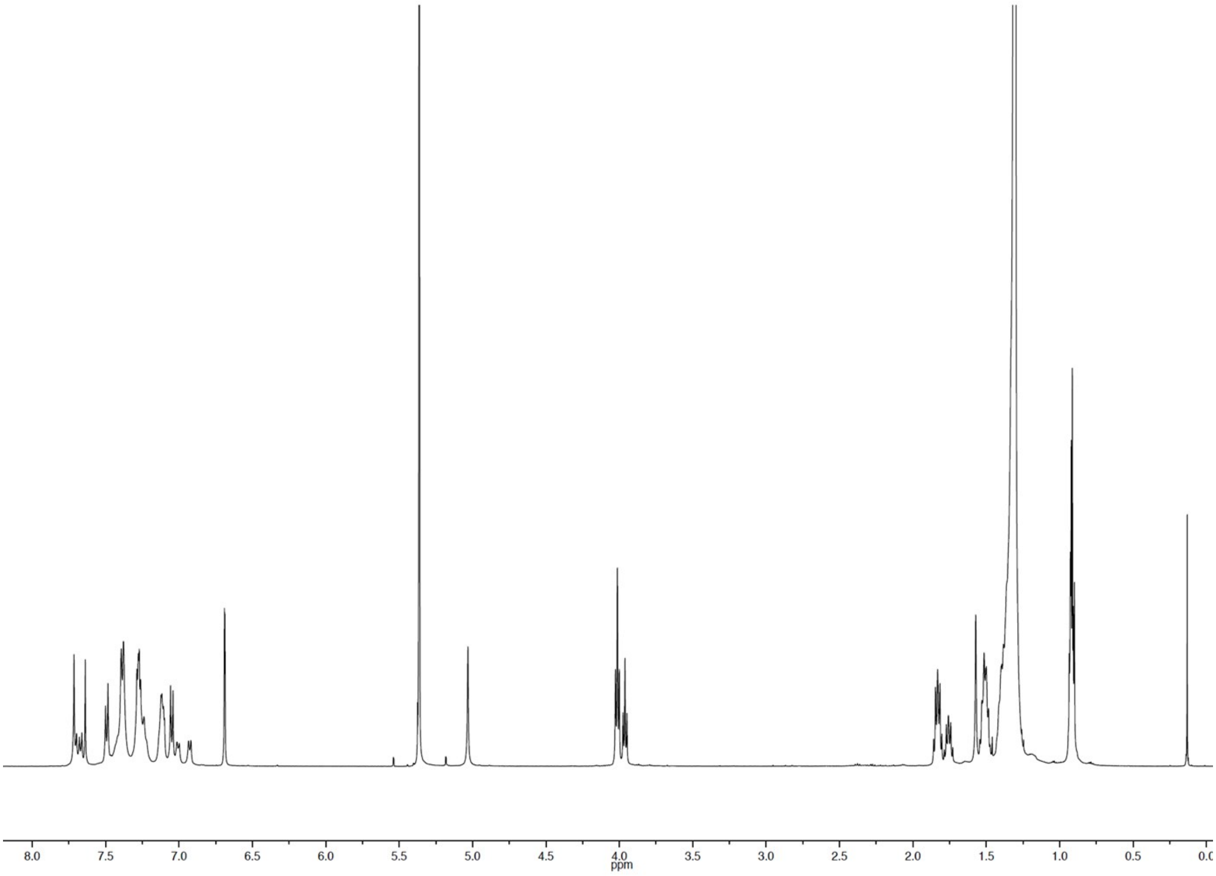
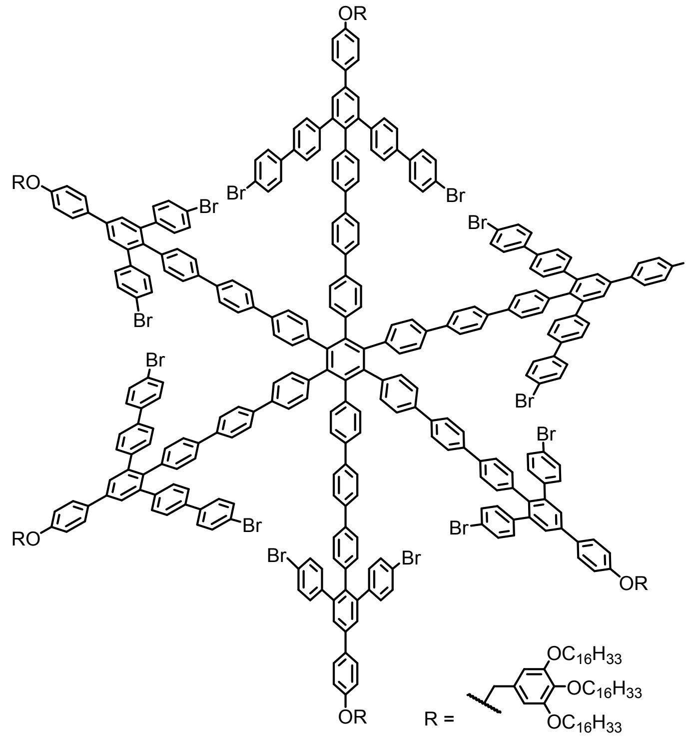


Figure S4: ^{1}H NMR spectrum of **8a** (CD_2Cl_2).

8b



Under an Ar atmosphere, **7b** (36.9 mg, 5.12 µmol), 3,4,5-tris-(hexadecyloxy)benzyl chloride (43.4 mg, 50.1 µmol) and Cs_2CO_3 (496 mg, 1.52 mmol) in DMF (10 mL) and toluene (5 mL) were stirred at 95 °C for 18 h. The solvent was removed under reduced pressure, and the residue was dissolved in DCM and acidified with 1 M aqueous HCl. The aqueous layer was extracted with DCM. The organic phase was washed with water, 10 % aqueous HCl, and brine, and dried over $MgSO_4$. After evaporation of the solvent the crude product was purified by recGPC to yield **8b** (44.5 mg, 4.62 µmol, 90 %) as a colorless solid.

Formula: $C_{624}H_{798}Br_{12}O_{24}$

Mol weight: 9642.07 g/mol

^{1}H- MR (400 MHz, CD_2Cl_2, RT): δ [ppm] = 7.71 – 7.65 (m, 12H), 7.63 (d, J = 8.5 Hz, 6H), 7.60 (s, 6H), 7.48 – 7.32 (m, 60H), 7.31 – 7.15 (m, 48H), 7.11 – 6.95 (m, 42H), 6.89 (d, J = 7.8 Hz, 6H), 6.65 (s, 12H), 4.99 (s, 12H), 3.97 (t, J = 6.5 Hz, 24H), 3.92 (t, J = 6.6 Hz, 12H), 1.84 – 1.74 (m, 24H), 1.74 – 1.67 (m, 12H), 1.49 – 1.41 (m, 36H), 1.38 – 1.19 (m, 432H), 0.92 – 0.80 (m, 54H).

^{13}C NMR (176 MHz, CD_2Cl_2, RT): δ [ppm] = 153.85, 142.59, 141.96, 138.31, 132.61, 132.32, 132.18, 131.37, 131.10, 129.01, 128.66, 128.47, 127.36, 126.63, 126.31, 121.20, 115.80, 106.47, 73.90, 71.02, 69.60, 32.52, 32.51, 30.94, 30.36, 30.34, 30.32, 30.30, 30.26, 30.25, 30.24, 30.21, 30.02, 29.96, 29.95, 26.74, 26.71, 23.28, 14.46.

MS (MALDI-TOF pos, DCTB), *m/z*: 9681.2 $[M+K]^+$.9665.2 $[M+Na]^+$. Calculated exact mass: 9623.14 Da.

GPC (THF, vs. PS): $M_p = 13.23 \times 10^3$ g/mol.

