Supporting Information for:

Quantitative mass determination of conjugated polymers for single molecule conformation analysis: enhancing rigidity with macrocycles

Klaus Becker, Gerald Gaefke, Jasmin Rolffs, Sigurd Höger*, and John M. Lupton*

Photonics and Optoelectronics Group, Department of Physics and CeNS, Ludwig Maximilians University of Munich, 80799 Munich, Germany, Department of Physics and Astronomy, University of Utah, Salt Lake City, UT 84112, USA and Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn, 53121 Bonn, Germany

Table of Contents:

1 Synthesis and fractionations of 1 and 2

Polymers of **1** and **2** were obtained by oxidative acetylene coupling of the corresponding bisacetylenes (see chapter 5.2.1 and chapter 5.3.1) and subsequent fractionation by GPC. Figure S1 displays the GPC traces of the fractionated polymer samples. Molecular weights are given relative to PS.

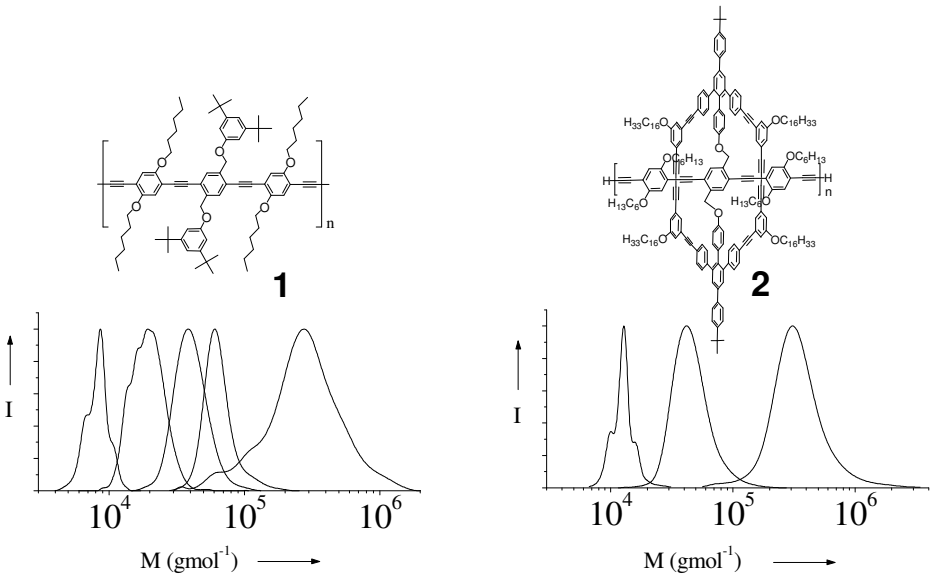


Figure S1: GPC traces (UV detection) of fractionated polymer samples **1** and **2**.

2 Calibrating the molecular weight distribution of the polymers using long-chain oligomers

In order to assess the absolute molecular weight of the polymer samples (see Figure S1) we synthesized defined oligomers of **1** and **2**. In both cases polymerization of the dimer (Figure S2, blue) provides well resolved peak molecular weights upon the 12mer in the GPC traces. By polymerization of the octamer of **1** we obtained distinguishable peaks upon the 64mer (Figure S2, red). Figure S2 illustrates how the oligomer GPC spectra can be used to assign the peaks observed in the polydisperse polymer sample.

Our results demonstrate that the scaling factor, which is generally used to carry out molecular weight determinations using conventional standards such as polystyrene, is actually molecular weight dependent, i.e. rather a scaling function.

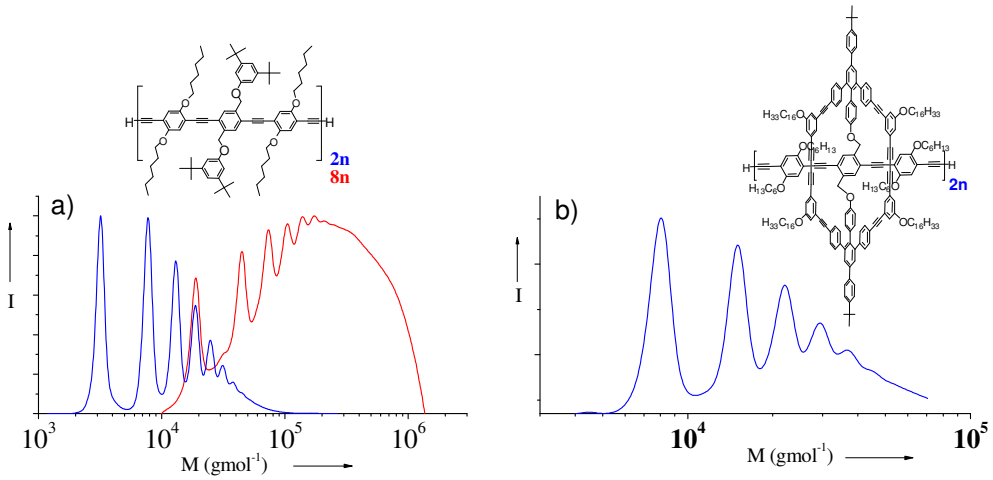


Figure S2: GPC traces of polymerized dimer (polymer of **13b** and **35**, blue) and octamer (polymer of **18**, red, extract of the normalized GPC curve) of **1** (**a**) and **2** (**b**).

n	M_p (g/mol; GPC *vs* PS standard)	M (g/mol; calculated)
1	1400	1164
2	3200	2325
4	7750	4649
6	13050	6972
8	18700	9296
10	24800	11619
12	31300	13942
16	45200	18589
24	74200	27883
32	105000	37176
40	140000	46470
48	174000	55763
56	211000	65057
64	246000	74350

Table S1: Observed (GPC) and calculated molecular weights of oligomers of **1**.

n	M_p (g/mol; GPC *vs* PS standard)	M (g/mol; calculated)
1	4300	3114
2	8050	6227
4	14950	12452
6	22100	18677
8	29400	24902
10	36650	31127
12	45000	37352

Table S2: Observed (GPC) and calculated molecular weights of oligomers of **2**.

3 UV/Vis spectra of the oligomers

As discussed in Ref. [1], encapsulating of the polymer chain does not modify the electronic properties of the backbone – the low-energy part of the UV/Vis spectra remains unchanged. Figure S3 summarizes the UV/Vis spectra of the model oligomers in comparison to the polymers **1** and **2**, illustrating that the longer oligomers are indistinguishable from the polymers.

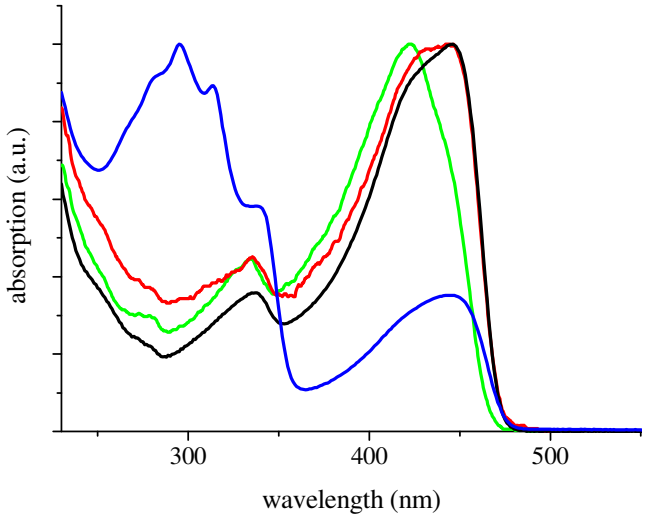


Figure S3: Absorbance of dimer **12** (green), tetramer **14** (red), polymer **1** (black), and polymer **2** (blue).

4 Enhanced photostability of encapsulated versus open polymer chain

Encapsulation of the polymer chain reduces the tendency to photo-oxidize under high intensity excitation. Figure S4(a) compares the fluorescence spectra of the bare **1** and encapsulated polymer **2**, which are found to be virtually identical. However, the two samples are easily distinguished in terms of their photophysical stability, which is assessed under constant UV illumination of the polymer solution by a pulsed nitrogen laser at 335 nm. As shown in Figure S4(b), the photoluminescence intensity of the bare polymer **1** decays much faster than that of the encapsulated polymer **2** due to photo-oxidation. The increased stability of the ring polymer **2** is most likely due to the improved rigidity of the polymer backbone, which minimizes conformational fluctuations required to drive irreversible photochemistry. At present, however, it cannot be excluded that the encapsulating rings also provide a simple physical shielding functionality for the polymer backbone, preventing access of singlet oxygen to the backbone as required for photo-oxidation to occur. Note that at 335 nm excitation most of the absorption (>85%) occurs in the conjugated ring rather than in the backbone. However, due to efficient energy transfer from the ring to the backbone, the residence time of excitations on the ring is limited to a few picoseconds [1], minimizing the probability of irreversible photochemistry and quenching occurring directly on the ring.

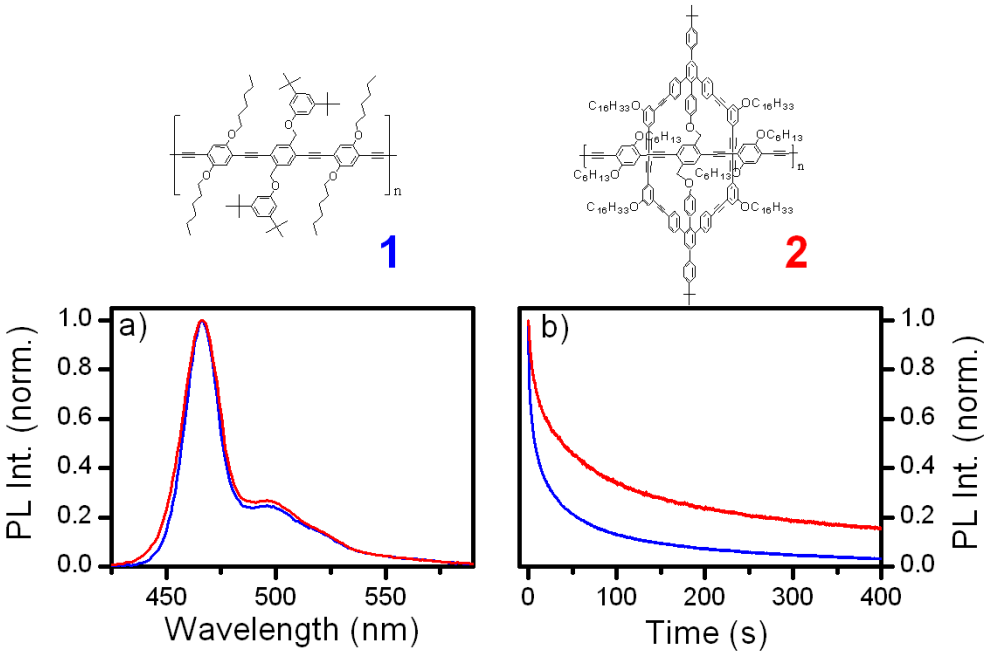


Figure S4: a) Fluorescence spectra of **1** and **2** in solution under excitation at 335 nm. b) Decay of the fluorescence intensity of the two compounds under illumination by a pulsed nitrogen laser at 335 nm.

