Self-assembled monolayers of clamped oligo(phenylene-ethynylene-butadiynylene)s

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Supporting Information

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1 General information

1.1 Synthesis and separation

Reagents were purchased at reagent grade from commercial sources and used without further purification. All air-sensitive reactions were performed applying standard Schlenk techniques under Ar atmosphere and – if not otherwise indicated – using dry solvents (THF, piperidine, CH_2Cl_2). The latter were dried, distilled and stored under Ar according to standard methods. Workup solvents were either used in “p.a.” quality or purified by distillation. All solids and olis were dried overnight at r.t. under vacuum prior to characterization and further processing. ^1H and ^{13}C NMR spectra were recorded on Bruker AM 300, AM 400 and AM 500 spectrometers (300, 400 and 500 MHz for ^1H; 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 $CDCl_3$ (^1H: 7.26, ^{13}C: 77.0) and CD_2Cl_2 (^1H: 5.32, ^{13}C: 53.5). Deuterated solvents were obtained from Deutero GmbH, Germany. Mass spectra were measured on a Finnigan ThermoQuest MAT 95 XL (EI-MS), and a Bruker Daltronics autoflex TOF/TOF (MALDI-MS; matrix material: DCTB, no salts added). Thin layer chromatography was performed on silica gel coated aluminium plates (Macherey-Nagel, Alugramm SIL G/UV_{254}, 0.2 mm silica gel coating with fluorescence indicator). Column chromatography was performed using silica gel 60 M (Macherey-Nagel, 40-63 μm) as stationary phase. Gel permeation chromatography (GPC) was performed in THF (*p.a.* grade, stabilized with 2.5 ppm BHT) at r.t. 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 (Polymer Standards Service, Mainz, Germany, 10^3 Å, 5 μ, 20 mm x 300 mm) was employed. The system was operated at a flow rate of 6 mL/min.

1.2 Scanning tunneling microscopy (STM)

Scanning tunneling microscopy (STM) measurements were performed under ambient conditions at the 1,2,4-trichlorobenzene (TCB)/HOPG interface, applying 10^{-4} M–10^{-6} M solutions of the respective oligomer. In some cases the adlayers were thermally annealed at 60–80 °C for ≤ 1 min. The experimental setup consists of an Agilent 5500 AFM/STM, placed on a Halcyonics actively damping microscopy workstation and being isolated with a homebuilt acoustic damping box. Mechanically cut Pt/Ir (80/20) tips were used and further modified *in situ* by applying short voltage pulses. Highly oriented pyrolytic graphite (HOPG) substrates were obtained from SPI Inc. in SPI-II quality and freshly cleaved before each experiment. STM images were *in situ* calibrated by subsequent immediate acquisition of an additional image at reduced bias voltage, so that the atomic lattice of HOPG is visible and can be used as a calibration grid. Respective data processing was performed using the SPIP 5 (Image Metrology) software package. All molecular models shown are based on force-field geometry optimized backbone structures (with a graphene layer as interaction partner), using Spartan `08 (Wavefunction Inc.).

1.3 Molecular modeling

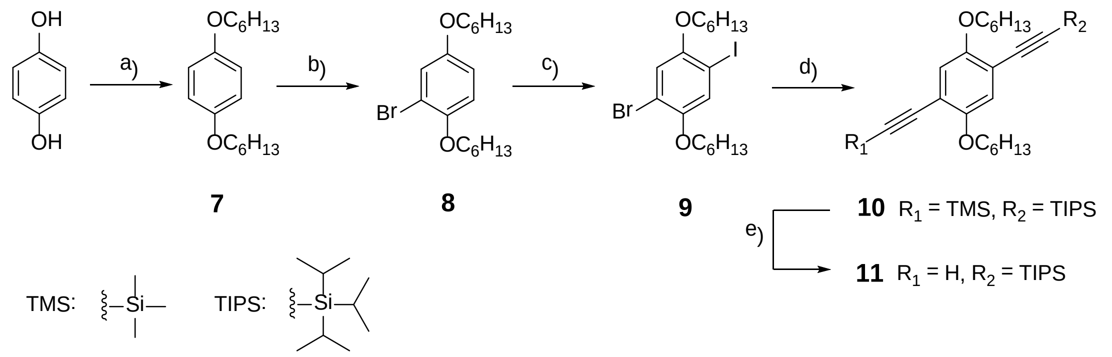
Molecular modeling was performed using Spartan ’08 (Wavefunction, Inc.). Equilibrium geometries of the backbone structures were obtained using molecular mechanics (based on the Merck Molecular Force Field (MMFF)) and a graphene monolayer with fixed atom positions as interaction partner. Alkoxy sidechains were subsequently attached with the alkoxy-backbone angles as observed by STM.