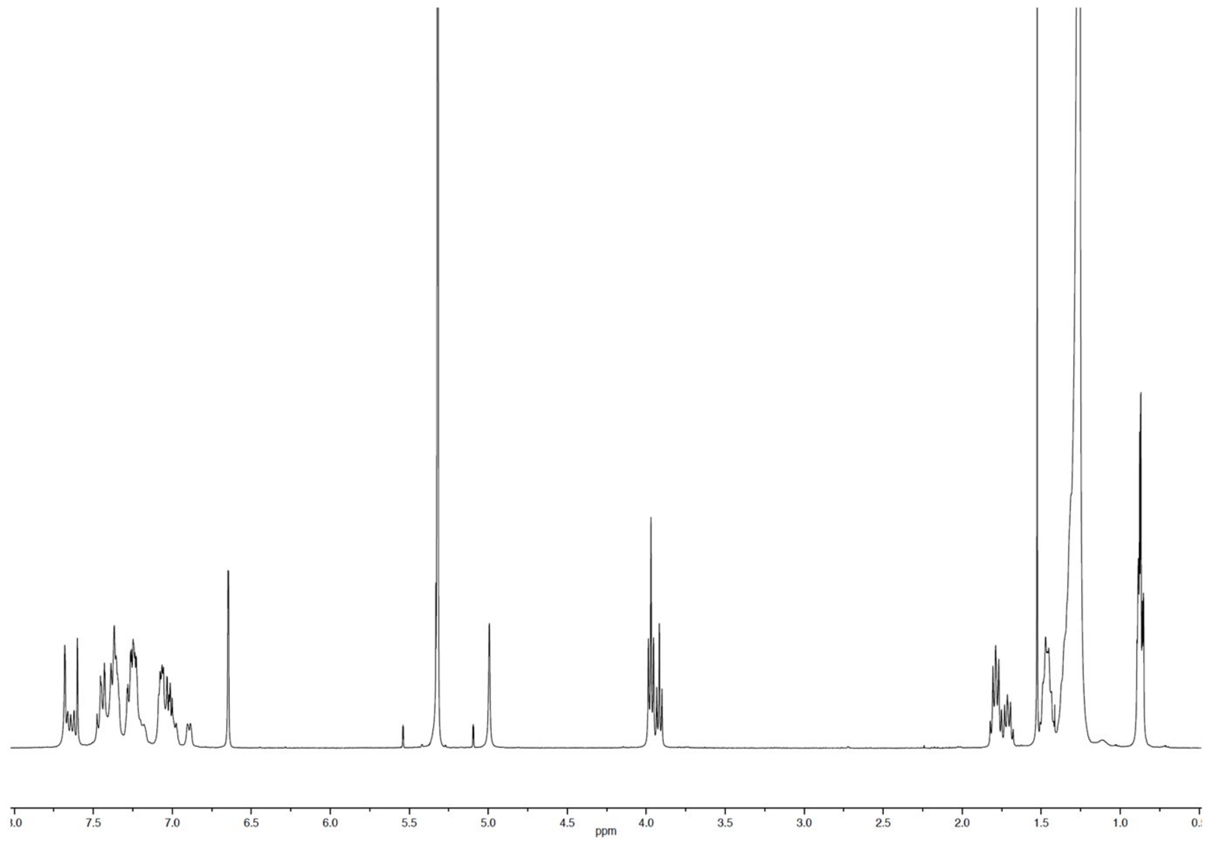
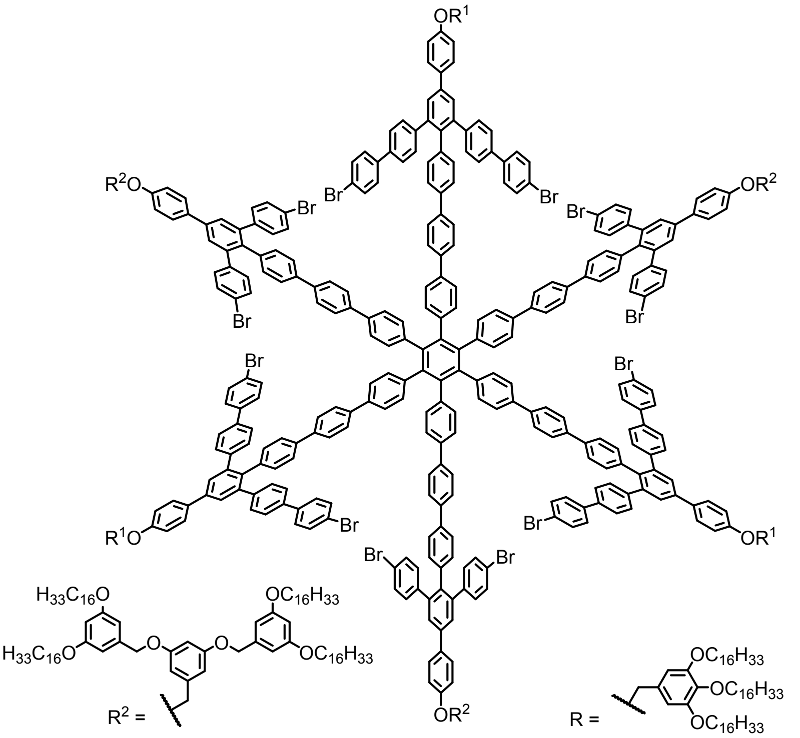


Figure S5: ^{1}H NMR spectrum of **8b** (CD_2Cl_2).

9



Under an Ar atmosphere, **7a** (20.6 mg, 2.86 µmol), 3,5-bis[3,5-bis(hexadecyloxy)benzyloxy]benzyl chloride (66.0 mg, 50.8 µmol), and Cs_2CO_3 (110 mg, 337 µmol) in DMF (10 mL) and toluene (5 mL) were stirred at 95 °C for 18 h. The solvent was removed under reduced pressure, and the residue was dissolved in DCM and acidified with 1 M aqueous HCl. The aqueous layer was extracted with DCM. The organic phase was washed with water, 10 % aqueous HCl, and brine, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by recGPC to yield **9** (24.8 mg, 2.25 µmol, 79 %) as a colorless solid.

Formula: $C_{714}H_{930}Br_{12}O_{33}$

Mol weight: 11000.11 g/mol

^{1}H NMR (400 MHz, CD_2Cl_2, RT): δ [ppm] = 7.71 – 7.65 (m, 12H), 7.65 – 7.59 (m, 12H), 7.50 – 7.34 (m, 60H), 7.31 – 7.16 (m, 48H), 7.11 – 6.95 (m, 42H), 6.90 (d, *J* = 7.9 Hz, 6H), 6.69 (d, *J* = 2.2 Hz, 6H), 6.65 (s, 6H), 6.55 (t, *J* = 2.6 Hz, 3H), 6.53 (d, *J* = 2.3 Hz, 12H), 6.38 (t, *J* = 2.3 Hz, 6H), 5.05 (s, 6H), 4.99 (s, 6H), 4.97 (s, 12H), 3.97 (t, *J* = 6.5 Hz, 12H), 3.92 (t, *J* = 6.6 Hz, 30H), 1.83 – 1.67 (m, 42H), 1.50 – 1.39 (m, 42H), 1.38 – 1.20 (m, 504H), 0.92 – 0.82 (m, 63H).

^{13}C NMR (176 MHz, CD_2Cl_2, RT): δ [ppm] = 161.14, 160.71, 153.86, 139.68, 137.69, 132.65, 132.35, 132.20, 131.39, 131.12, 129.17, 129.05, 128.68, 128.50, 127.39, 126.64, 126.30, 115.82, 106.86, 106.49, 106.22, 101.20, 73.91, 71.03, 70.66, 69.61, 68.69, 32.51, 30.94, 30.28, 30.24, 30.20, 30.18, 30.03, 29.99, 29.95, 29.84, 28.58, 26.72, 26.61, 23.27, 14.47.

MS (MALDI-TOF pos, DCTB), *m/z*: 11039.2 $[M+K]^+$.11023.3 $[M+Na]^+$. Calculated exact mass: 10980.13 Da.

GPC (THF, vs. PS): $M_p = 14.67 \times 10^3$ g/mol.

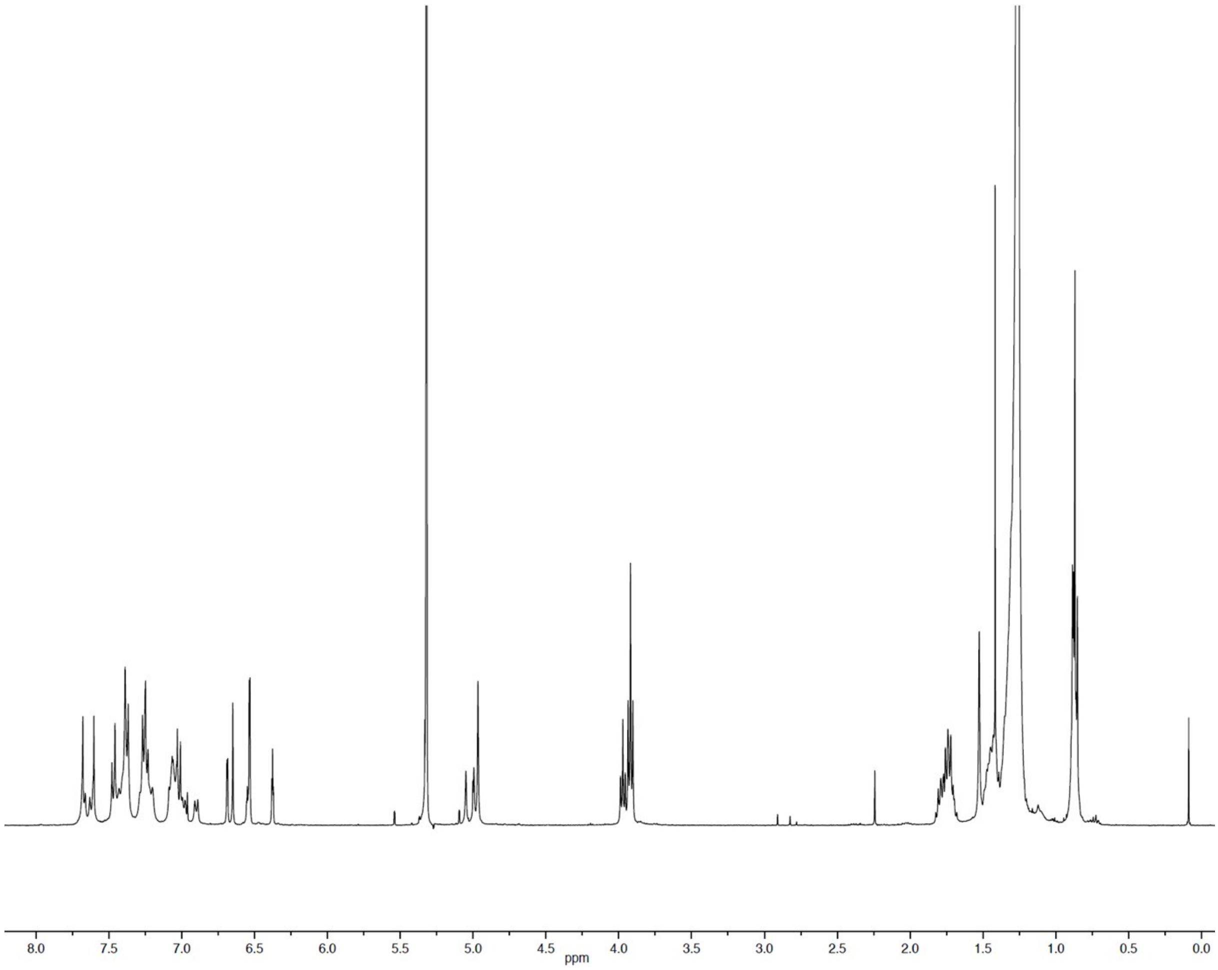
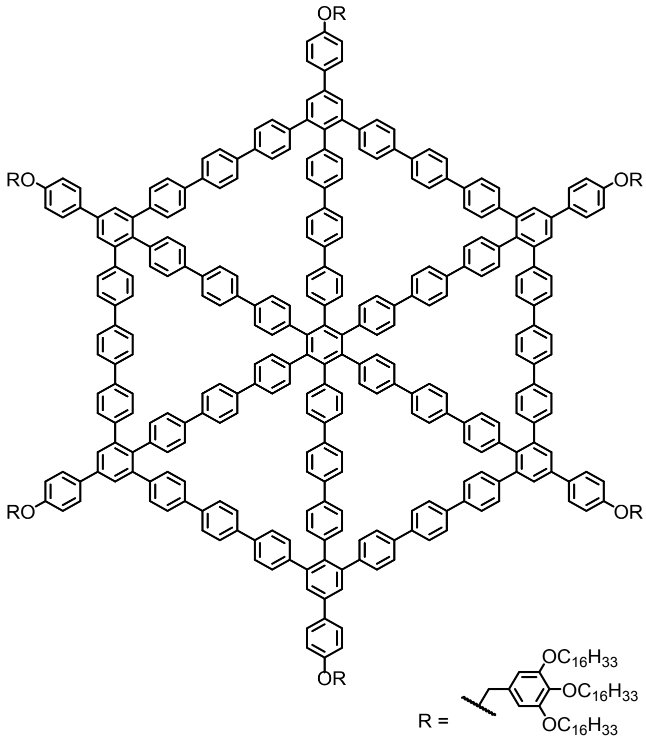


Figure S6: ^{1}H NMR spectrum of **9** (CD_2Cl_2).