5 Synthesis

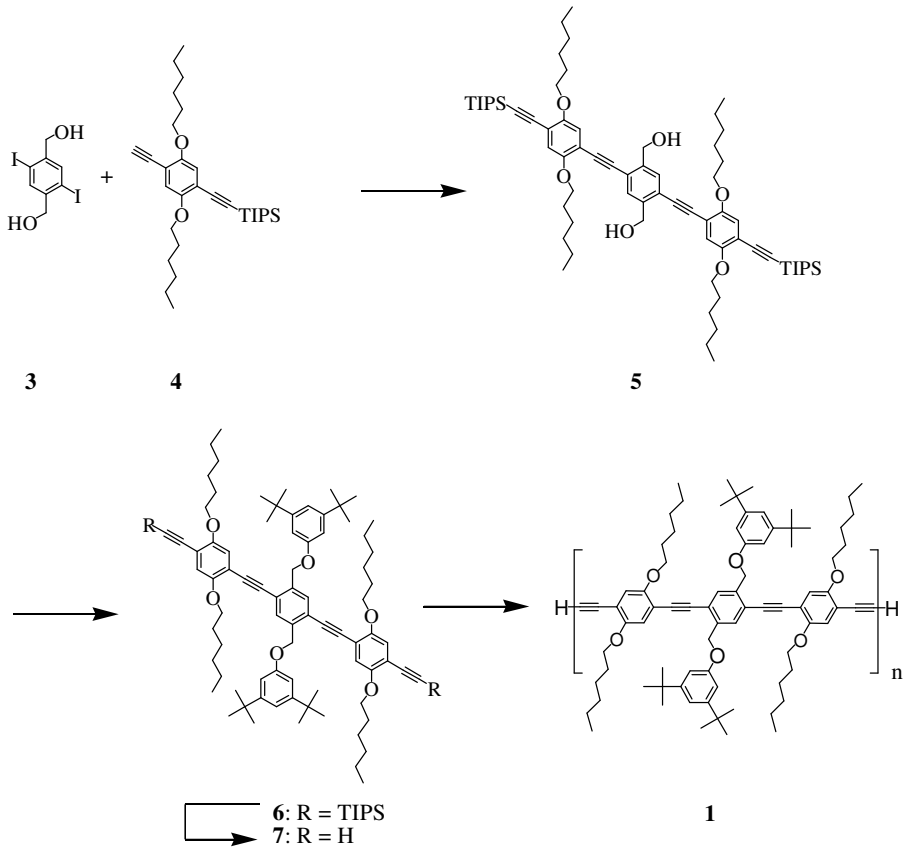
5.1 General methods

Commercially available chemicals were used as received, unless otherwise stated. All air sensitive reactions were carried out using standard Schlenk techniques under argon (4.7). THF was distilled from sodium and piperidine, pyridine and CH_2Cl_2 from CaH_2. Prior to characterization and further processing, all solids and oils were dried overnight at room temperature under vacuum. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300, DPX 400 and DRX 500 (300, 400, and 500 MHz for ^1H and 75.5, 100.6 and 125.8 MHz for ^{13}C). Chemical shifts are given in parts per million (ppm) referenced to residual ^1H or ^{13}C signals in deuterated solvents. Mass spectra were measured on a Finnigan ThermoQuest MAT 95 XL (EI-MS), AEI MS-5 (EI-HRMS) and a Bruker Daltronics autoflex TOF/TOF (MALDI-MS; matrix material: *trans*-2-[3-(4-t-Butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), dithranol). UV/Vis absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer using 10 mm quartz cuvettes. Fluorescence experiments were run on a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer in all-transparent quartz cuvettes by monochromatic excitation at the indicated wavelength. Melting points were determined using a Leica DMLB microscope with resistive heating socket controlled by a Leica LMW transformer and a Testo 925 digital thermometer. Thin layer chromatography was conducted on silica gel coated aluminium plates (Macherey-Nagel, Alugramm SIL G/UV254, 0.25 mm coating with fluorescence indicator). Silica gel 60 M (Macherey-Nagel, 0.04-0.063 mm) was used as the stationary phase for column chromatography. Gel permeation chromatography (GPC) was performed in THF (HPLC grade, stabilized with 2.5 ppm BHT) at room temperature. GPC analyses were run on an Agilent Technologies system at a flow rate of 1 mL/min using an IsoPump G1310 A, a UV detector (G1314B) and PSS columns (Polymer Standards Service, Mainz, Germany; 10^2, 10^3, and 10^5 Å, 5µ, 8 x 300 mm). For the oligomer separation, a Shimadzu Recycling GPC system, equipped with a LC-20 AD pump, a SPD-20 A UV detector and a set of three preparative columns from PSS (10^3 Å,

5µ, 20 x 300 mm) was employed. The system operated at a flow rate of 6 mL/min. Unless otherwise indicated, all molecular weights were determined versus universal PS calibration (standards from PSS). TLC was performed with Macherey-Nagel Alugram SIL G/UV 254 precoated aluminum sheets. Merck silica gel 60, 230-400 mesh ASTM was used for column chromatography. Radial chromatography was performed on a Chromatotron (Harrison Research Europe) using Merck silica gel 60 PF 254 containing gypsum.

5.2 1 and oligomers of 1

5.2.1 1



Scheme S1: Synthesis of **1**.

*2,5-Diiodo-1,4-bis-(hydroxymethyl)benzene **3***

3 was synthesized according to literature procedure [S2].

*1,4-Dihexyloxy-2-ethynyl-5-(2-triisopropylsilylethynyl)benzene **4***

The compound was synthesized according to literature procedure [S3] starting from 1,4-dihexyloxy-2,5-diiodobenzene.

5

4 (739 mg, 1.53 mmol) was added to a solution of $Pd(PPh_3)_2Cl_2$ (30 mg, 0.043 mmol), CuI (15 mg, 0.078 mmol), PPh_3 (30 mg, 0.114 mmol) and **3** (200 mg, 0.51 mmol) in THF (8 mL) and piperidine (4 mL). After stirring overnight at room temperature, the mixture was poured into Et_2O (100 mL) and H_2O (50 mL). The organic layer was separated, washed with water (2 x 30 mL) and brine (30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Product purification was performed by column chromatography on silica gel (petroleumether-CH_2Cl_2, 1:1, 0:1; R_f = 0.55, 0:1) to give **5** (1.05 g, 0.69 mmol, 86 %) as a pale yellow solid. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.55 (s, 2H), 6.98-6.93 (m, 4H), 4.82 (s, 4H), 4.05-3.92 (m, 8H), 2.81 (br. s, 2H), 1.91-1.70 (m, 8H), 1.55-1.24 (m, 24H), 1.13 (s, 42H), 0.93-0.83 (m, 12H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 154.24, 153.28, 142.34, 131.10, 131.09, 121.89, 116.57, 116.53, 116.11, 116.01, 114.64, 114.57, 112.76, 112.74, 102.85, 102.82, 97.11, 97.07, 92.75, 92.73, 92.45, 70.94, 70.92, 69.45, 69.36, 63.94, 63.91, 31.67, 31.55, 29.39, 28.99, 25.84, 25.68, 22.66, 22.63, 22.62, 22.41, 18.70, 14.07, 14.01, 11.37, 10.60, 10.47 ppm; MS (MALDI TOF, matrix: DCTB) $C_{70}H_{106}O_6Si_2$ (1098.8): *m/z* (%) 1098.7 (100) $[M]^+$.

6

Diisopropyl azodicarboxylate (DIAD) (82 mg, 0.40 mmol) was slowly added to a solution of **5** (100 mg, 0.09 mmol), 3,5-di-*tert*-butylphenol (56 mg, 0.27 mmol) und PPh_3 (106 mg, 0.40 mmol) in THF (4 mL) at 0 °C. The mixture was allowed to reach room temperature, stirred overnight and then poured into Et_2O (100 mL) and H_2O (30 mL). The organic layer was separated, washed with water (2 x 30 mL) and brine (30 mL), and dried

over $MgSO_4$ and concentrated *in vacuo*. Product purification was performed by column chromatography on silica gel (petroleumether-CH_2Cl_2, 3:1, 2:1; R_f = 0.88, 2:1) to give **6** (110 mg, 0.075 mmol, 83 %) as a pale yellow solid. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.75 (s, 2H), 7.01-6.98 (m, 2H), 6.91 (s, 4H), 6.86-6.83 (m, 4H), 5.36 (s, 4H), 3.97-3.84 (m, 8H), 1.80-1.62 (m, 8H), 1.50-1.14 (m, 60H), 1.12 (s, 42H), 0.91-0.74 (m, 12H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 158.15, 154.20, 153.43, 152.04, 138.63, 130.44, 121.64, 117.09, 116.08, 115.08, 114.28, 113.38, 109.41, 102.93, 96.74, 93.04, 92.06, 69.49, 69.21, 67.42, 34.94, 31.68, 31.41, 31.37, 29.40, 29.14, 25.86, 25.58, 22.63, 22.49, 18.70, 14.08, 13.97, 11.36, 1.01 ppm; MS (MALDI TOF, matrix: DCTB) $C_{98}H_{146}O_6Si_2$ (1475.1): *m/z* (%)1475.1 (100) $[M]^+$.

7

TBAF (1 M solution in THF; 0.36 mL, 0.36 mmol) was added to a solution of **6** (110 mg, 0.08 mmol) in THF (15 mL). After stirring overnight the mixture was poured into Et_2O (100 mL) and H_2O (20 mL). The organic layer was separated, washed with water (3 x 30 mL) and brine (30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. After adding MeOH the precipitate was collected by filtration. Drying *in vacuo* gave **7** (86 %, 80 mg, 0.069 mmol) as a yellow solid. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.75 (s, 2H), 7.01-6.98 (m, 2H), 6.94 (s, 4H), 6.85-6.82 (m, 4H), 5.36 (s, 4H), 3.95-3.87 (m, 8H), 3.36 (s, 2H), 1.82-1.61 (m, 8H), 1.50-1.14 (m, 60H), 0.92-0.74 (m, 12H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ =158.18, 154.06, 153.52, 152.08, 138.74, 130.52, 121.66, 117.27, 116.67, 115.14, 114.05, 112.94, 109.43, 92.71, 92.24, 82.45, 79.98, 69.62, 69.47, 67.48, 34.95, 31.52, 31.41, 31.36, 31.32, 29.12, 29.08, 25.60, 25.57, 22.58, 22.49, 14.01, 13.96 ppm; MS (MALDI TOF, matrix: DCTB) $C_{80}H_{106}O_6$ (1162.8): *m/z* (%)1162.8 (100) $[M]^+$; 1412.9 (6) $[M + DCTB]^+$; GPC *vs.* PS: M_p = 1400 g/mol.

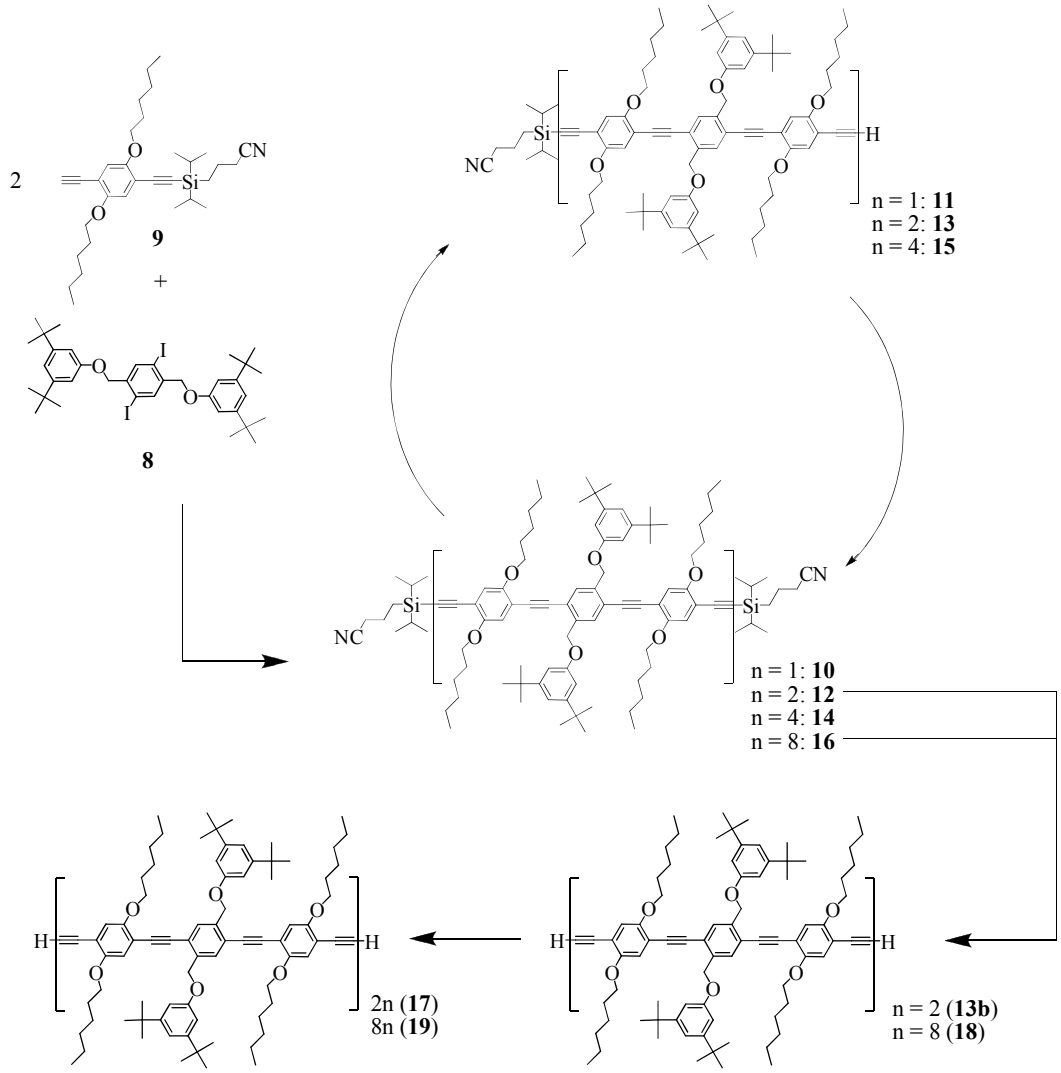
1

To a solution of **7** (10 mg, 0.009 mmol) in *o*-dichlorobenzene (1 mL) was added TMEDA (5 mg, 0.04 mmol) and CuCl (2 mg, 0.02 mmol). Then a slow stream of dried air was piped into the solution via a canula for 30 min at the beginning of the reaction and after 12 h. After stirring for 20 h at room temperature, the mixture was poured into CH_2Cl_2 (50

mL) and H_2O (30 mL). The organic layer was separated, washed with water (2 x 20 mL) and brine (20 mL), and dried over $MgSO_4$. The crude product was purified by filtration through a short silica gel filled column. After reducing the solvent volume *in vacuo* and adding MeOH the precipitate was collected by filtration. Drying *in vacuo* gave **1** (90 %, 9 mg) as a yellow solid. ^{1}H NMR (250 MHz, $C_2D_2Cl_4$): δ = 7.85 (s, 2H), 7.06-6.92 (m, 6H), 6.87 (s, 4H), 5.38 (s, 4H), 4.02-3.84 (m, 8H), 1.87-1.61 (m, 12H), 1.54-1.14 (m, 90H), 0.94-0.74 (m, 20H) ppm; GPC *vs.* PS: M_w = 78000 g/mol, M_n = 24600 g/mol, D = 3.2.