1a



In a glove box under Ar, **8a** (7.2 mg, 0.747 µmol) was placed in a microwave tube, $Ni(COD)_2$ (10.0 mg, 36.4 µmol) and 2,2´-bipyridine (5.0 mg, 32.0 µmol) were added, and the tube was closed with a septum. Then, the tube was transferred out of the glove box, and under the exclusion of light THF (8.00 mL) and COD (0.25 mL) were added. The mixture was heated in a microwave oven at 300 W and 120 °C for 12 min. The solvent was removed under reduced pressure, and the crude product was filtered through a plug of silica gel (DCM). After purification by recGPC, **1a** (1.1 mg, 0.127 µmol, 17 %) was obtained as a cream-colored solid.

Formula: $C_{624}H_{798}O_{24}$

Mol weight: 8683.22 g/mol

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, RT): δ [ppm] = 7.95 – 6.86 (m, 180H), 6.74 (br s, 12H), 5.11 (br s, 12H), 4.08 (br s, 36H), 1.99 – 1.77 (m, 36H), 1.65 – 1.16 (m, 468H), 1.01 – 0.90 (m, 54H).

MS (MALDI-TOF pos, DCTB), *m/z*: 8726.0 $[M+K]^+$, 7912.1 $[M-C_{55}H_{103}O_3(R)+K]^+$, 7096.9 $[M-2(C_{55}H_{103}O_3(R))+K]^+$. Calculated exact mass: 8676.12 Da.

GPC (THF, vs. PS): $M_p = 13.02 \times 10^3$ g/mol.

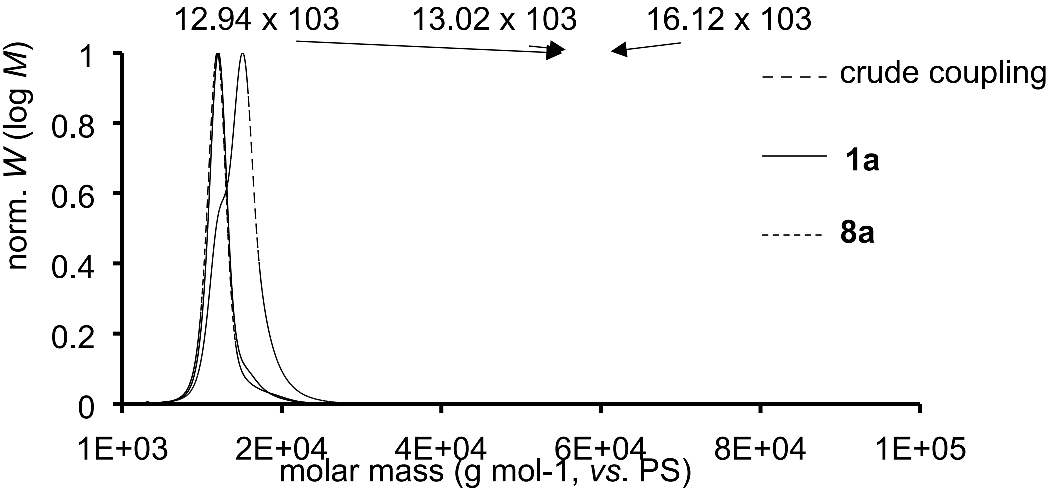


Figure S7: Product distribution after the Yamamoto coupling towards **1a**. Main peak in the crude product is a higher oligomer, most probably a dimeric species.

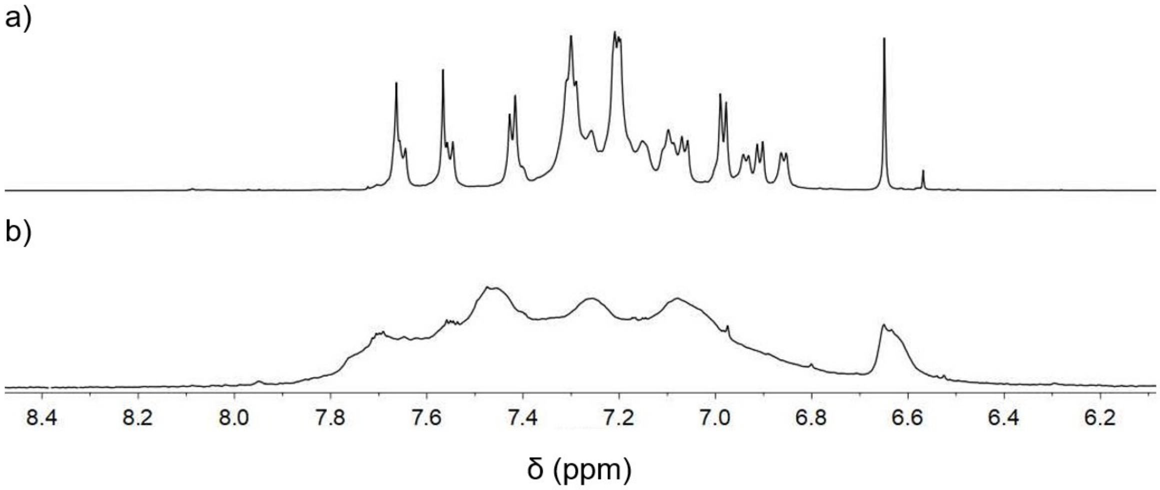


Figure S8: The aromatic regions of the ^{1}H NMR-spectra of **8a** (a) and **1a** (b), both in CD_2Cl_2.

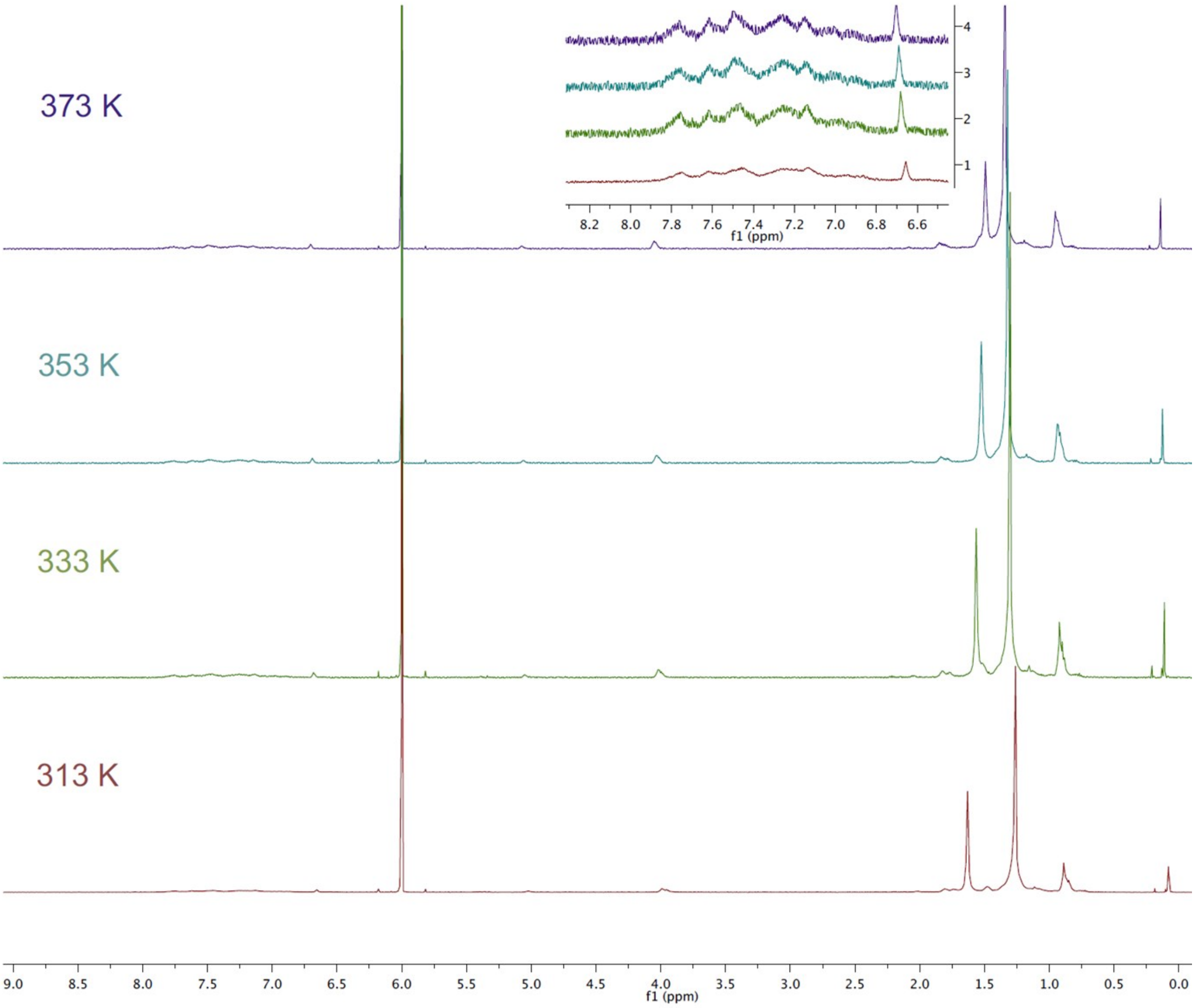


Figure S9: VT ^{1}H NMR of **1a** ($C_2D_2Cl_4$).