5.2.2 Oligomers of 1

The iterative synthesis is based on the recently presented 3-cyanopropyl-diisopropylsilyl (CPDIPS) acetylene [S4] and described in Scheme S2. In the first step of the synthetic cycle the diprotected bisacetylene is partially deprotected under statistical conditions. Therefore, a small amount of water (5%) was added slowing down the fluoride-induced desilylation. In consequence of the high polarity of the CPDIPS group, the R_f values of the resulting three species (starting material, monoprotected bisacetylene, completly deprotected bisacetylene) differ considerably even for the higher oligomers. Therefore, the conversion can be well controlled by TLC and the crude product can be separated easily by chromatography on silica gel. To complete the cycle, monoprotected species are dimerized under Glaser-Hay condition in high yield. The molecular weight is doubled in every cycle which results in exponential growth.



Scheme S2: Iterative synthesis of oligomers of **1**.

8

A suspension of 1,4-diiodo-2,5-bis(bromomethyl)benzene (1.03 mg, 1.99 mmol) [S2], 3,5-di-*tert*-butylphenol (906 mg, 4.39 mmol) and K_2CO_3 (1100 mg, 7.96 mmol) in DMF (15 mL) was heated to 65 °C and stirred overnight. After cooling to room temperature, the mixture was poured into CH_2Cl_2 (200 mL) and H_2O (100 mL). The organic layer was separated, washed with water (3 x 50 mL) and brine (50 mL), and dried over $MgSO_4$. After the solution was concentrated to 10 mL MeOH (10 mL) was added and the white precipitate was collected by filtration. Drying *in vacuo* yielded **8** (1.18 g, 1.54 mmol, 77 %) as white solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.04 (s, 2H), 7.09 (t, *J* = 1.6 Hz,

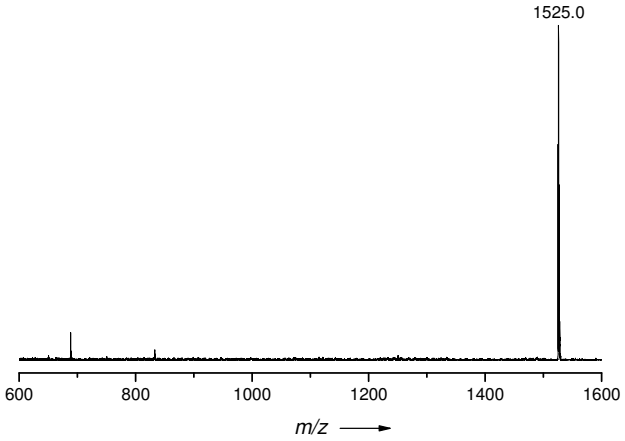
2H), 6.85 (d, *J* = 1.6 Hz, 4H), 5.01 (s, 4H), 1.33 (s, 36H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.87, 152.37, 140.89, 138.80, 115.78, 109.50, 97.00, 73.12, 35.03, 31.45 ppm; MS (EI) $C_{36}H_{48}I_2O_2$ (711.2): *m/z* (%) 711.1 (52) $[M]^+$.

1-{2-[(3-Cyanopropyl)diisopropylsilyl]ethynyl}-4-ethynyl-3,5-dihexyloxybenzene ***9***

9 was synthesized according to literature procedure [S4]

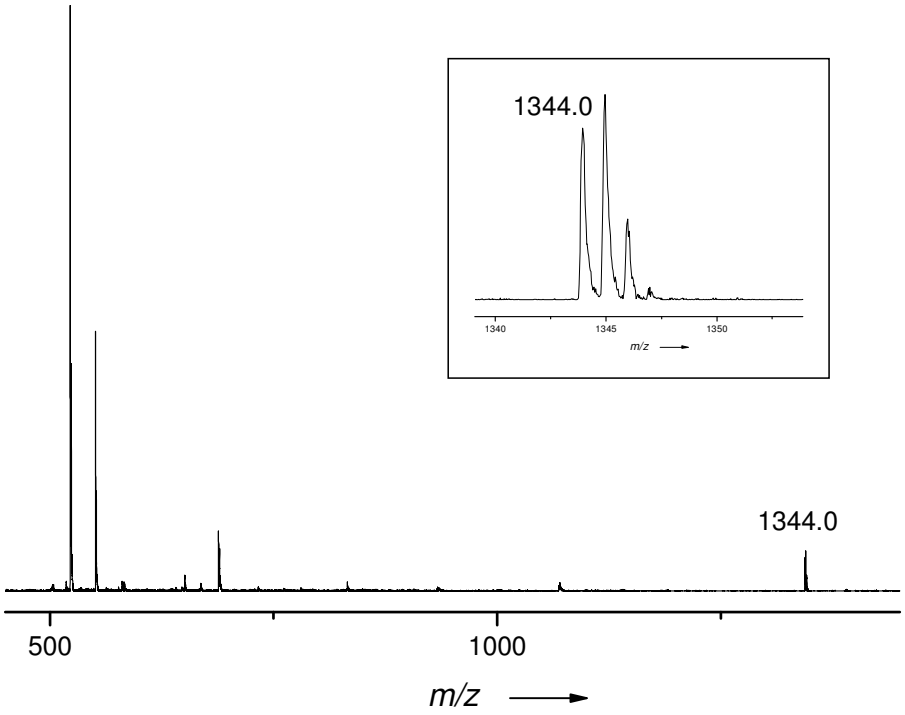
10

9 (865 mg, 1.685 mmol) was added to a solution of $Pd(PPh_3)_2Cl_2$ (30 mg, 0.043 mmol), CuI (15 mg, 0.078 mmol), PPh_3 (30 mg, 0.114 mmol) and **8** (615 mg, 0.802 mmol) in THF (8 mL) and piperidine (4 mL). After stirring overnight at room temperature, the mixture was poured into CH_2Cl_2 (150 mL) and H_2O (50 mL). The organic layer was separated, washed with water (2 x 50 mL) and brine (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Filtration of the crude product through a short silica gel filled column (petroleumether-CH_2Cl_2, 1:1, 1:2, 1:4, R_f = 0.44 bei 2:1) gave **10 (**1.05 gm, 0.69 mmol, 86 %) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 2H), 7.03-7.00 (m, 2H), 6.96-6.92 (m, 4H), 6.88-6.86 (m, 4H), 5.39 (s, 4H), 3.99-3.89 (m, 8H), 2.43 (t, *J* = 7.0 Hz, 4H), 1.92-1.82 (m, 4H), 1.81-1.67 (m, 8H), 1.52-1.31 (m, 16H), 1.27 (s, 36H), 1.25-1.19 (m, 8H), 1.16-1.08 (m, 28H), 0.94-0.78 (m, 16H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.51, 154.57, 153.90, 152.58, 139.30, 130.83, 122.15, 120.12, 117.29, 116.46, 115.55, 114.17, 114.01, 109.76, 104.09, 95.98, 93.40, 92.39, 69.92, 69.63, 67.69, 35.23, 32.02, 31.79, 31.55, 29.75, 29.58, 26.18, 26.00, 23.05, 22.90, 21.71, 21.06, 18.38, 18.14, 14.24, 14.15, 12.18, 9.98 ppm; MS (MALDI TOF; matrix: DCTB) $C_{100}H_{144}N_2O_6Si_2$ (1525.1): *m/z* (%)1525.0 (100) $[M]^+$.



11

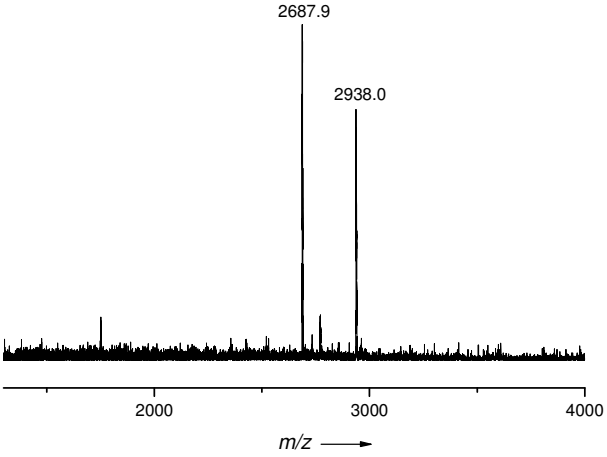
To a solution of **10** (865 mg, 0.567 mmol) in THF (20 mL) and H_2O (1 mL) was added TBAF (1 M solution in THF; 510 µL, 0.510 mmol) at 0 °C. The mixture was stirred at room temperature, while conversion was followed by TLC. After 6h the reaction was stopped by adding H_2O (20 mL) and the mixture was poured into Et_2O (150 mL). The organic layer was separated, washed with H_2O (2 x 30 mL) and brine, and dried over $MgSO_4$. Product isolation via column chromatography (petroleumether-CH_2Cl_2, 2:1, 3:2 1:1, 2:3; R_f = 0.65 in 2:3) on silica gel gave **11** (307 mg, 40 %, 0.228 mmol) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (s, 2H), 7.05-7.01 (m, 2H), 6.99-6.94 (m, 4H), 6.89-6.85 (m, 4H), 5.40 (s, 2H), 5.39 (s, 2H), 3.98-3.89 (m, 8H), 3.39 (s, 1H), 2.43 (t, *J* = 7.0 Hz, 2H), 1.92-1.67 (m, 10H), 1.52-1.31 (m, 16H), 1.28 (s, 36H), 1.25-1.19 (m, 8H), 1.16-1.08 (m, 14H), 0.94-0.78 (m, 14H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 158.52, 158.50, 154.57, 154.44, 153.95, 153.90, 152.59, 139.33, 139.31, 130.85, 122.19, 122.11, 120.12, 117.63, 117.29, 116.94, 116.47, 115.57, 114.26, 114.18, 114.00, 113.30, 109.76, 104.09, 95.99, 93.40, 93.17, 92.37, 92.36, 82.75, 80.30, 69.93, 69.92, 69.89, 69.63, 67.72, 67.68, 35.23, 32.02, 31.92, 31.79, 31.78, 31.54, 29.75, 29.57, 29.53, 26.18, 25.99, 23.05, 22.98, 22.90, 21.71, 21.06, 18.38, 18.14, 14.24, 14.18, 14.15, 12.18, 9.98 ppm; MS (MALDI TOF; matrix: DCTB) $C_{90}H_{125}NO_6Si$ (1343.9): *m/z* (%) 1344.0 (8) $[M]^+$.



12

To a solution of **11** (290 mg, 0.216 mmol) in CH_2Cl_2 (5 mL) was added TMEDA (25 mg, 32 µL, 0.216 mmol) and CuCl (21 mg, 0.216 mmol). Then a slow stream of dried air was piped into the solution via a canula for 30 min at the beginning of the reaction and after 12 h. After stirring for 20 h at room temperature, the mixture was poured into CH_2Cl_2 (100 mL) and H_2O (50 mL). The organic layer was separated, washed with water (3 x 20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Product isolation via column chromatography (petroleumether-CH_2Cl_2, 2:1, 1:1, 1:2; R_f = 0.40, 1:2) on silica gel gave **12** (264 mg, 0.098 mmol, 91 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 4H), 7.03-7.00 (m, 4H), 6.97-6.93 (m, 4H), 6.92-6.89 (m, 4H), 6.88-6.85 (m, 8H), 5.39 (s, 4H), 5.38 (s, 4H), 3.99-3.88 (m, 16H), 2.43 (t, *J* = 7.0 Hz, 4H), 1.94-1.66 (m, 20H), 1.49-1.29 (m, 32H), 1.27 (s, 72H), 1.25-1.19 (m, 16H), 1.15-1.08 (m, 28H), 0.94-0.78 (m, 28H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.26, 158.22,

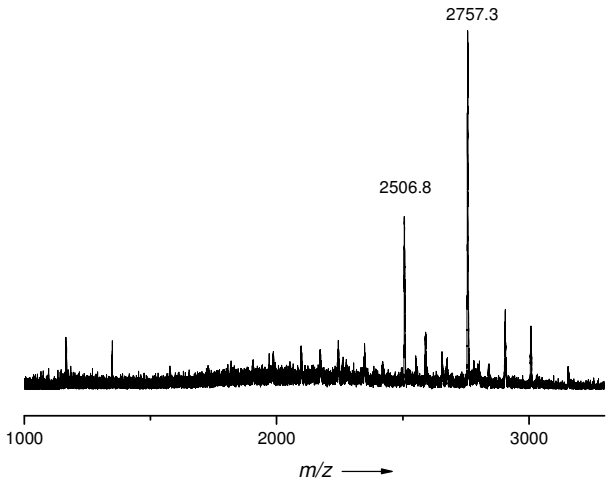
154.95, 154.27, 153.58, 153.51, 152.14, 138.83, 138.79, 130.59, 121.81, 121.64, 119.82, 117.23, 117.07, 116.75, 116.09, 115.20, 114.59, 113.89, 113.69, 112.96, 109.50, 109.49, 103.91, 95.44, 93.07, 92.94, 92.89, 92.32, 79.69, 79.51, 69.81, 69.59, 69.51, 69.20, 67.58, 67.50, 65.90, 35.01, 31.69, 31.59, 31.47, 31.44, 31.42, 29.42, 29.21, 29.15, 29.11, 25.85, 25.67, 25.65, 25.63, 22.71, 22.65, 22.55, 21.34, 20.83, 18.29, 18.05, 15.33, 14.12, 14.09, 14.02, 11.86, 9.70 ppm; MS (MALDI TOF; matrix: DCTB) $C_{180}H_{248}N_2O_{12}Si_2$ (2685.8): *m/z* (%) 2938.0 (74) $[M + DCTB]^+$, 2687.9 (100) $[M]^+$.