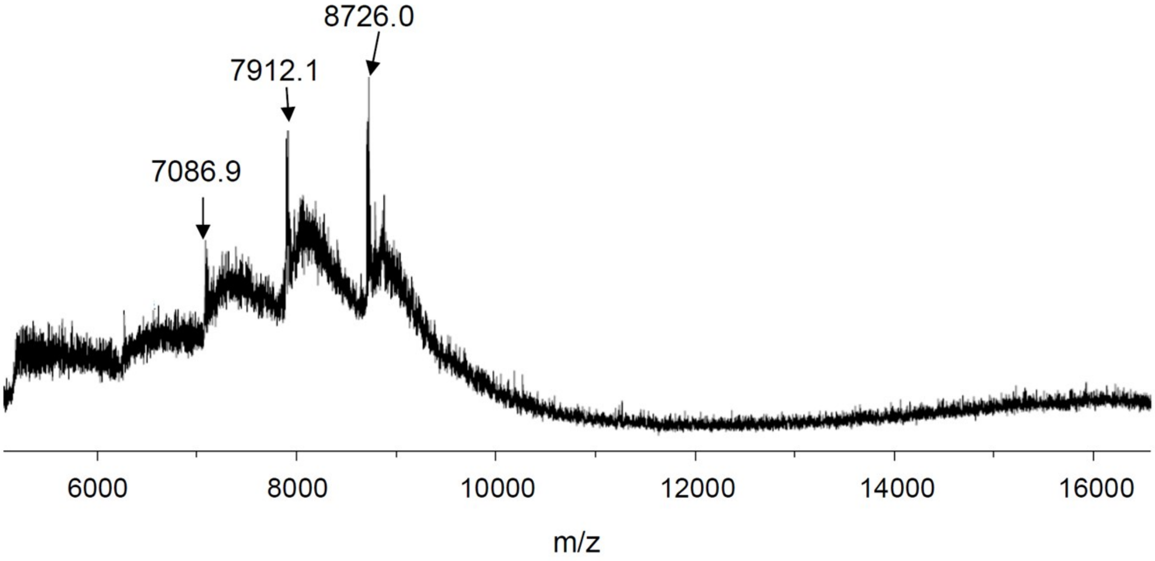


Figure S10: MALDI-TOF-spectrum of **1a**: $[M+K]^+$, calculated: 8722.1 Da, found: 8726.0 Da; $[M-C_{55}H_{103}O_3+K]^+$, calculated: 7910.4 Da, found: 7912.1 Da; $[M-2(C_{55}H_{103}O_3)+Na]^+$, calculated: 7082.6 Da, found: 7086.9 Da.

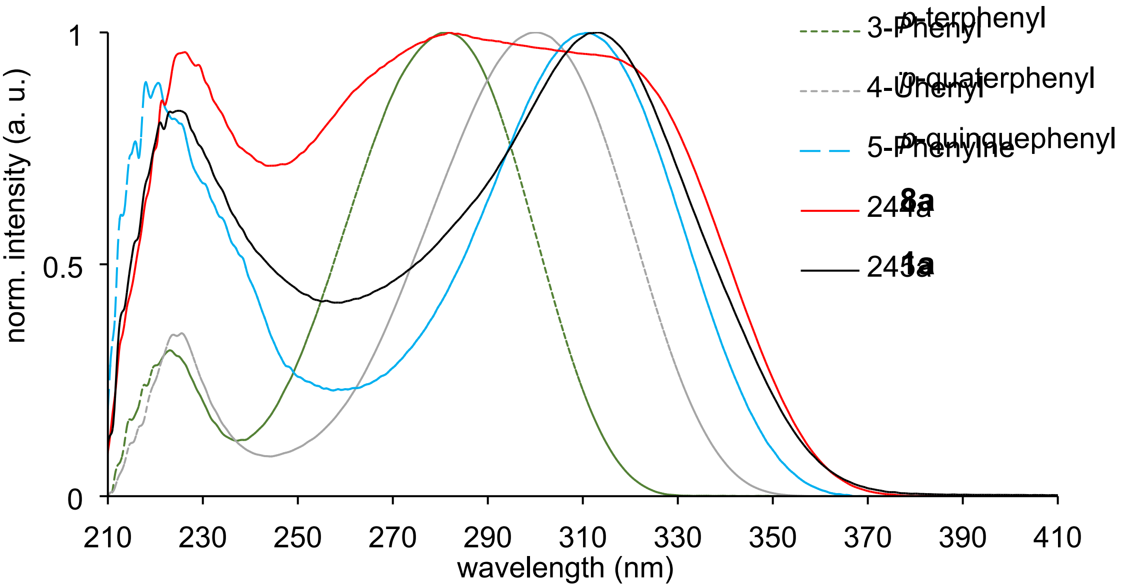
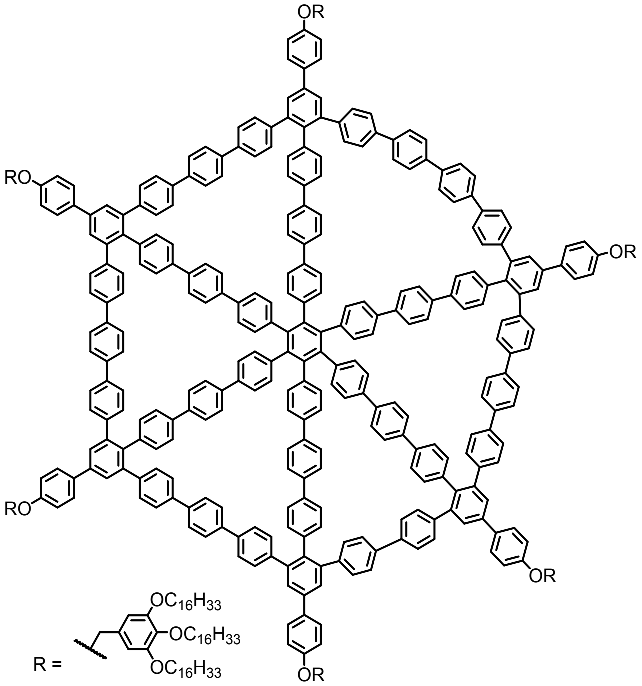


Figure S11: UV/vis-spectra of selected *p*-phenylenes, **8a** and **1a** in THF at RT. The chromophores of different lengths in **8a** and the defined chromophores in **1a** result in a dramatic change of the precursors and wheel absorption spectrum upon Yamamoto coupling. The well-defined absorption spectrum of **1a** also indicates the defined structure.

1b



In a glove box under Ar, **8b** (7.5 mg, 0.778 µmol) was placed in a microwave tube, Ni(COD)$_2$ (10.0 mg, 36.4 µmol) and 2,2´-bipyridine (5.0 mg, 32.0 µmol) were added, and the tube was closed with a septum. Then, the tube was transferred out of the glove box, and under the exclusion of light THF (8.00 mL) and COD (0.25 mL) were added. The mixture was heated in a microwave oven at 300 W and 120 °C for 12 min. The solvent was removed under reduced pressure, and the crude product was filtered through a plug of silica gel (DCM). After purification by recGPC, **1b** (0.5 mg, 0.0576 µmol, 7 %) was obtained as a cream-colored solid.

Formula: $C_{624}H_{798}O_{24}$

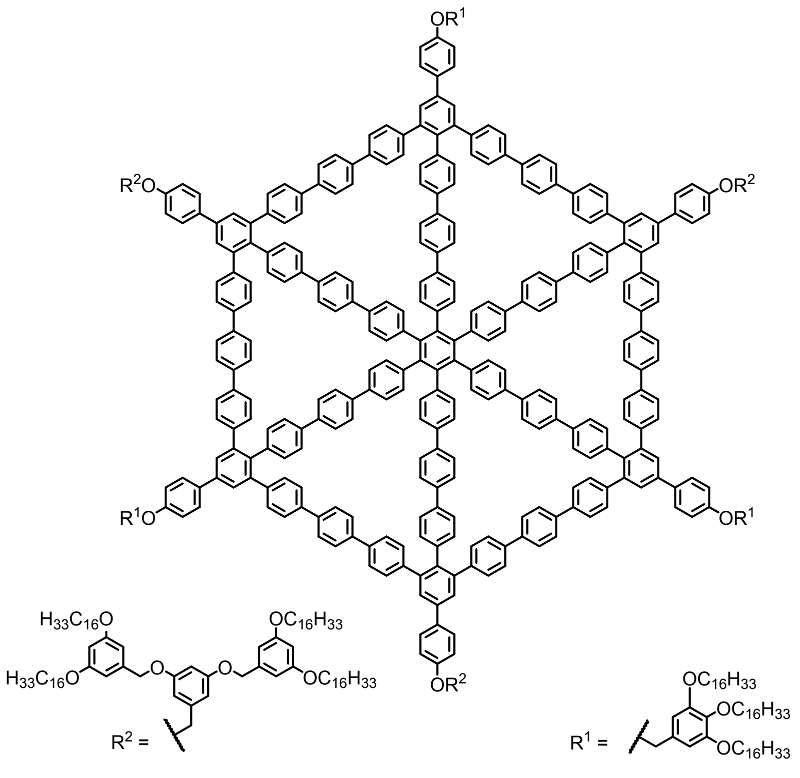
Mol weight: 8683.22 g/mol

GPC (In THF, vs. PS): M_p = 12807 g/mol.