13

To a solution of **12** (359 mg, 0.134 mmol) in THF (4 mL) and H_2O (200 µL) was added TBAF (1 M solution in THF; 120 µL, 0.120 mmol) at 0 °C. The mixture was stirred at room temperature, while conversion was followed by TLC. After 6 h the reaction was stopped by adding H_2O (5 mL) and the mixture was poured into Et_2O (100 mL). The organic layer was separated, washed with H_2O (2 x 20 mL) and brine (20 mL) and dried over $MgSO_4$. Product isolation via radial chromatography (petroleumether-CH_2Cl_2, 2:1, 3:2 1:1; R_f = 0.32 in 1:1) on silica gel gave **13** (137 mg, 46 %, 0.054 mmol) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82 (s, 4H), 7.04-7.02 (m, 4H), 6.98-6.94 (m,

6H), 6.93-6.91 (m, 2H), 6.89-6.87 (m, 8H), 5.43-5.38 (m, 8H), 4.00-3.91 (m, 16H), 3.36 (s, 1H), 2.44 (t, J = 7.0 Hz, 2H), 1.94-1.68 (m, 18H), 1.55-1.33 (m, 32H), 1.29 (s, 72H), 1.25-1.21 (m, 16H), 1.16-1.10 (m, 14H), 0.95-0.89 (m, 12H), 0.87-0.80 (m, 14H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.17, 158.15, 158.13, 154.86, 154.18, 154.02, 153.50, 153.42, 152.06, 138.75, 138.72, 130.51, 125.48, 124.85, 121.72, 121.69, 121.60, 121.56, 119.75, 117.21, 117.12, 116.95, 116.64, 116.62, 115.97, 115.13, 114.48, 113.98, 113.79, 113.59, 112.92, 112.86, 112.85, 109.41, 103.83, 95.37, 93.00, 92.86, 92.85, 92.82, 92.77, 92.25, 92.22, 82.47, 79.95, 79.61, 79.44, 69.70, 69.57, 69.49, 69.41, 69.10, 67.48, 67.45, 67.40, 34.93, 31.62, 31.51, 31.39, 31.36, 31.34, 30.29, 29.68, 29.44, 29.40, 29.34, 29.13, 29.09, 29.07, 29.03, 25.77, 25.60, 25.58, 25.55, 22.64, 22.58, 22.57, 22.48, 21.26, 20.75, 18.22, 17.98, 14.06, 14.02, 14.00, 13.96, 11.77, 9.61 ppm; MS (MALDI TOF, matrix: DCTB) $C_{170}H_{229}NO_{12}Si$ (2504.7): *m/z* (%) 2757.3 (100) $[M + DCTB]^+$; 2506.8 (48) $[M]^+$.



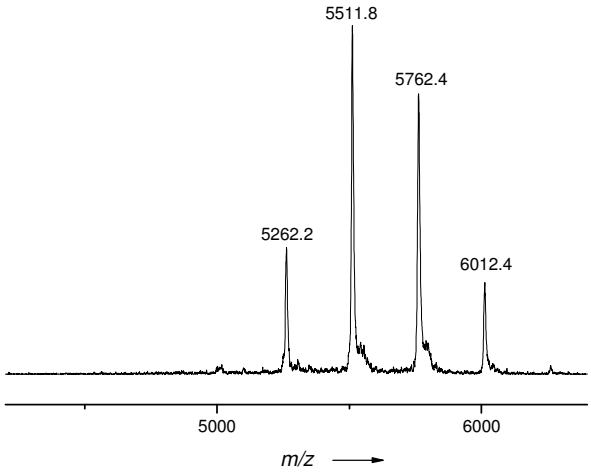
13b

13b was isolated from the crude product of **13** by radial chromatography (petroleumether-CH_2Cl_2, 2:1, 3:2 1:1; R_f = 0.89 in 1:1) on silica gel yielding **13b** (78 mg, 25 %, 0.034 mmol) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (s, 4H), 7.03-7.00 (m, 4H), 6.97-6.93 (m, 8H), 6.89-6.86 (m, 8H), 5.39 (s, 8H), 3.99-3.90 (m,

16H), 3.35 (s, 2H), 1.86-1.66 (m, 16H), 1.57-1.17 (m, 120H), 0.96-0.78 (m, 24H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.19, 154.89, 154.06, 153.53, 152.09, 138.77, 130.54, 121.71, 117.28, 117.18, 116.70, 115.16, 114.53, 114.04, 112.96, 112.91, 109.44, 92.83, 82.47, 79.63, 79.46, 69.75, 69.62, 69.47, 69.46, 67.49, 34.95, 31.52, 31.41, 31.36, 29.69, 29.12, 29.09, 29.05, 25.61, 25.57, 22.58, 22.49, 14.03, 14.00, 13.96 ppm; MS (MALDI TOF, matrix: DCTB) $C_{160}H_{210}O_{12}$ (2323.6): *m/z* (%) 2573.8 (65) $[M + DCTB]^+$; 2323.6 (100) $[M]^+$.

14

To a solution of **13** (178 mg, 0.071 mmol) in CH_2Cl_2 (2 mL) was added TMEDA (11 µL, 0.07 mmol) and CuCl (7 mg, 0.07 mmol). Then a slow stream of dried air was piped into the solution via a canula for 30 min at the beginning of the reaction and after 12 h. After stirring for 20 h at room temperature, the mixture was poured into CH_2Cl_2 (100 mL) and H_2O (30 mL). The organic layer was separated, washed with water (3 x 20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Product isolation via column chromatography (petroleumether-CH_2Cl_2, 1:1, 2:3, 1:3; R_f = 0.21, 1:1) on silica gel gave **14** (150 mg, 0.030 mmol, 85%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (s, 8H), 7.07-7.03 (m, 8H), 7.02-6.96 (m, 12H), 6.96-6.93 (m, 4H), 6.93-6.87 (m, 16H), 5.43 (s, 16H), 4.04-3.92 (m, 32H), 2.46 (t, *J* = 7.0 Hz, 4H), 1.97-1.69 (m, 36H), 1.61-1.34 (m, 64H), 1.31 (s, 144H), 1.28-1.22 (m, 32H), 1.19-1.11 (m, 28H), 0.99-0.91 (m, 24H), 0.90-0.81 (m, 28H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.18, 158.17, 158.14, 154.88, 154.19, 153.52, 153.44, 152.07, 152.06, 138.78, 138.76, 138.72, 130.54, 130.51, 121.74, 121.67, 121.56, 119.70, 117.14, 116.99, 116.67, 116.01, 115.13, 114.51, 114.49, 113.81, 113.62, 112.91, 112.88, 103.85, 95.36, 93.02, 93.00, 92.96, 92.86, 92.25, 79.61, 79.52, 79.46, 69.72, 69.50, 69.42, 69.11, 67.47, 67.41, 34.92, 34.75, 31.61, 31.55, 31.51, 31.39, 31.36, 31.34, 31.20, 29.34, 29.13, 29.08, 29.04, 25.76, 25.59, 25.57, 25.55, 22.63, 22.57, 22.47, 21.27, 20.72, 18.21, 17.97, 14.04, 14.01, 13.94, 11.77, 9.61 ppm; MS (MALDI TOF, matrix: DCTB) (5007.4): *m/z* (%) 6012.4 (27) $[M + 4 DCTB]^+$, 5762.4 (81) $[M + 3 DCTB]^+$, 5511.8 (100) $[M + 2 DCTB]^+$, 5262.2 (37) $[M + DCTB]^+$.

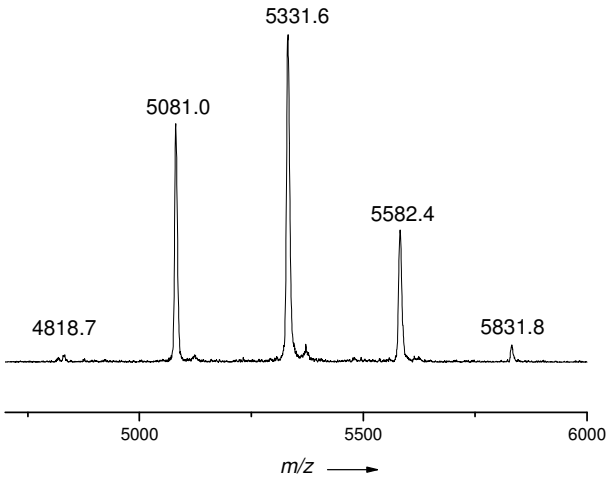


15

To a solution of **14** (150 mg, 0.030 mmol) in THF (860 µL) and H_2O (43 µL) was added TBAF (1 M solution in THF; 30 µL, 0.030 mmol) at 0 °C. After 1 min, 1 mL of THF was additionally added. After 15 minutes TLC indicated that the conversion was above 50 % the reaction was stopped by adding H_2O (1 mL). The mixture was poured into CH_2Cl_2 (50 mL). The organic layer was separated, washed with H_2O (2 x 10 mL) and brine (10 mL), and dried over $MgSO_4$. Product isolation via column chromatography (petroleumether-CH_2Cl_2, 3:2 1:1, 1:2; R_f = 0.21 in 1:1) on silica gel gave **15** (41 mg, 28 %, 0.008 mmol) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 8H), 7.05-7.01 (m, 8H), 6.99-6.91 (m, 16H), 6.90-6.86 (m, 16H), 5.40 (s, 16H), 4.01-3.90 (m, 32H), 3.36 (s, 1H), 2.44 (t, *J* = 7.0 Hz, 2H), 1.95-1.67 (m, 34H), 1.59-1.33 (m, 64H), 1.29 (s, 144H), 1.26-1.19 (m, 32H), 1.17-0.09 (m, 14H), 0.96-0.79 (m, 50H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ =158.18, 158.16, 154.89, 154.21, 154.05, 153.53, 153.45, 152.09, 138.79, 138.77, 130.55, 130.54, 121.74, 121.71, 121.68, 121.62, 121.57, 119.74, 117.26, 117.17, 117.01, 116.69, 116.03, 115.15, 114.51, 114.03, 113.83, 113.63, 112.96, 112.92, 109.43, 93.01, 92.87, 92.83, 92.79, 92.25, 92.23, 79.63, 79.46, 69.74, 69.61, 69.52, 69.45, 69.13, 67.49, 67.43, 34.94, 31.62, 31.52, 31.40, 31.37, 31.35, 29.35, 29.14, 29.09, 29.05, 25.78, 25.61, 25.59, 25.56, 22.64, 22.58, 22.49, 21.28, 20.75, 18.22, 17.98, 14.06, 14.02, 14.00, 13.95, 11.79, 9.63 ppm; MS (MALDI TOF, matrix: DCTB)

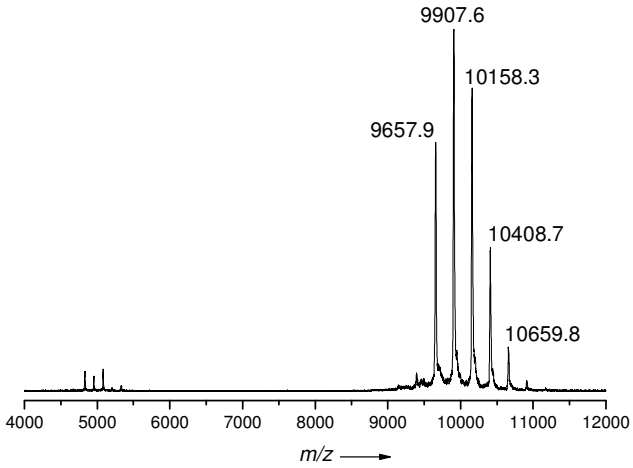
$C_{330}H_{437}NO_{24}Si$ (4826.3): *m/z* (%) 5831.8 (6) [M + 4 DCTB] $^{+}$, 5582.4 (41) [M + 3 DCTB]$^{+}$, 5331.6 (100) [M + 2 DCTB]$^{+}$, 5081.0 (81) [M + DCTB]$^{+}$.