STM: Further analytical validation was performed by scanning tunneling microscopy (as often performed for molecular spoked wheel compounds, see Refs. S4 and S5) and is described in the Main Text.

UV/vis and fluorescence spectroscopy: See Figs. S14 and S15.

2



In a glove box under Ar, **9** (7.0 mg, 0.636 µmol) was placed in a microwave tube, Ni(COD)$_2$ (14.0 mg, 51.3 µmol) and 2,2´-bipyridine (7.4 mg, 47.4 µmol) were added, and the tube was closed with a septum. Then, the tube was transferred out of the glove box, and under the exclusion of light THF (8.00 mL) and COD (0.25 mL) were added. The mixture was heated in a microwave oven at 300 W and 120 °C for 12 min. The solvent was removed under reduced pressure, and the crude product was filtered through a plug of silica gel (DCM). After purification by recGPC, **2** (2.3 mg, 0.229 µmol, 33 %) was obtained as a cream-colored solid.

Formula: $C_{714}H_{930}O_{33}$

Mol weight: 10041.26 g/mol

^{1}H NMR (400 MHz, CD_2Cl_2, RT): δ [ppm] = 7.87 – 6.81 (m, 180H), 6.71 – 6.49 (m, 27H), 6.37 (br s, 6H), 5.06 – 4.87 (m, 24H), 3.92 (br s, 42H), 1.75 (br s, 42H), 1.53 – 1.00 (m, 546H), 0.96 – 0.74 (m, 63H).

MS (MALDI-TOF pos, DCTB), *m/z*: 10206.8 $[2M+DCTB+2K]^{2+}$, 10149.9 $[M+Ag]^+$, 10083.9 $[M+K]^+$, 10067.9 $[M+Na]^+$. Calculated exact mass: 10033.11 Da.

GPC (In THF, vs. PS): $M_p = 14.03 \times 10^3$ g/mol.

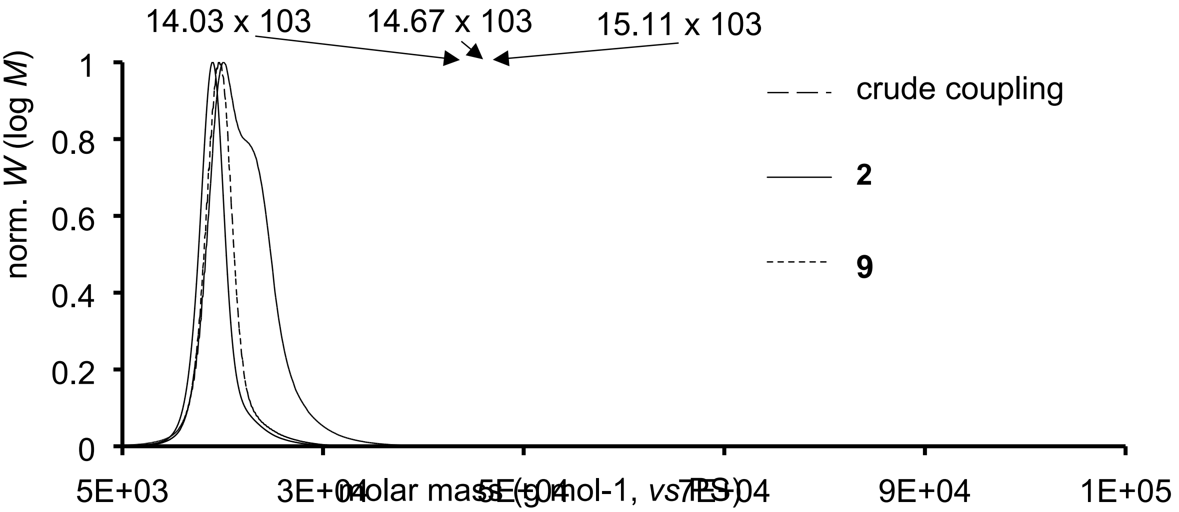


Figure S12: Product distribution after the Yamamoto coupling towards **2**. Main peak in molar mass distribution of the crude product is the spoked wheel **2**. At present it is not clear why the molecular weight of **2** in the crude cyclization product and in the purified compound differ so dramatically.

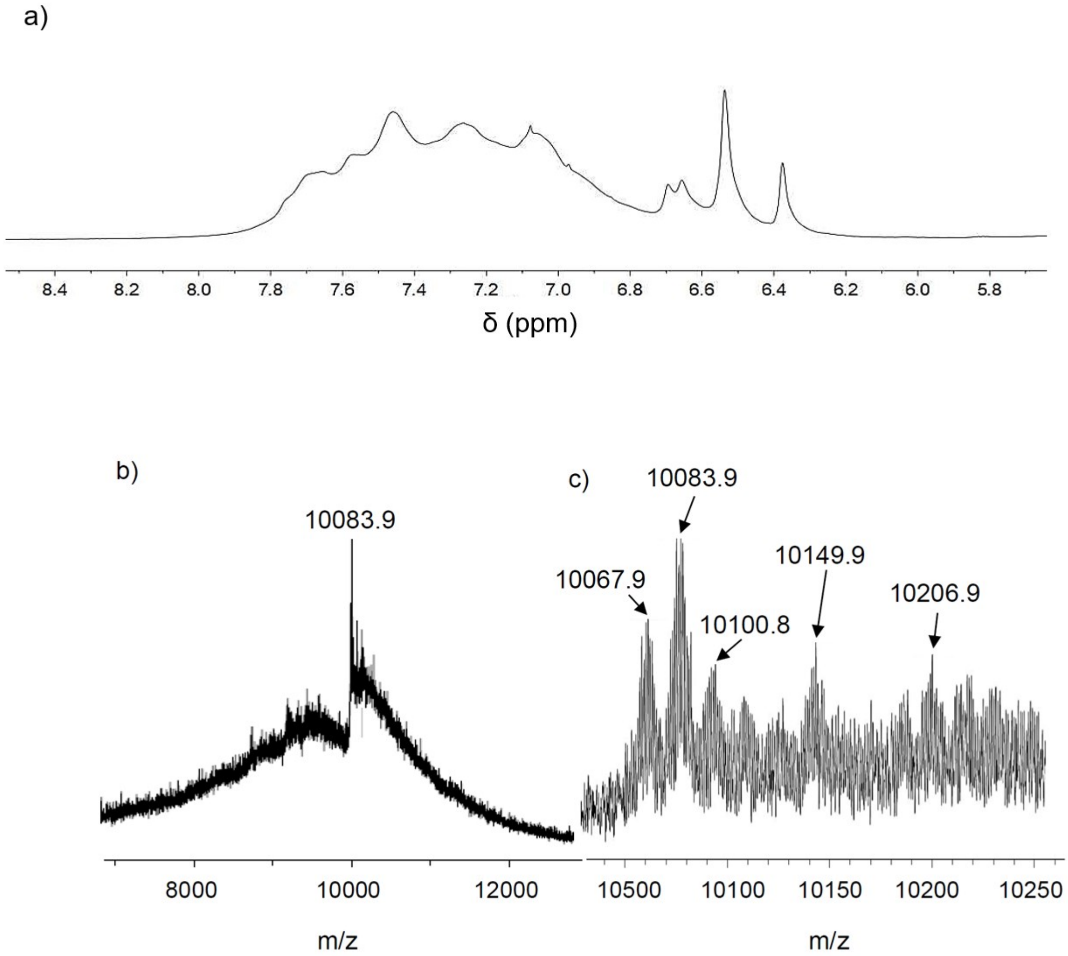


Figure S13: Analytical data for **2**: a) ^{1}H NMR-spectrum in CD_2Cl_2; b) MALDI-TOF spectrum, c) magnification of the relevant region: $[M+K]^+$, calculated: 10080.1 Da, found: 10083.9 Da; $[M+Na]^+$, calculated: 10063.1 Da, found: 10067.9; $[M+Ag]^+$, calculated: 10148.0 Da, found: 10149.9 Da; $[2M+DCTB+2K]^{2+}$, calculated: 10205.2, found: 10206.9 Da.

UV/Vis- and fluorescence spectra

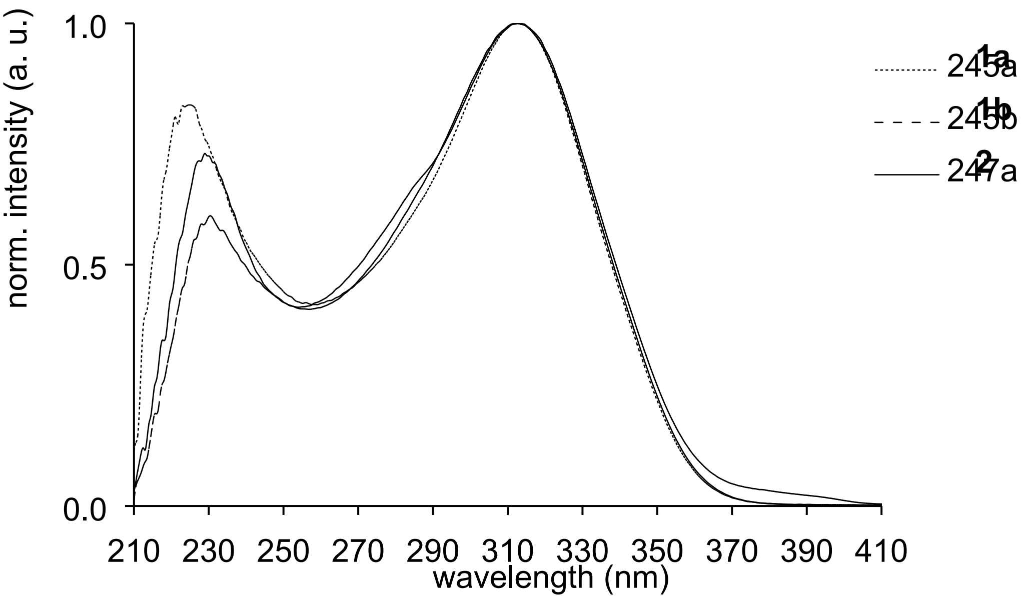


Figure S14: UV/vis-spectra of **1a**, **1b**, and **2** in THF at RT. All longest wavelength maxima are at λ = 313 nm.