16

To a solution of **15** (38 mg, 0.008 mmol) in CH_2Cl_2 (500 µL) was added TMEDA (2 µL, 0.02 mmol) and CuCl (2 mg, 0.02 mmol). Then a slow stream of dried air was piped into the solution via a canula for 30 min at the beginning of the reaction and after 12 h. After stirring for 20 h at room temperature, the mixture was poured into CH_2Cl_2 (50 mL) and H_2O (20 mL). The organic layer was separated, washed with water (3 x 20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Product isolation via column chromatography (petroleumether-CH_2Cl_2, 1:1, 2:3, 1:3; R_f = 0.19 in 1:1) on silica gel gave **16** (24 mg, 0.0025 mmol, 63 %) as a yellow solid.^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (s, 16H), 7.07-7.03 (m, 16H), 7.01-6.92 (m, 32H), 6.92-6.88 (m, 32H), 5.41 (s, 32H), 4.03-3.91 (m, 64H), 2.46 (t, *J* = 7.0 Hz, 4H), 1.97-1.68 (m, 68H), 1.60-1.34 (m, 128H), 1.31 (s, 288H), 1.28-1.21 (m, 64H), 1.18-1.10 (m, 28H), 0.96-0.78 (m, 100H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.19, 158.16, 154.89, 154.21, 153.53, 153.45, 152.09, 138.79, 138.73, 130.56, 130.54, 121.68, 119.74, 117.18, 117.05, 117.03, 116.70,

116.64, 116.04, 115.26, 115.16, 115.07, 115.05, 114.53, 114.52, 114.48, 114.46, 113.84, 113.64, 112.92, 109.53, 109.44, 109.36, 92.90, 92.88, 92.86, 79.52, 79.51, 79.49, 79.47, 79.46, 79.43, 69.75, 69.53, 69.45, 69.14, 67.50, 67.45, 34.95, 31.63, 31.61, 31.57, 31.52, 31.49, 31.41, 31.36, 31.32, 29.36, 29.14, 29.09, 29.05, 25.78, 25.61, 25.59, 25.56, 22.64, 22.58, 22.49, 21.28, 20.76, 18.23, 17.99, 14.06, 14.02, 13.96, 11.80, 9.64 ppm; MS (MALDI TOF, matrix: DCTB) $C_{660}H_{872}N_2O_{48}Si_2$ (9650.5): *m/z* (%) 10659.8 (13) [M + 4 DCTB]$^+$, 10408.7 (40)[M + 3 DCTB]$^+$, 10158.3 (84) [M + 2 DCTB]$^+$, 9907.6 (100) [M + 1 DCTB]$^+$, 9657.9 (69) [M]$^+$.



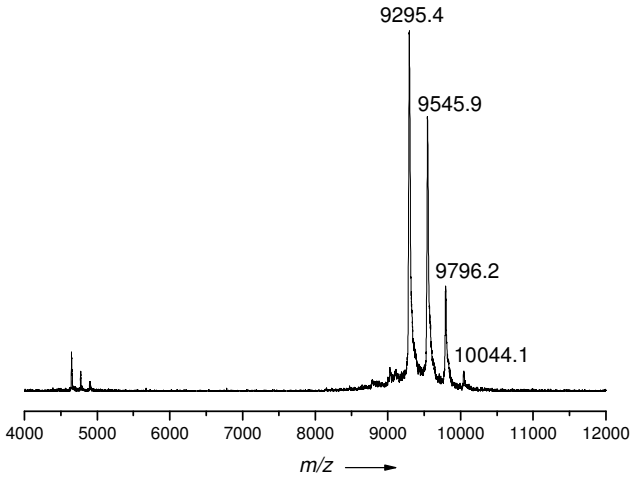
17

To a solution of **13b** (6 mg, 0.0026 mmol) in *o*-dichlorobenzene (1 mL) was added TMEDA (2.3 mg, 3.0 µL, 0.020 mmol) and CuCl (1.5 mg, 0.015 mmol). Then a slow stream of dried air was piped into the solution via a canula for 30 min. After stirring for 2 h at room temperature, the mixture was poured into CH_2Cl_2 (50 mL) and H_2O (30 mL). The organic layer was separated, washed with water (2 x 20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. After adding MeOH the precipitate was collected by filtration. Drying *in vacuo* gave **17** (83 %, 5 mg) as a yellow solid.

n	M_p (g/mol; GPC *vs* PS-standard)	M (g/mol; calculated)
2	3200	2325
4	7750	4649
6	13050	6972
8	18700	9296
10	24800	11619
12	31300	13942

18

TBAF (1 M solution in THF; 10 µL, 0.01 mmol) was added to a solution of **16** (18 mg, 0,0019 mmol) in THF (2 mL). After stirring overnight the mixture was poured into CH_2Cl_2 (50 mL) and H_2O (20 mL). The organic layer was separated, washed with water (3 x 20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. After adding MeOH the precipitate was collected by filtration. Drying *in vacuo* gave **18** (91 %, 16 mg, 0.0017 mmol) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (s, 16H), 7.04-7.00 (m, 16H), 6.98-6.93 (m, 32H), 6.89-6.86 (m, 32H), 5.39 (s, 32H), 4.02-3.90 (m, 64H), 3.35 (s, 2H), 1.88-1.66 (m, 64H), 1.56-1.17 (m, 480H), 0.97-0.88 (m, 96H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.25, 154.96, 154.90, 154.12, 153.59, 152.16, 152.04, 138.86, 138.84, 130.62, 130.61, 121.76, 121.74, 121.72, 117.24, 116.75, 116.71, 115.23, 115.21, 115.18, 115.17, 115.16, 114.59, 114.57, 113.01, 112.98, 109.50, 109.44, 92.98, 92.95, 92.94, 92.93, 92.91, 92.88, 79.68, 79.66, 79.56, 79.54, 79.53, 69.81, 69.52, 67.56, 35.02, 31.59, 31.47, 31.42, 29.76, 29.16, 29.12, 25.68, 25.63, 22.65, 22.56, 14.10, 14.07, 14.03 ppm; MS (MALDI TOF, matrix: DCTB) C640H834O48 (9288.3): *m/z* (%) 10044.1 (5) $[M + 3\ DCTB]^+$, 9796.2 (31) $[M + 2\ DCTB]^+$, 9545.9 (77) $[M + 1\ DCTB]^+$, 9295.4 (100) $[M]^+$.



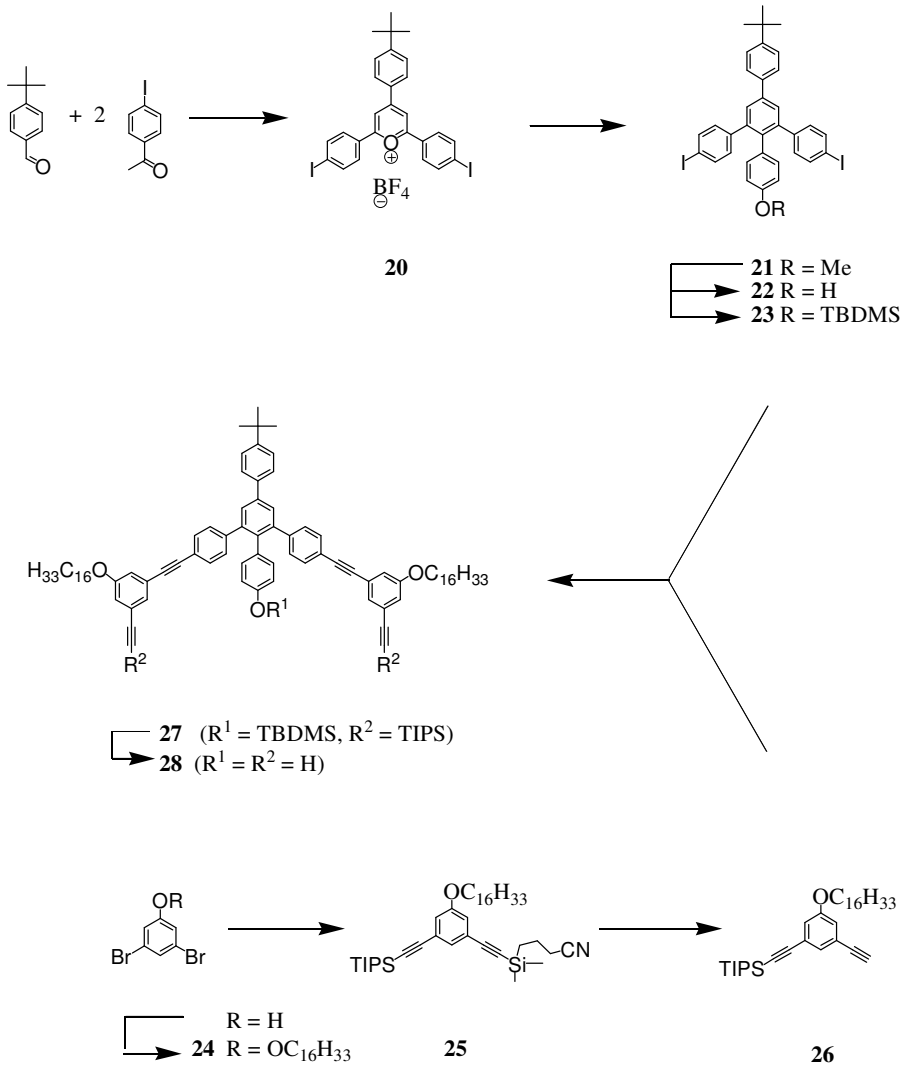
19

To a solution of **18** (6 mg, 0.0006 mmol) in *o*-dichlorobenzene (0.4 mL) was added TMEDA (3 mg, 4.0 µL, 0.026 mmol) and CuCl (2 mg, 0.02 mmol). Subsequently, a slow stream of dried air was piped into the solution via a canula for 30 min. After stirring for 3 h at room temperature, the mixture was poured into CH_2Cl_2 (50 mL) and H_2O (30 mL). The organic layer was separated, washed with water (2 x 20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. After adding MeOH the precipitate was collected by filtration. Drying *in vacuo* gave **19** (83 %, 5 mg) as a yellow solid.

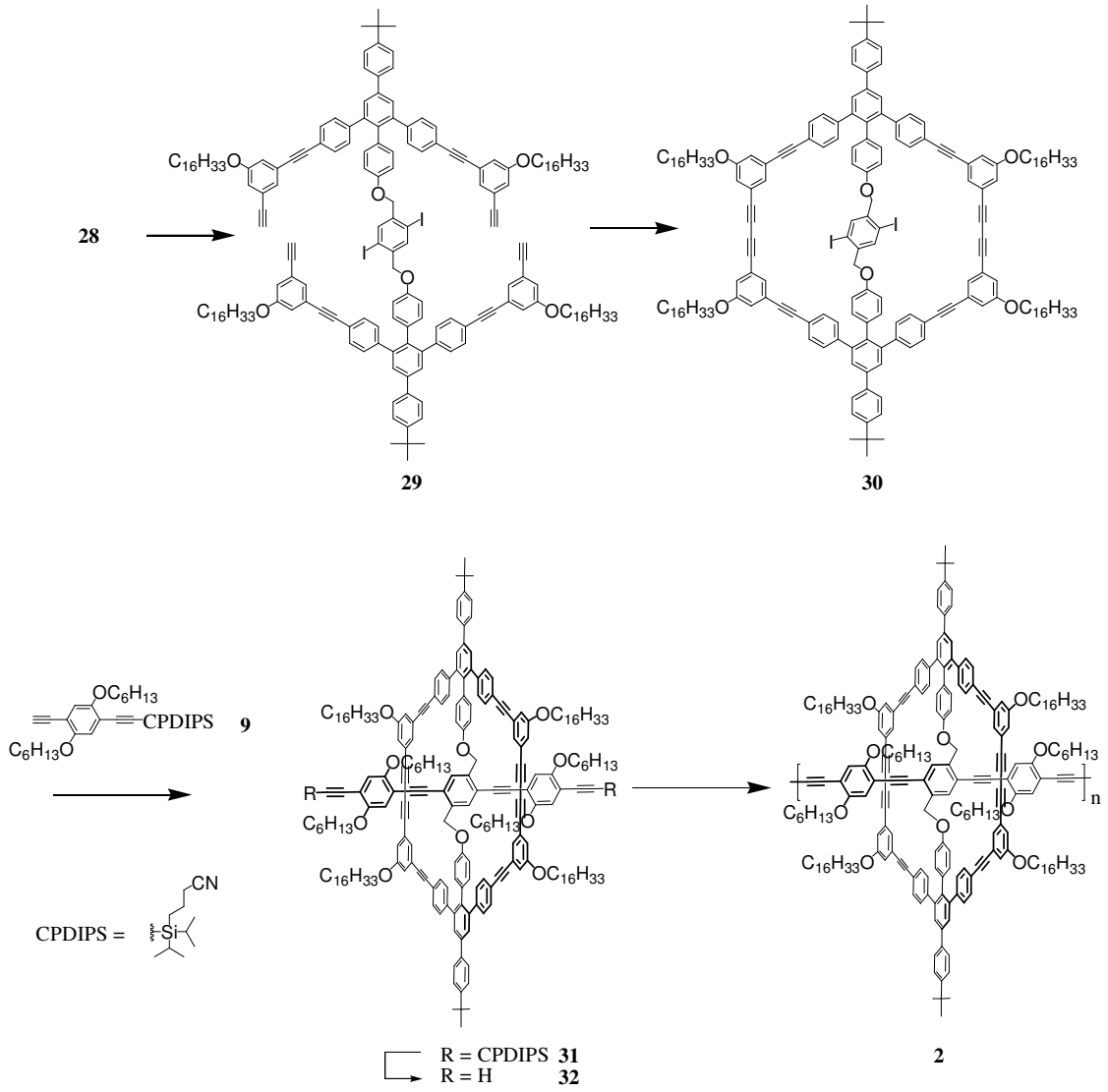
n	**M_p (g/mol; GPC *vs* PS-standard)**	**M (g/mol; calculated)**
8	18700	9296
16	45200	18589
24	74200	27883
32	105000	37176
40	140000	46470
48	174000	55763
56	211000	65057
64	246000	74350

5.3 2 and oligomers of 2

5.3.1 2



Scheme S3: Synthesis of the macrocycle "half rings".



Scheme S4: Synthesis of polymer **2**.

*4-(4-tert-Butylphenyl)-2,6-di-(4-iodophenyl)pyryliumtetrafluoroborate **20***

20 was synthesized according to literature procedure. [S5]

*4''-tert-Butyl-4-methoxy-2',6'-bis-(p-iodophenyl)-[1,1';4',1'']terphenyl **21***

A mixture of **20** (10.0 g, 14.2 mmol), sodium 4-methoxyphenylacetate (23.2 g, 123.3 mmol; prepared from 4-methoxyphenylacetic acid and sodium methylate (0.5 M) in methanol and subsequent evaporation of the solvent) in acetic anhydride (120 mL) was stirred at 150 °C for 3 h. After cooling to room temperature the precipitate was collected

by filtration and washed with water and MeOH. Drying *in vacuo* gave **21** (6.07 g, 60 %, 8.52 mmol) as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.62-7.57 (m, 4H), 7.53-7.45 (m, 6H), 6.89-6.85 (m, 4H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 3.69 (s, 3H), 1.36 (s, 9H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): *δ* = 157.9, 150.8, 141.5, 141.4, 140.2, 137.2, 137.1, 136.8, 132.5, 131.8, 130.8, 128.3, 126.8, 125.8, 113.1, 92.2, 55.0, 34.6, 31.3 ppm; MS (EI) $C_{35}H_{30}I_2O$ (720.0): *m/z* (%) 720.0 (100) $[M]^+$.

4''-tert-Butyl-2',6'-bis-(p-iodophenyl)-[1,1';4',1'']terphenyl-4-ol ***22***

BBr_3 (6.8 mL, 6.8 mmol, 1 M solution in CH_2Cl_2) was slowly added to a mixture of **21** (3.25 g, 4.51 mmol) in CH_2Cl_2 (50 mL) at -78 °C. After stirring at this temperature for 1 h the mixture was allowed to warm to room temperature overnight. Subsequently, H_2O (100 mL) and MeOH (100 mL) were added and the resulting mixture was poured into Et_2O (100 mL). The organic layer was separated, washed with water (2 x 40 mL) and brine (40 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via column chromatography (petroleumether-CH_2Cl_2, 1:1, 0:1; R_f = 0.26, CH_2Cl_2) to yield **22** (2.7 g, 3.82 mmol, 85 %) as a pale yellow solid. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.62-7.45 (m, 10H), 6.92-6.84 (m, 4H), 6.73-6.66 (m, 2H), 6.56-6.48 (m, 2H), 4.82 (s, 1H), 1.34 (s, 9H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): *δ* = 154.0, 150.9, 114.8, 125.9, 126.8, 128.0, 128.3, 128.9, 131.0, 131.8, 132.7, 132.8, 136.8, 136.9, 137.1, 137.2, 138.1, 140.3, 141.5, 141.6, 114.8, 92.3, 34.6, 31.4 ppm; MS (EI) $C_{34}H_{28}I_2O$ (706.0): *m/z* (%) 706.0 (100) $[M]^+$, 579.1 (5) $[M– I]^+$.

4''-tert-Butyl-2',6'-bis-(p-iodophenyl)-[1,1';4',1'']terphenyl-4-yloxy-tert-butyl-dimethyl-silan ***23***

tert-Butyldimethylsilyl chloride (960 mg, 2.12 mmol) was added to a mixture of **22** (1.5 g, 2.12 mmol) and imidazole (0.96 g, 6.37 mmol) in DMF (10 mL). After stirring overnight, the mixture was poured into Et_2O (150 mL) and H_2O (50 mL). The organic layer was separated, washed with water (40 mL), HOAc (10 %, 40 mL), H_2O (40 mL), NaOH-solution (10 %, 40 mL), H_2O (40 mL) and brine (40 mL). After drying over $MgSO_4$ the solvent was evaporated *in vacuo*. The crude product was purified via column chromatography (petroleumether-CH_2Cl_2, 3:1, 2:1; R_f = 0.75, 2:1) to give **23** (1.65 g, 2.01

mmol, 95 %) as a white solid. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.64-7.56 (m, 4H), 7.52-7.45 (m, 6H), 6.89-6.84 (m, 4H), 6.69-6.64 (m, 2H), 6.56-6.51 (m, 2H), 1.34 (s, 9H), 0.92 (s, 9H), 0.11 (s, 6H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.0, 150.9, 141.4, 140.3, 138.1, 137.5, 137.3, 136.9, 136.8, 132.6, 132.5, 131.9, 131.8, 131.7, 128.9, 128.1, 127.9, 126.8, 125.9, 124.5, 119.8, 92.2, 34.6, 31.4, 25.8, 18.5, 4.4 ppm; MS (EI) $C_{40}H_{42}I_2OSi$ (820.1): *m/z* (%) 820.1 $[M]^+$.

1,3-Dibromo-5-hexadecyloxybenzene ***24***

A mixture of 3,5-dibromophenol (4.57 g, 18.16 mmol), hexadecyl bromide (6.89 g, 22.59 mmol), K_2CO_3 (11.16 g, 80.78 mmol) and KI (~ 20 mg) in DMF (2 mL) was stirred for 15 h at 60°C. After cooling to room temperature, the mixture was poured into Et_2O (200 mL) and H_2O (100 mL). The organic layer was separated, washed with water (50 mL), NaOH-solution (10 %, 50 mL) and brine (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via column chromatography (petroleumether-CH_2Cl 3:1, 2:1; R_f = 0.88 in 2:1) and recrystallization from CH_2Cl_2/*i*-propanol to give **24** (91 %, 7.89 g, 16.5 mmol) as a white solid. M.p. 48.3-48.9 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.22 (t, $^4J_{HH}$ = 1.7 Hz, 1H), 6.98 (d, $^4J_{HH}$ = 1.7 Hz, 2H), 3.91 (t, $^3J_{HH}$ = 6.5 Hz, 2H), 1.79-1.72 (m, 2H), 1.46-1.39 (m, 2H), 1.26 (s, 24H), 0.89-0.87 (m, 3H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.4, 126.1, 123.1, 116.9, 68.6, 31.9, 29.6, 28.9, 25.9, 22.7, 14.1 ppm; MS (EI) $C_{22}H_{36}Br_2O$ (476.1): *m/z* (%) 476.1 (100) $[M]^+$, 397.2 (5) $[M-Br]^+$, 251.8 (70) $[M-C_{16}H_{33}]^+$.

3-[2-(3-Cyanopropyl)dimethylsilylethinyl]-5-(2-triisopropylsilylethinyl)-hexadecyloxybenzene ***25***

To a solution of **24** (7.89 g, 16.6 mmol), $Pd(PPh_3)_2Cl_2$ (1.17 g, 1.67 mmol), CuI (0.32 g, 1.69 mmol) und PPh_3 (0.23 g, 0.88 mmol) in THF (45 mL) and piperidine (3.3 mL, 2.83 mg, 33 mmol) was added (tri*iso*propylsilyl) acetylene (782 mg, 3.77 mmol) via a syringe. After stirring for 3 h, (3-cyanopropyl)-dimethylsilyl acetylene (2.83 g, 18.73 mmol) was added and the mixture stirred for 12 h. The mixture was poured into Et_2O (150 mL) and H_2O (50 mL). The organic layer was separated, washed with water (2 x 50 mL) and brine (50 mL) and dried over $MgSO_4$. Product isolation was performed by column

chromatography (petroleumether-CH_2Cl_2 3:1, 2:1, 1:1; R_f = 0.38 in 2:1) to give **25** (4.87 g, 7.5 mmol, 45 %) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ =7.15 (t, 1H, $^4J_{HH}$= 1.4 Hz), 6.96-6.91 (m, 2H), 3.93 (t, 2H, $^3J_{HH}$= 6.5 Hz), 2.43 (t, 2H, $^3J_{HH}$= 7.1 Hz,), 1.86-1.72 (m, 4H), 1.47-1.39 (m, 2H), 1.34-1.26 (m, 24H), 1.11 (s, 21H), 0.89-0.82 (m, 5H), 0.25 (s, 6H) ppm; ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 158.6, 127.8, 124.7, 123.7, 118.9, 117.9, 105.7, 92.3, 91.1, 68.3, 31.9, 29.6, 29.3, 25.9, 22.7, 20.6, 20.5, 18.7, 15.7, 14.1, 11.3 ppm; MS (EI) $C_{41}H_{69}NOSi_2$ (647.49): *m/z* (%) 604.4 (100) $[M - C_3H_7]^+$.

3-Ethinyl-5-(2-triiopropylsilylethinyl)-hexadecyloxybenzene ***26***

K_2CO_3 (0.97 g, 7.00 mmol) was added to a solution of **25** (2.38 g, 3.67 mmol) in THF (20 mL) and MeOH (10 mL). After stirring for 1 h at room temperature, the mixture was poured into Et_2O (100 mL) and H_2O (40 mL). The organic layer is separated, washed with water (2 x 40 mL) and brine (40 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via column chromatography (petroleumether, R_f = 0.35) and digested with warm MeOH to give **26** (1,5 g, 2.89 mmol, 78 %) as a slightly yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (t, 1H, $^4J_{HH}$= 1.3 Hz), 6.98 (dd, 1H, $^4J_{HH}$= 1.3 Hz, $^4J_{HH}$= 3.8 Hz), 6.95 (dd, 1H, $^4J_{HH}$= 1.3 Hz, , $^4J_{HH}$= 3.8 Hz), 3.94 (t, 2H, $^3J_{HH}$= 6.5 Hz), 3.04 (s, 1H), 1.79-1.72 (m, 2H), 1.47-1.40 (m, 2H), 1.26 (s, 24H), 1.12 (s, 21H), 0.89-0.86 (m, 3H) ppm; ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 158.6, 128.1, 124.7, 123.1, 118.8, 118.1, 105.9, 91.2, 82.9, 77.3, 68.3, 31.9, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.1, 25.9, 22.7, 18.6, 14.1, 11.3 ppm. MS (EI) C35H58OSi (522.4) *m/z* (%) 522.4 (7) $[M]^+$, 479.4 (100) $[M- C_3H_7]^+$.

27

To a solution of **23** (722 mg, 0.88 mmol), $Pd(PPh_3)_2Cl_2$ (30 mg, 0.043 mmol), CuI (15 mg, 0.079 mmol) und PPh_3 (30 mg, 0.114 mmol) in THF (20 mL) and piperidine (8 mL) was added **26** (1.016 g, 1.92 mmol). After stirring for 3 h, the mixture was poured into Et_2O (150 mL) and H_2O (50 mL). The organic layer was separated, washed with water (2 x 50 mL) and brine (50 mL) and dried over $MgSO_4$. Product purification was performed by column chromatography (petroleumether-CH_2Cl_2 3:1; R_f = 0.92, 2:1) to give **27** (1.6 g, contaminated with homocoupling product; separation in the next step) as a pale yellow

solid. ^{1}H-NMR (250 MHz, CD_2Cl_2): δ = 7.68-7.61 (m, 4H), 7.52-7.46 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 4H), 7.20-7.17 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 4H), 7.00-6.93 (m, 4H), 6.70 (d, *J* = 8.6, 2H), 6.53 (d, *J* = 8.6 Hz, 2H), 3.94 (t, *J* = 8.5 Hz, 4H), 1.82-1.68 (m, 4H), 1.50-1.13 (m, 61H), 1.12 (s, 42H), 0.92-0.81 (m, 15), 0.13 (s, 6H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): *δ* = 158.7, 154.1, 150.7, 142.2, 141.8, 140.1, 137.5, 137.4, 132.6, 131.9, 130.9, 129.9, 128.5, 127.6, 126.8, 125.8, 124.3, 120.8, 119.6, 118.3, 118.1, 117.5, 106.2, 90.9, 89.6, 88.8, 68.3, 68.2, 66.7, 34.6, 31.9, 31.4, 29.6, 29.4, 29.2, 26.0, 25.7, 22.7, 19.7, 18.4, 14.1, 11.3, 4.4 ppm; MS (MALDI TOF, matrix: DCTB) $C_{110}H_{156}O_3Si_3$ (1609.14): *m/z* (%) 1610.1 (100) $[M]^+$.

28

TBAF (1 M solution in THF; 9.5 mL, 9.5 mmol) was added to a solution of **27** (1.60 mg, 0.94 mmol) in THF (10 mL). After stirring for 18 h, the mixture was poured into Et_2O (150 mL) and H_2O (50 mL). The organic layer was separated, washed with water (2 x 30 mL) and brine (30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Product purification was performed by column chromatography (petroleumether-CH_2Cl_2 2:1, 1:1; R_f = 0.49, 1:1) to give **28** (1.02 g, 0.86 mmol, 92 %) as a pale yellow solid. ^{1}H-NMR (250 MHz, $C_2D_2Cl_4$): δ = 7.70-7.64 (m, 4H), 7.54-7.48 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 4H), 7.28-7.25 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 4H), 7.08-7.00 (m, 4H), 6.74 (d, *J* = 8.6, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 4.67 (s, 1H), 3.96 (t, *J* = 8.5 Hz, 4H), 3.14 (s, 2H), 1.85-1.71 (m, 4H), 1.50-1.20 (m, 61H), 0.93-0.85 (m, 6), ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): *δ* = 158.7, 153.9, 150.7, 142.3, 141.8, 140.2, 137.3, 132.8, 131.3, 131.1, 129.9, 128.3, 127.5, 126.8, 125.8, 124.5, 123.2, 120.8, 118.4, 118.2, 114.7, 89.7, 88.7, 82.8, 68.3, 34.6, 31.9, 31.3, 29.7, 29.6, 29.4, 29.1, 25.9, 22.7, 14.1 ppm; MS (MALDI TOF, matrix: DCTB) $C_{86}H_{102}O_3$ (1182.78): *m/z* (%) 1182.7 (100) $[M]^+$, 1432.9 (12) $[M + DCTB]^+$.