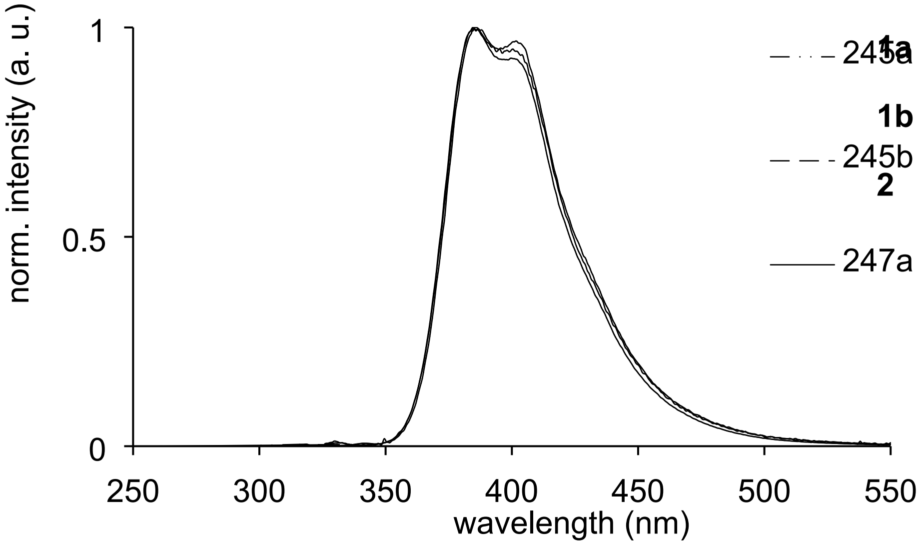
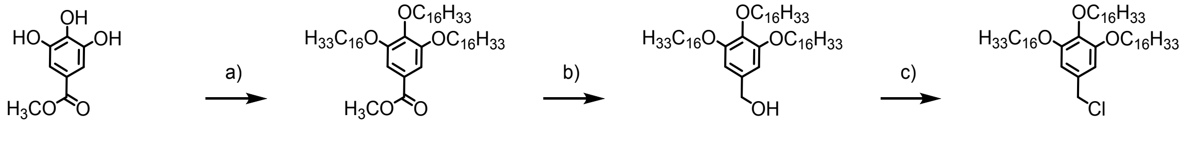


Figure S15: Fluorescence spectra of **1a**, **1b**, and **2** (exc. wavelength: 313 nm).

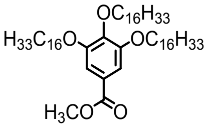
UV/vis and fluorescence spectra are reminiscent of Iyodas pentadecaphenylenes[S6].

2.4 Synthesis of the solubilizing side chains



Scheme S4: Synthesis of 3,4,5-tris(hexadecyloxy)benzyl chloride. a) 1-Bromohexadecane, K_2CO_3, DMF, 80 °C, 4 d, 55 %; b) $LiAlH_4$ (2.4 M in THF), THF, 0 °C, 30 min, RT, 12 h, 78 %; c) $SOCl_2$ in DMF, THF, 0 °C→RT over 18 h, 99 %.

29[S7]



Under an Ar atmosphere, methyl 3,4,5-trihydroxybenzoate (8.05 g, 43.7 mmol), 1-bromohexadecane (80.1 g, 262 mmol), and K_2CO_3 (25.3 g, 434 mmol) in DMF (100 mL) were heated to 80 °C for 4d. Chloroform was added to dissolve the precipitated product, and the organic layer was washed with water and brine and dried over $MgSO_4$. The solvent volume was reduced under reduced pressure, and the product was dissolved in DCM and precipitated by the addition of MeOH. The product was filtered off and dried under vacuum to yield **29** (20.7 g; 24,1 mmol; 55 %) as a slightly cream colored solid.

Formula: $C_{56}H_{104}O_5$

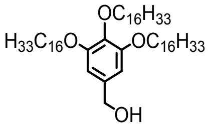
Mol weight: 857.44 g/mol.

^{1}H NMR (400 MHz, $CDCl_3$, RT) δ [ppm] = 7.25 (s, 2H), 4.03 - 3.99 (m, 6H), 3.89 (s, 3H), 1.85 - 1.70 (m, 6H), 1.51 - 1.43 (m, 6H), 1.36 - 1.23 (m, 72H), 0.90 - 0.86 (m, 9H).

^{13}C NMR (101 MHz, C*D*Cl$_3$, RT) δ [ppm] = 167.08, 152.96, 142.52, 124.79, 108.13, 73.63, 69.32, 52.24, 32.09, 30.49, 29.91, 29.89, 29.88, 29.84, 29.83, 29.80, 29.73, 29.56, 29.53, 29.47, 26.24, 26.22, 22.85, 14.27.

MS (EI, 70 eV, 200 °C) *m/z* = 856.7 [$M^{+\bullet}$], 632.4 [$M^{+\bullet}$- $C_{16}H_{33}$].

30[S7]



Under an Ar atmosphere, $LiAlH_4$ (2.4 M in THF, 15.26 mL, 36.62 mmol) was diluted with THF (50 mL), and the mixture was cooled to 0 °C. **29** (15.70 g, 18.31 mmol) in THF (150 mL) was slowly added, and the mixture was stirred at 0 °C for 30 min and at RT for 12 h. Water was carefully added, and the aqueous phase was washed with DCM. The combined organic phase was washed with water and brine, and dried over $MgSO_4$. The solvent volume was reduced and the product precipitated after the addition of MeOH. The product was filtered off and dried under vacuum to yield **30** (11.9 g; 14.4 mmol; 78 %) as a colorless solid.

Formula: $C_{55}H_{104}O_4$

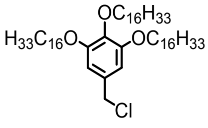
Mol weight = 829.43 g/mol.

^{1}H NMR (400 MHz, C*D*Cl$_3$, RT) δ [ppm] = 6.56 (s, 2H), 4.59 (s, 2H), 4.00 - 3.90 (m, 6H), 1.84 - 1.68 (m, 6H), 1.50 - 1.42 (m, 6H), 1.36 - 1.23 (m, 72H), 0.88 (t, $^3J_{HH}$ = 6.8 Hz, 9H).

^{13}C NMR (101 MHz, C*D*Cl$_3$, RT) δ [ppm] = 153.44, 137.78, 136.14, 105.52, 73.58, 69.27, 65.86, 32.09, 30.49, 29.93, 29.92, 29.90, 29.88, 29.84, 29.83, 29.81, 29.79, 29.58, 29.53, 26.30, 26.26, 22.85, 14.28.

MS (MALDI-pos, DCTB) *m/z* = 828.8 [$M^{+\bullet}$].

3,4,5-tris(hexadecyloxy)benzyl chloride[S7]



Under an Ar atmosphere, **30** (11.79 g, 14.23 mmol) was dissolved in THF (100 mL) and cooled to 0 °C. $SOCl_2$ (8.46 g, 71.13 mmol, ρ = 1.64 g/cm^3) in DMF (6 mL) was added dropwise, and the mixture stirred at 0 °C for 1 h and then at RT for 18 h. Water (10 mL) was slowly added, and the precipitated solid was redissolved by gentle heating of the organic/aqueous phase. After cooling, the precipitate was collected by filtration, washed with water and acetone and dried under vacuum to yield **3,4,5-tris(hexadecyloxy)benzyl chloride** (12.1 g; 6.17 mmol; 99 %) as a colorless solid.

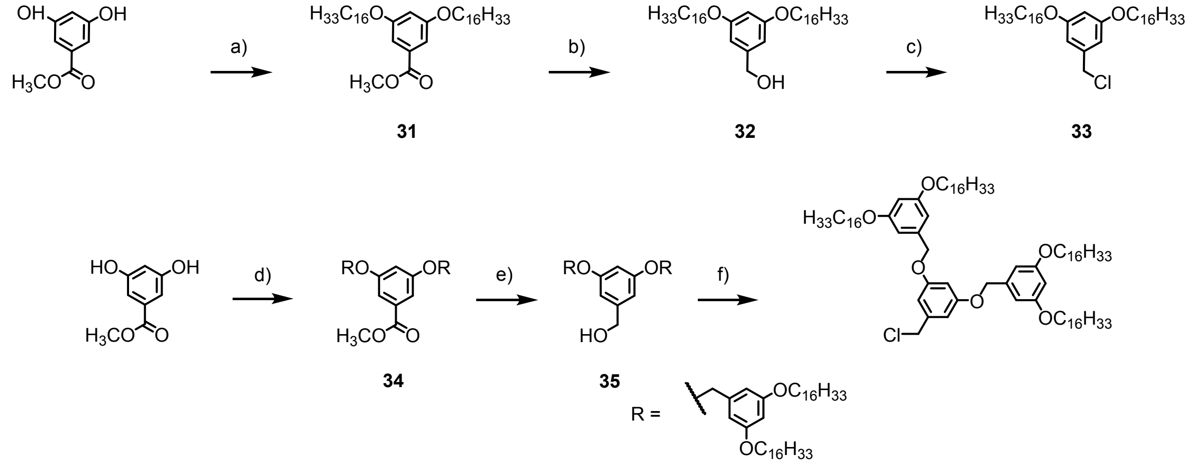
Formula: $C_{55}H_{103}ClO_3$

Mol weight = 847.88 g/mol.