29

A mixture of 1,4-diiodo-2,5-bis(bromomethyl)benzene [S2] (50 mg, 0.097 mmol), **28** (240 mg, 0.204 mmol) and K_2CO_3 (134 mg, 0.97 mmol) in DMF (5 mL) was stirred for 15 h at 50 °C. After cooling to room temperature, the mixture was poured into Et_2O (100 mL) and H_2O (50 mL). The organic layer was separated, washed with water (2 x 40 mL)

and brine (40 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via column chromatography (petroleumether-CH_2Cl_2 3:1, 2:1; R_f = 0.76, 2:1) and radial chromatography to give **29** (220 mg, 0.081 mmol, 83 %) as a pale yellow solid. ^{1}H-NMR (250 MHz, CD_2Cl_2): δ = 7.85 (s, 2H), 7.68-7.62 (m, 8H), 7.53 (m, 4H), 7.38-7.33 (m, 8H), 7.20-7.08 (m, 12H), 7.03-6.93 (m, 8H), 6.79 (d, *J* = 8.7 Hz, 4H), 6.63 (d, *J* = 8.7 Hz, 4H), 4.88 (s, 4H), 3.91 (t, *J* = 6.6 Hz, 8H), 3.09 (s, 4H), 1.80-1.66 (m, 8H), 1.50-1.14 (m, 122H), 0.90-0.79 (m, 12H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.7, 156.3, 150.7, 142.2, 141.8, 140.2, 140.9, 138.0, 137.3, 137.1, 132.7, 131.8, 131.1, 129.9, 128.3, 127.5, 126.8, 125.8, 124.5, 123.2, 120.8, 118.2, 114.0, 96.1, 89.8, 88.8, 82.8, 72.5, 68.3, 34.6, 31.9, 29.7, 29.6, 29.1, 25.9, 22.7, 14.1 ppm; MS (MALDI TOF, matrix: DCTB) $C_{180}H_{208}I_2O_6$ (2719.4): *m/z* (%) 2719.4 (100) $[M]^+$.

30

A solution of **29** (200 mg, 0.073 mmol) in pyridine (20 mL) was added to a suspension of CuCl (990 mg, 10.01 mmol) and $CuCl_2$ (200 mg, 1.49 mmol) in pyridine (40 mL) over 96 h. After the completion of the addition, the mixture was allowed to stir for an additional 4 d at room temperature and then was poured into CH_2Cl_2 (150 mL) and water (100 mL). The organic layer was extracted with water, NH_4OH solution (25%, 3 x 30 mL), water (30 mL), HOAc (10 %, 30 mL), water (30 mL), aqueous NaOH solution (30 %, 50 mL), and brine (30 mL) and dried over $MgSO_4$. After evaporation of the solvent to about 20 mL, the crude product was precipitated by the addition of methanol (100 mL) and collected by filtration. The product was purified by column chromatography (petroleumether-CH_2Cl_2 3:1, 2:1; R_f = 0.41, 2:1) to give **30** (185 mg, 0.068 mmol, 93 %) as a pale yellow solid. ^{1}H-NMR (250 MHz, CD_2Cl_2): δ = 8.05 (s, 2H), 7.75 (s, 4H), 7.67 (d, *J* = 8.5 Hz, 4H), 7.51 (d, *J* = 8.5 Hz, 4H), 7.33 (d, *J* = 8.2 Hz, 8H), 7.22 (s, 4H), 7.13 (d, *J* = 8.2 Hz, 8H), 7.07-6.98 (m, 8H), 6.71 (s, 8H), 4.89 (s, 4H), 3.95 (t, *J* = 6.6Hz, 8H), 1.83-1.68 (m, 8H), 1.50-1.14 (m, 122H), 0.90-0.79 (m, 12H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.7, 156.5, 150.7, 142.1, 141.8, 140.3, 138.5, 137.5, 132.7, 132.2, 130.9, 130.1, 128.1, 127.5, 126.9, 125.9, 124.7, 122.8, 120.8, 118.7, 118.5, 114.1, 96.6, 89.9, 88.3, 80.7, 73.9, 72.8, 68.4, 34.6, 31.9, 31.4, 29.7, 29.6, 29.6, 29.6, 29.4, 29.1, 25.9, 22.7,

14.1, 1,0 ppm; MS (MALDI TOF, matrix: DCTB) $C_{180}H_{204}I_2O_6$ (2715.4): *m/z* (%) 2715.4 (100) $[M]^+$.

31

To a solution of **30** (75 mg, 0.028 mmol), $Pd(PPh_3)Cl_2$ (10 mg, 0.014 mmol), CuI (5 mg, 0.05 mmol) und PPh_3 (10 mg, 0.04) in THF (5 mL) and piperidine (2 mL) was added **9** (36 mg, 0.07 mmol). After stirring for 15 h, the mixture was poured into Et_2O (100 mL) and H_2O (50 mL). The organic layer was separated, washed with water (2 x 50 mL) and brine (50 mL) and dried over $MgSO_4$. Product purification was performed by radial chromatography (petroleumether-CH_2Cl_2 3:1, 2:1; R_f = 0.65, 2:1) to give **31** (70 mg, 0.02 mmol, 72 %) as a pale yellow solid. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 7.83 (s, 2H), 7.74 (s, 4H), 7.67 (d, *J* = 8.5 Hz, 4H), 7.52 (d, *J* = 8.5Hz, 4H), 7.32 (d, *J* = 8.4 Hz, 8H), 7.19 (t, *J* = 1.3 Hz, 4H), 7.12 (d, *J* = 8.3 Hz, 8H), 7.04 (m, 4H), 6.98 (m, 4H), 6.95 (d, *J* = 4.3 Hz, 4H), 6.83-6.65 (m, 8H), 5.28 (s, 4H), 4.03 (t, *J* = 6.4 Hz, 4H), 3.96 (t, *J* = 6.5 Hz, 8H), 3.89 (t, *J* = 6.4 Hz, 4H), 3.75 (t, *J* = 6.7 Hz, 8H), 2.37 (t, *J* = 6.9 Hz, 4H), 1.86 (t, *J* = 6.6 Hz, 12H), 1.82-1.76 (m, 16H), 1.62-1.53 (m, 4H), 1.52-1.42 (m, 16H), 1.39 (s, 18H), 1.09-1.06 (m, 36H), 0.88 (t, *J* = 6.8 Hz, 24H), 0.85-0.75 (m, 24H), 0.08 (s, 12H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.7, 157.1, 154.3, 153.4, 150.7, 142.1, 141.8, 140.3, 137.9, 137.4, 132.6, 131.5, 130.9, 130.0, 128.2, 127.7, 126.8, 125.8, 124.7, 122.8, 121.0, 120.7, 119.8, 118.4, 118.3, 117.1, 115.9, 113.9, 113.6, 103.8, 95.3, 94.5, 93.1, 89.9, 88.4, 80.7, 74.0, 69.5, 69.2, 68.3, 67.9, 34.6, 31.9, 31.4, 25.9, 25.7, 25.6, 22.7, 22.6, 21.2, 20.7, 18.2, 17.9, 14.1, 14.0, 11.8, 9.5, 1.0 ppm; MS (MALDI TOF, matrix: DCTB) $C_{244}H_{300}N2O_{10}Si_2$ (3474.3): *m/z* (%) 3724.5 (15) $[M + DCTB]^+$, 3474.3 (100) $[M]^+$.

32

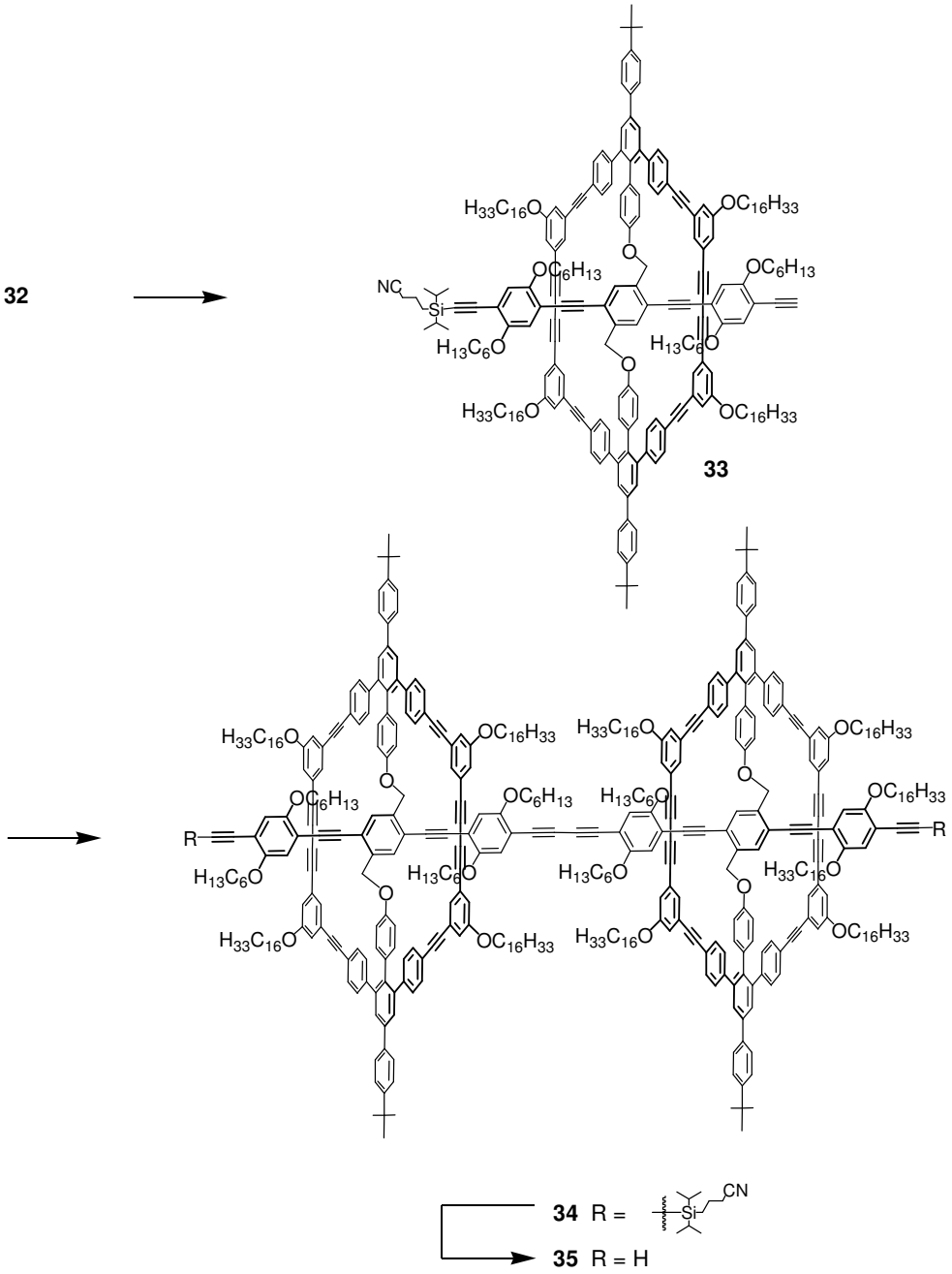
TBAF (1 M solution in THF; 0.3 mL, 0.3 mmol) was added to a solution of **31** (70 mg, 0.02 mmol) in THF (2 mL). After stirring for 10 h, the mixture was poured into CH_2Cl_2 (50 mL) and H_2O (20 mL). The organic layer was separated, washed with water (3 x 20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was filtered through a short silica gel column. Drying *in vacuo* gave **32** (25 mg, 0.08 mmol, 40 %) as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.87 (s, 2H), 7.75 (s,

4H), 7.68 (d, *J* = 8.4 Hz, 4H), 7.53 (d, *J* = 8.5 Hz, 4H), 7.32 (d, *J* = 8.3 Hz, 8H), 7.21 (s, 4H), 7.12 (d, *J* = 8.3 Hz, 8H), 7.04 (m, 4H), 7.00 (m, 4H), 6.98 (s, 2H), 6.95 (s, 2H), 6.76 (d, *J* = 8.7 Hz, 4H), 6.71 (d, *J* = 8.7 Hz, 4H), 5.28 (s, 4H), 4.03-3.94 (m, 16H), 3.28 (s, 2H), 1.83-1.69 (m, 16H), 1.52-1.16 (m, 146H), 0.91-0.78 (m, 24H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.7, 157.2, 154.1, 153.4, 150.7, 142.1, 141.8, 140.3, 138.1, 137.9, 137.5, 132.6, 131.6, 130.9, 130.4, 130.1, 129.5, 128.2, 127.6, 126.8, 125.8, 124.7, 122.9, 121.2, 120.8, 118.5, 118.4, 117.5, 116.7, 113.9, 113.2, 92.9, 91.9, 89.8, 88.4, 82.4, 80.7, 79.9, 73.9, 69.6, 69.5, 68.3, 67.8, 34.6, 31.9, 29.7, 29.6, 29.4, 29.1, 26.0, 25.8, 25.5, 22.7, 22.6, 22.5, 14.1, 14.0, 13.9, 1,0 ppm; MS (MALDI TOF, Matrix: DCTB) $C_{224}H_{262}O_{10}$ (3112.0): *m/z* (%) 3612.2 (5) $[M + 2\ DCTB]^+$, 3362.3 (15) $[M + DCTB]^+$, 3112.0 (100) $[M]^+$; GPC *vs.* PS: M_p = 4300 g/mol.