^{1}H NMR (400 MHz, C*D*Cl$_3$, RT) δ [ppm] = 6.56 (s, 2H), 4.51 (s, 2H), 4.00 - 3.90 (m, 6H), 1.84 - 1.69 (m, 6H), 1.50 - 1.43 (m, 6H), 1.38 - 1.22 (m, 72H), 0.88 (t, $^3J_{HH}$ = 6.8 Hz, 9H).

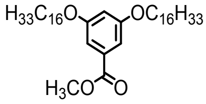
^{13}C NMR (101 MHz, C*D*Cl$_3$, RT) δ [ppm] = 153.36, 138.46, 132.44, 107.23, 73.60, 69.30, 47.15, 32.09, 30.49, 29.91, 29.90, 29.88, 29.84, 29.83, 29.81, 29.77, 29.57, 29.54, 26.28, 26.25, 22.85, 14.28.

MS (MALDI-pos, DCTB) *m/z* = 846.8 [$M^{+\bullet}$].



Scheme S5: Synthesis of 3,5-bis[3,5-bis(hexadecyloxy)benzyloxy]benzyl chloride. a) 1-Bromohexadecane, K_2CO_3, DMF, 90 °C, 1 d, 89 %; b) $LiAlH_4$, THF, 0 °C 1 h, RT, 12 h, 82 %; c) $SOCl_2$, DMF, THF, 0 °C→RT, 14 h, 90 %; d) **14**, K_2CO_3, acetone, 75 °C, 4 d, 75 %; e) $LiAlH_4$, THF, 0 °C→RT, 18 h, 96 %; f) $SOCl_2$, THF, DMF, RT, 18 h, 89 %.

31[S8]



Under an Ar atmosphere, methyl 3,5-dihydroxybenzoate (5.05 g, 29.8 mmol), 1-bromohexadecane (45.4 g, 149 mmol), and K_2CO_3 (16.5 g, 119 mmol) in DMF (100 mL) were heated to 90 °C for 18 h. DCM was added, and the organic layer was washed with water and brine, and dried over $MgSO_4$. The solvent volume was reduced under reduced pressure, and the product precipitated by the addition of MeOH. The product was filtered off and dried under vacuum to yield **31** (16.3 g; 26,4 mmol; 89 %) as a slightly cream colored solid.

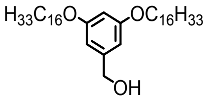
Formula: $C_{40}H_{72}O_4$

Mol weight: 617.01 g/mol.

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ [ppm] = 7.15 (d, *J* = 2.3 Hz, 2H), 6.63 (t, *J* = 2.3 Hz, 1H), 3.96 (t, *J* = 6.5 Hz, 4H), 3.89 (s, 3H), 1.83 - 1.69 (m, 4H), 1.46 - 1.41 (m, 4H), 1.31 - 1.26 (m, 48H), 0.90 - 0.85 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, RT): δ [ppm] = 167.15, 160.29, 131.94, 107.76, 106.73, 68.47, 52.32, 32.08, 29.85, 29.83, 29.81, 29.75, 29.73, 29.52, 29.51, 29.33, 26.16, 22.85, 14.27.

32[S8]



Under an Ar atmosphere, $LiAlH_4$ (2.4 M in THF, 6.75 mL, 16.2 mmol) was diluted with THF (20 mL) and cooled to 0 °C. **31** (5.03 g, 8.51 mmol) in THF (80 mL) was slowly added, and the mixture was stirred at 0 °C for 1 h and at RT for 16 h. Water was carefully added, and the mixture was acidified by the addition of aqueous 10 % HCl (25 mL). The aqueous phase was washed with DCM. The combined organic phase was washed with water and brine, and dried over $MgSO_4$. The solvent volume was reduced, and the product precipitated from warm DCM by the addition of MeOH. The product was filtered off, and dried under vacuum to yield **32** (4.09 g; 6,94 mmol; 82 %) as a slightly cream colored solid.

Formula: $C_{39}H_{72}O_3$

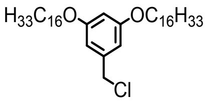
Mol weight = 588.99 g/mol.

^{1}H NMR (400 MHz, $CDCl_3$, RT) δ [ppm] = 6.50 (d, J = 2.2 Hz, 2H), 6.38 (t, J = 2.3 Hz, 1H), 4.62 (s, 2H), 3.93 (t, J = 6.6 Hz, 4H), 1.80 - 1.72 (m, 4H), 1.48 - 1.39 (m, 4H), 1.36 - 1.23 (m, 48H), 0.91 - 0.85 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, RT) δ [ppm] = 160.69, 143.31, 105.21, 100.71, 68.23, 65.65, 32.09, 29.86, 29.84, 29.83, 29.82, 29.77, 29.74, 29.55, 29.52, 29.42, 26.21, 22.85, 14.28.

MS (EI, 70 eV, 180 °C) m/z = 588.5 [$M^{+\bullet}$], 572.5 [$M^{+\bullet}$- OH]. Calculated exact mass: 588.55 Da.

33[S8]



Under an Ar atmosphere **32** (4.06 g, 6.89 mmol) was dissolved in THF (50 mL) and cooled to 0 °C. $SOCl_2$ (8.21 g, 68.9 mmol, ρ = 1.64 g/cm^3) in DMF (10 mL) was added dropwise, and the mixture was stirred at 0 °C for 1 h and then at RT for 12 h. The mixture was cooled to 0 °C, and water (10 mL) was slowly added. DCM was added to dissolve the precipitated solid and the aqueous phase was washed with DCM. The combined organic phase was washed with water and brine and dried over $MgSO_4$. The solvent volume was reduced, and the product precipitated from warm DCM by the addition of MeOH. The product was filtered off, and dried under vacuum to yield **33** (3.75 g; 6.17 mmol; 90 %) as a slightly cream colored solid.

Formula: $C_{39}H_{71}ClO_2$

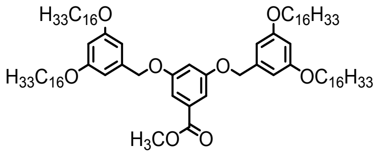
Mol weight = 607.45 g/mol.

^{1}H NMR (400 MHz, $CDCl_3$, RT) δ [ppm] = 6.51 (d, J = 2.2 Hz, 2H), 6.39 (t, J = 2.2 Hz, 1H), 4.50 (s, 2H), 3.93 (t, J = 6.5 Hz, 4H), 1.81 - 1.70 (m, 4H), 1.49 - 1.39 (m, 4H), 1.37 - 1.22 (m, 48H), 0.92 - 0.85 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, RT) δ [ppm] = 160.61, 139.45, 107.06, 101.45, 68.28, 46.61, 32.09, 29.86, 29.84, 29.82, 29.76, 29.73, 29.54, 29.52, 29.38, 26.19, 22.85, 14.28.

MS (EI, 70 eV) m/z = 606.5 [$M^{+\bullet}$], 572.6 [$M^{+\bullet}$- Cl + H]. Calculated exact mass: 606.51Da.

34[S9]



Under an Ar atmosphere, **33** (8.45 g, 13.9 mmol), methyl 3,5-dihydroxybenzoate (1.17 g, 6.96 mmol) and K_2CO_3 (5.77 g, 41.7 mmol) in acetone (100 mL) were heated 4 d to 75 °C for 4 d. The solvent was removed under reduced pressure, and the residue was dissolved in DCM, and acidified with 1 M aqueous HCl. The aqueous layer was extracted with DCM. The organic phase was washed with water, 10 % aqueous HCl and brine, and dried over $MgSO_4$. After evaporation of the solvent, **34** (6.86 g; 5.24 mmol, 75 %) was obtained as a slightly cream colored solid.

Formula: $C_{85}H_{148}O_8$

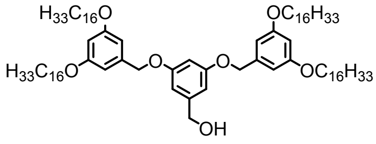
Mol weight: 1310.12 g/mol.

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ [ppm] = 7.28 (d, *J* = 2.3 Hz, 2H), 6.79 (t, *J* = 2.3 Hz, 1H), 6.55 (d, *J* = 2.2 Hz, 4H), 6.41 (t, *J* = 2.2 Hz, 2H), 3.94 (t, *J* = 6.6 Hz, 8H), 3.90 (s, 3H), 1.78 – 1.71 (m, 8H), 1.47 – 1.41 (m, 8H), 1.35 – 1.26 (m, 96H), 0.88 (t, *J* = 6.9 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, RT): δ [ppm] = 166.91, 160.68, 159.91, 138.72, 132.14, 108.52, 107.34, 105.87, 101.06, 70.46, 68.24, 52.39, 32.09, 29.86, 29.85, 29.84, 29.82, 29.78, 29.75, 29.57, 29.52, 29.42, 26.22, 22.85, 14.27.

MS (MALDI-TOF pos, DCTB), *m/z*: 1309.1 $[M]^+$, 571.6 $[C_{39}H_{71}O_2]^+$. Calculated exact mass: 1309.12 Da.

35[S9]



Under an Ar atmosphere, **34** (5.64 g, 4.31 mmol) in THF (150 mL) was cooled in an ice bath. $LiAlH_4$ (1.92 mL, 4.74 mmol, 2.4 M in THF) was added, stirred at 0 °C for 30 min and then at RT for 18 h. A concentrated aqueous $NaHCO_3$ solution was slowly added until no more gas evolved. DCM was added, the organic layer was separated, and the aqueous layer was extracted with DCM. The organic phase was washed with water, 10 % aqueous HCl and brine, and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the crude product was dissolved in DCM (10 mL) and precipitated from MeOH (50 mL). After drying in vacuum, **35** (5.27 g; 4.11 mmol, 96 %) was obtained as a colorless solid.

Formula: $C_{86}H_{148}O_7$

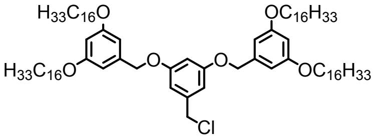
Mol weight: 1282.11 g/mol.

^{1}H NMR (500 MHz, $CDCl_3$, RT): δ [ppm] = 6.61 (d, *J* = 2.2 Hz, 2H), 6.55 – 6-53 (m, 5H), 6.40 (t, *J* = 2.3 Hz, 2H), 4.95 (s, 4H), 4.63 (s, 2H), 3.93 (s, 8H), 1.78 – 1.71 (m, 8H), 1.47 – 1.41 (m, 8H), 1.35 – 1.26 (m, 96H), 0.88 (t, *J* = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$, RT): δ [ppm] = 160.66, 160.32, 143.49, 139.12, 105.89, 105.86, 101.49, 100.95, 70.28, 68.24, 65.51, 32.09, 29.86, 29.85, 29.82, 29.78, 29.75, 29.58, 29.52, 29.43, 26.22, 22.85, 14.27.

MS (MALDI-TOF pos, DCTB), *m/z*: 1281.2 $[M]^+$, 571.6 $[C_{39}H_{71}O_2]^+$. Calculated exact mass: 1281.12 Da.

3,5-bis[3,5-bis(hexadecyloxy)benzyloxy]benzyl chloride



Under an Ar atmosphere, $SOCl_2$ (0.36 mL, 4.94 mmol) was slowly added to a solution of **35** (5.27 g, 4.11 mmol) in THF (100 mL) and DMF (0.35 mL, 4.94 mmol). The mixture was stirred at RT for 2 d. The solution was poured onto ice and the organic layer was separated. The aqueous layer was extracted with DCM. The organic phase was washed with water, 10 % aqueous HCl and brine, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (Cy:DCM = 2:1, R_f = 0.50) and **3,5-bis[3,5-bis(hexadecyloxy)benzyloxy]benzyl chloride** (4.76 g; 3.66 mmol, 89 %) was obtained as a white solid.

Formula: $C_{85}H_{147}ClO_6$

Mol weight: 1300.56 g/mol.

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ [ppm] = 6.62 (d, *J* = 2.2 Hz, 2H), 6.58 – 6.53 (m, 5H), 6.40 (t, *J* = 2.3 Hz, 2H), 4.95 (s, 4H), 4.51 (s, 2H), 3.93 (t, *J* = 6.6 Hz, 8H), 1.81 – 1.71 (m, 8H), 1.48 – 1.39 (m, 8H), 1.38 – 1.20 (m, 96H), 0.87 (t, *J* = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$, RT): δ [ppm] = 160.67, 160.24, 139.63, 138.92, 107.80, 105.88, 102.23, 101.03, 70.36, 68.25, 46.47, 32.09, 29.86, 29.85, 29.84, 29.82, 29.78, 29.75, 29.57, 29.52, 29.43, 26.22, 14.28.

MS (MALDI-TOF pos, DCTB), *m/z*: 1299.2 $[M]^+$, 571.6 $[C_{39}H_{71}O_2]^+$. Calculated exact mass: 1299.09 Da.

3 Time-resolved PL spectroscopy

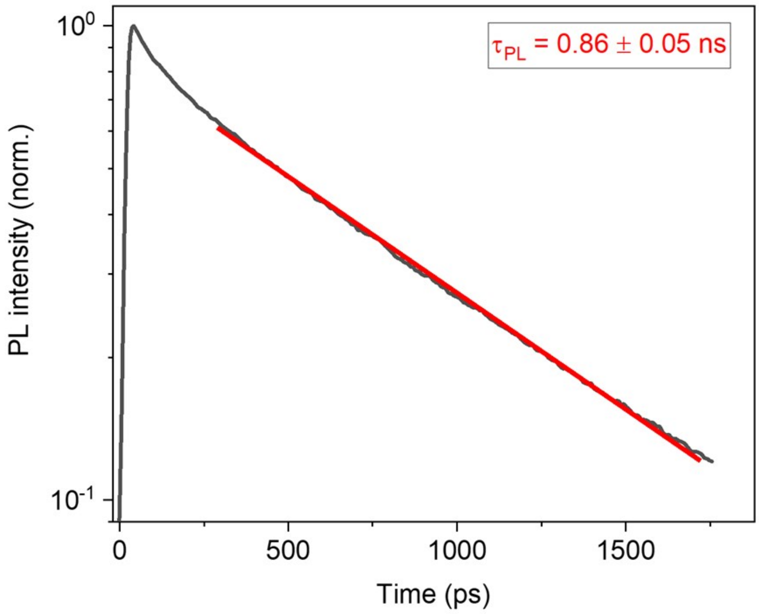


Figure S16: Time-resolved PL intensity of **1a**.

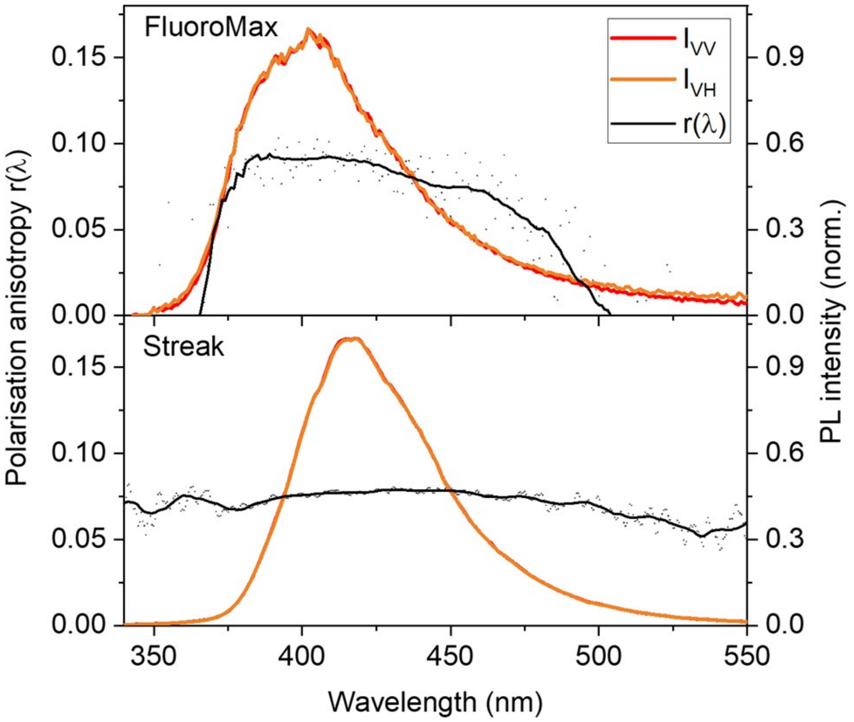


Figure S17: Wavelength dependence of the steady-state and time-integrated time-resolved polarisation anisotropy.

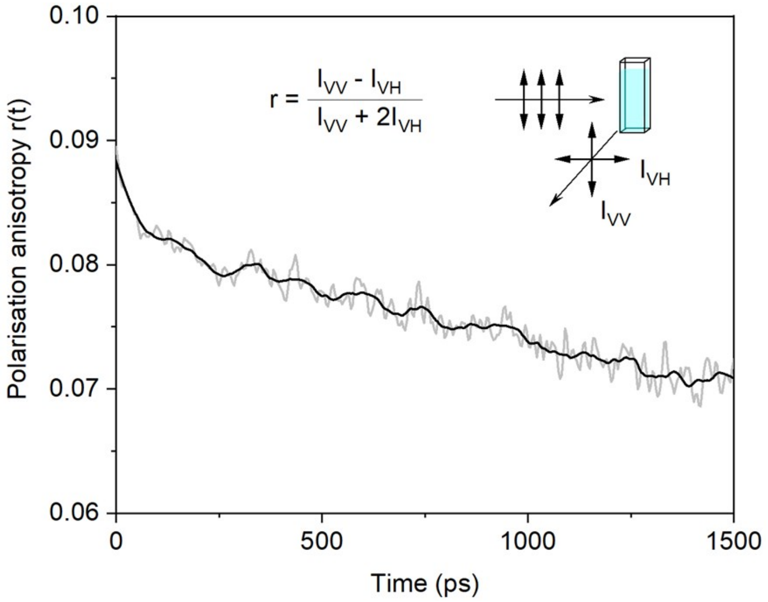


Figure S18: Time-resolved PL polarisation anisotropy.

4 References

S1) S. Henzel, S. Becker, D. Hennen, T. J. Keller, J. Bahr, S.-S. Jester, S. Höger, *ChemPlusChem* **2021**, *86*, 803.

S2) L.-Q. Dieu, A. Devaux, I. Lopez-Duarte, M. V. Martinez-Diaz, D. Bruehwiler, G. Calzaferri, T. Torres, *Chem. Commun.* **2008**, 1187.

S3) A. Idelson, C. Sterzenbach, S.-S. Jester, C. Tschierske, U. Baumeister, S. Höger, *J. Am. Chem. Soc.* **2017**, *139*, 4429.

S4) R. May, S.-S. Jester, S. Höger*, J. Am. Chem. Soc*. **2014**, *136*, 16732.

S5) S.-H. Jung, W. Pisula, A. Rouhanipur, H. J. Räder, J. Jacob, K. Müllen, *Angew. Chem. Int. Ed.* **2006**, *45*, 4685.

S6) M. J. Rahman, H. Shimizu, Y. Araki, H. Ikeda, M. Iyoda, *Chem. Comm.* **2013**, *49*, 9251.

S7) V. Percec, M. Peterca, Y. Tsuda, B. M. Rosen, S. Uchida, M. R. Imam, G. Ungar, P. A. Heiney, *Chem. Eur. J.* **2009**, *15*, 8994.

S8) J.-R. Gong, S.-B. Lei, L. J. Wan, G.-J. Deng, Q.-H. Fan, C.-L. Bai, *Chem. Mater.* **2003**, *15*, 3098.

S9) Y.-P. Sun, W. Huang, Y. Lin, F. Yi; K. Fu, A. Kitaygorodskiy, L. A. Riddle, Y. J. Yu, D. L. Carroll, *Chem. Mater.* **2001**, *13*, 2864.