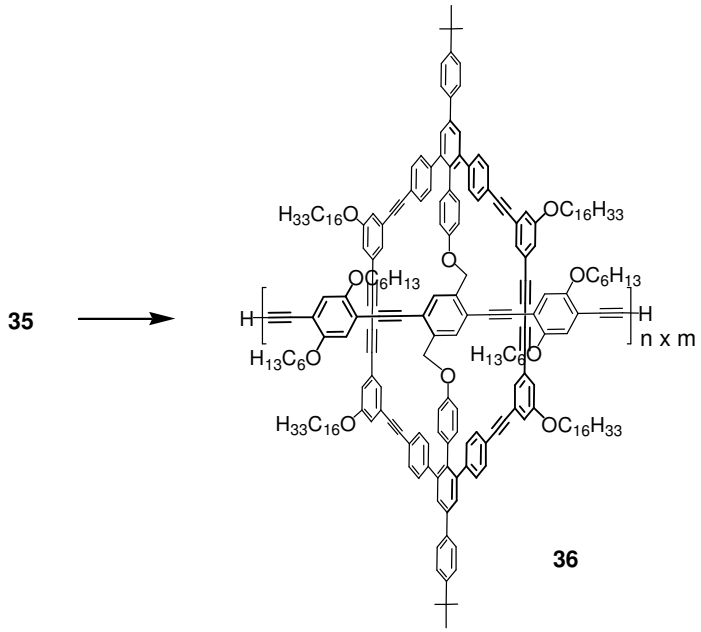
2

To a solution of **32** (17 mg, 0.005 mmol) in *o*-dichlorobenzene (1 mL) was added TMEDA (2 drops) and CuCl (5 mg, 0.05 mmol). Subsequently, a slow stream of dried air was piped into the solution via a canula for 30 min at the beginning of the reaction and after 12 h. After stirring for 24 h at 35 °C, the mixture was poured into CH_2Cl_2 (50 mL) and H_2O (30 mL). The organic layer was separated, washed with water (2 x 20 mL) and brine (20 mL) and dried over $MgSO_4$. The crude product was purified by filtration through a short silica gel filled column. After reducing the solvent volume *in vacuo* and adding MeOH the precipitate was collected by filtration. Drying *in vacuo* gave **2** (94 %, 16 mg) as a yellow solid. ^{1}H-NMR (250 MHz, CD_2Cl_2): δ = 7.86 (s, 2H), 7.78 (s, 4H), 7.73-7.66 (m, 4H), 7.55-7.50 (m, 4H), 7.38-7.30 (m, 8H), 7.20-7.11 (m, 12H), 7.08-6.99 (m, 8H), 6.91 (s, 2H), 6.83-6-66 (m, 10H), 5.33-5.25 (m, 4H), 4.05-3.97 (m, 16H), 1.83-1.65 (m, 16H), 1.48-1.12 (m, 146H) 0.90-0.74 (m, 24H) ppm; GPC *vs.* PS: M_w = 91400 g/mol, M_n = 42600 g/mol, D = 2.1.

5.3.2 Oligomers of 2



Scheme S5: Synthesis of the dimer of **2**.



Scheme S6: Synthesis of the oligomers of **2**.

33

To a solution of **32** [S1] (103 mg, 0,029 mmol) in THF (900 µL) and H_2O (44 µL) was added TBAF (1 M solution in THF; 27 µL, 0.027 mmol) at 0 °C. The mixture was stirred at room temperature, while conversion was followed by TLC. After 21 h the reaction was stopped by adding H_2O (1 mL) and the mixture was poured into CH_2Cl_2 (50 mL). The organic layer was separated, washed with H_2O (2 x 20 mL) and brine (20 mL) and dried over $MgSO_4$. Product isolation via radial chromatography (petroleumether-CH_2Cl_2, 1:4; R_f = 0.22 in 2:1) on silica gel gave **33** (28 mg, 29 %, $8.5 \cdot 10^{-3}$ mmol) as a yellow solid.^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.87 (s, 1H), 7.83 (s, 1H), 7.74 (s, 4H), 7.67 (d, $^3J_{HH}$= 8.2 Hz, 4H), 7.52 (d, $^3J_{HH}$= 8.4 Hz, 4H), 7.32 (d, $^3J_{HH}$= 8.2 Hz, 8H), 7.22 (s, 2H), 7.17 (s, 2H), 7.13-7.11 (d, $^3J_{HH}$= 8.3 Hz, 8H), 7.04 (dd, $^4J_{HH}$= 2.3 Hz, $^4J_{HH}$= 3.6 Hz, 4H), 7.00-6.97 (m, 6H), 6.94 (s, 1H), 6.89 (s, 1H), 6.81 -6.69 (m, 8H), 5.29 (s, 2H), 5.25 (s, 2H), 4.06-3.89 (m, 16H), 3.28 (s, 1H), 2.35 (t, $^3J_{HH}$= 6.9 Hz, 2H), 1.86-1.63 (m, 21H), 1.51-1.42 (m, 16H), 1.39 (s, 18H), 1.27 (s, 120H), 1.08-1.04 (m, 14H), 0.90-0.75 (m, 31H) ppm;^{13}C-NMR (400 MHz, $CDCl_3$): δ = 158.8, 158.7, 157.2, 154.3, 154.1, 153.4, 150.7, 142.1, 141.8, 140.3, 18.3, 137.9, 137.8, 137.5, 132.7, 132.6, 131.6, 130.9, 130.0, 128.2,

127.7, 127.6, 126.8, 125.9, 124.7, 124.6, 122.9, 122.8, 121.4, 120.9, 120.8, 120.7, 119.8, 118.5, 118.4, 117.3, 116.5, 116.1, 114.1, 113.8, 113.2, 95.4, 93.1, 92.9, 92.1, 91.9, 89.9, 88.4,88.3, 80.7, 80.6, 80.0, 74.0, 73.9, 69.7, 69.6, 69.4, 69.2, 68.4, 34.6, 31.9, 31.6, 31.5, 31.4, 29.7, 29.6, 29.4, 29.3, 29.1, 25.9, 25.8, 25.7, 25.5, 22.7, 21.2, 20.7, 18.2, 17.9, 14.1, 14.0, 13.9, 11.8, 9.5, 1.0 ppm; MS (MALDI TOF, matrix: DCTB) $C_{224}H_{261}O_{10}$, (3293.1): *m/z* (%) 3543.4 (13) $[M + DCTB]^+$; 3293.2 (100) $[M]^+$.

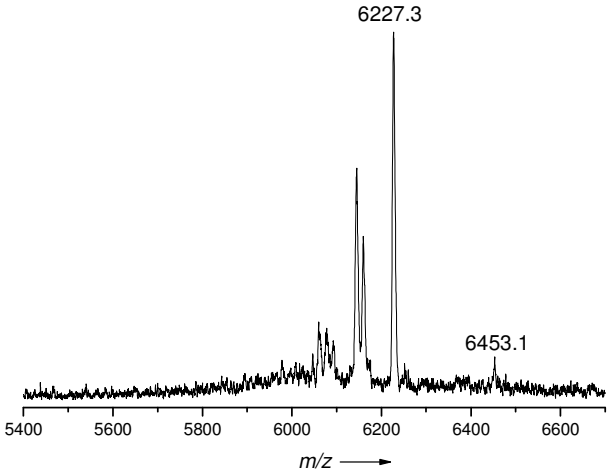
34

To a solution of **33** (0.026 g, 7.88 µmol) in CH_2Cl_2 (1 mL) was added TMEDA (1.76 µL, 0.01 mmol) and CuCl (1 mg, 0.01 mmol). Subsequently, a slow stream of dried air was piped into the solution via a canula for 30 min at the beginning of the reaction and after 12 h. After stirring for 3 d at room temperature, the mixture was poured into CH_2Cl_2 (50 mL) and H_2O (20 mL). The organic layer was separated, washed with H_2O (3 x 20 mL), HOAc solution (10 %, 20 mL), NH_3 solution (25 %, 20 mL), H_2O and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Product isolation via radial chromatography (petroleumether-CH_2Cl_2, 4:1; R_f = 0.24 in 2:1) on silica gel gave **34** (16 mg, 2.33 µmol, 59 %) as a yellow solid. M.p. 140.1-142.7 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.89 (s, 2H), 7.82 (s, 2H), 7.74 (d, $^4J_{HH}$= 1.1 Hz, 8H), 7.67 (dd, $^4J_{HH}$= 1.1 Hz, $^3J_{HH}$= 8.4 Hz, 8H), 7.52 (dd, $^4J_{HH}$= 1.7 Hz, $^3J_{HH}$= 8.4 Hz, 8H), 7.31 (dd, $^4J_{HH}$= 1.1 Hz, $^3J_{HH}$= 8.3 Hz, 16H), 7.24 (t, $^4J_{HH}$= 1.3 Hz, 4H), 7.15 (t, $^4J_{HH}$= 1.3 Hz, 4H), 7.11 (d, $^3J_{HH}$= 8.3 Hz, 16H), 7.04-7.02 (m, 12H), 6.99-6.98 (m, 8H), 6.96 (s, 2H), 6.94 (s, 2H), 6.84 (s, 2H), 6.8-6.61 (m, 16H), 5.30 (s, 4H), 5.24 (s, 4H), 4.07 (t, $^3J_{HH}$= 6.3 Hz, 4H), 3.99-3.94 (m, 24H), 3.90 (t, $^3J_{HH}$= 6.3 Hz, 4H), 2.34 (t, $^3J_{HH}$= 6.8 Hz, 4H), 1.84-1.72 (m, 41H), 1.69-1.64 (m, 4H), 1.46-1.39 (m, 82H), 1.31-1.22 (m, 266H), 1.07-1.04 (m, 28H), 0.89-0.74 (m, 66H) ppm; ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 158.8, 158.7, 157.1, 154.9, 154.3, 153.4, 150.7, 142.1, 141.1, 140.3, 138.0, 137.9, 137.5, 131.6, 130.9, 130.8, 130.1, 128.2, 127.7, 127.6, 126.8, 125.9, 124.7, 124.6, 122.9, 122.8, 122.7, 120.8, 119.8, 118.6, 118.5, 118.3, 116.1, 114.1, 113.7, 89.9, 89.8, 88.5, 88.3, 80.8, 74.1, 73.8, 69.7, 69.6, 69.3, 69.2, 68.3, 34.6, 31.9, 31.6,31.5, 31.4, 29.7, 19.6, 19.4, 29.3, 29.1, 26.0, 25.8, 25.7, 25.6, 22.7, 22.6, 21.2, 20.7, 18.2, 17.9, 14.1, 14.0, 11.8, 9.5 ppm; MS (MALDI TOF, matrix:

DCTB) $C_{468}H_{560}N_2O_{20}Si_2$ (6589.6): *m/z* (%) 6840.6 $[M + DCTB]^+$; 6772.6 $[M + DCTB–C_4H_6N]^+$; 6589.8 $[M]^+$; 6521.6 $[M - C_4H_6N]^+$.

35

TBAF (1 M solution in THF; 30 µL, 0.030 mmol) was added to a solution of **34** (50 mg, 0.008 mmol) in THF (2 mL). After stirring for 1 h the reaction was stopped by adding water (2 mL) and the mixture was poured into CH_2Cl_2 (50 mL). The organic layer was separated, washed with water (3 x 20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Product purification was performed by radial chromatography (petroleumether-CH_2Cl_2 1/1, R_f = 0.98) followed by recycling GPC. Drying *in vacuo* gave **35** (30 %, 15 mg, 0.0024 mmol) as a yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.89 – 7.84(m, 8H), 7.74 (s, 8H), 7.69-7.64 (m, 8H), 7.54-7.48 (m, 8H), 7.33-7.27 (m, 16H), 7.22-7.16(m, 8H), 7.13-7.07 (m, 16H), 7.04-7.01 (m, 12H), 7.00-6.94 (m, 12H), 6.88 (s, 2H), 6.80-6.59 (m, 16H), 5.30-5.22 (m, 8H), 4.04-3.89 (m, 32H), 3.27 (s, 2H), 1.82-1.67, 1.52-1.16 (m, 292H), 0.91-0.78 (m, 48H) ppm.; MS (MALDI TOF, Matrix: Dithranol) $C_{468}H_{562}O_{20}$ (6226.9): *m/z* (%) 6453.1 $[M+Dithranol]^+$ (13); 6227.3 $[M]^+$ (100).



36

To a solution of **35** (6.7 mg, 0.0011 mmol) in *o*-dichlorobenzene (0.7 mL) was added TMEDA (8 mg, 10 µL, 0.066 mmol) and CuCl (3 mg, 0.03 mmol). A slow stream of dried air was then piped into the solution via a canula for 30 min at the beginning of the reaction and after 12 h. After stirring for 45 h at room temperature, the mixture was poured into toluene (50 mL) and H_2O (20 mL). The organic layer was separated, washed with water (2 x 20 mL), NH_3 solution (25 %) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. After adding MeOH the precipitate was collected by filtration. Drying *in vacuo* gave **36** as a yellow solid.

n	**M_p (g/mol; GPC *vs* PS standard)**	**M (g/mol; calculated)**
2	8050	6227
4	14950	12452
6	22100	18677
8	29400	24902
10	36650	31127
12	45000	37352

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