The molecular models shown in Figure 4c and f, Main Text, were obtained by force field-based geometry optimization on HOPG including the relaxation of alkoxy substituents.

2 Synthetical strategy

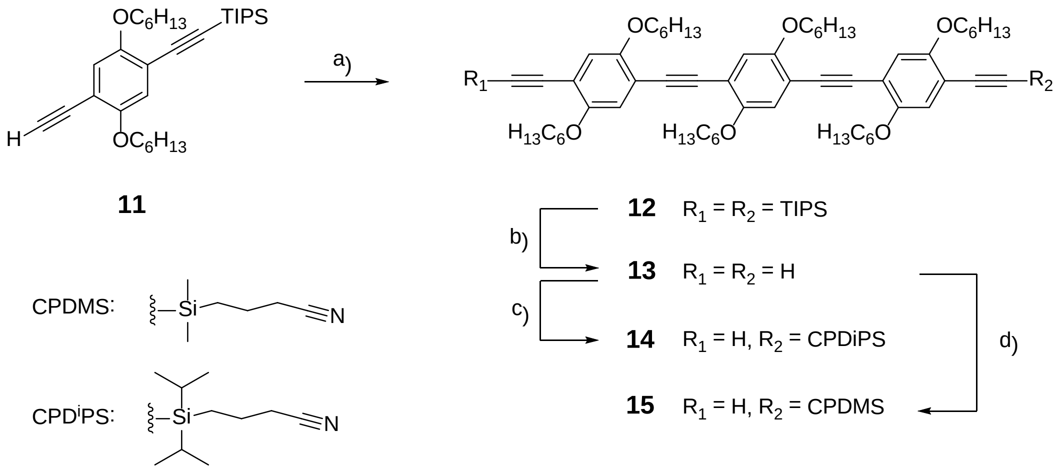
2.1 Synthesis of symmetrically and asymmetrically substituted oPEs and oPEBs

The synthesis of symmetrically and asymmetrically substituted oligo(phenylene-ethynylenes) (oPEs) and oligo(phenylene-ethynylene-butadiynylenes) (oPEBs) starts with the preparation of the monoprotected bisacetylene **11**, which is further required for the preparation of higher oligomers. The reaction sequence starts with a Williamson ether synthesis of the commercial available hydroquinone and 1-bromohexane, introducing the hexyloxy sidechains for reasons of solubility, followed by a monobromination and a subsequent iodination to obtain **9**. The bromine and iodine atoms in **9** offer the possibility of a selective Sonogashira-Hagihara reaction, which is applied in the next step. The trimethylsilyl (TMS)-protected acetylene as well as the triisopropylsilyl (TIPS)-protected acetylene are introduced in a one pot reaction, obtaining the asymmetrically substituted bisacetylene **10** in good yields. Finally the TMS group is deprotected in the presence of potassium carbonate and methanol, while the TIPS group is stable under these conditions.



Scheme S1: a) 1-bromohexane, K_2CO_3, KI, DMF, 70 °C, 80 %, b) Br_2, NaOAc, HOAc, $CHCl_3$, 30 °C, 52 %, c) I_2, KIO_3, H_2SO_4 (conc.), H_2O, HOAc, CCl_4, reflux, 66 %, d) TIPS-acetylene, $Pd(PPh_3)Cl_2$, CuI, PPh_3, piperidine, THF, r.t., TMS-acetylene, 50 °C, 76 %, e) K_2CO_3, methanol, THF, r.t., 83 %.

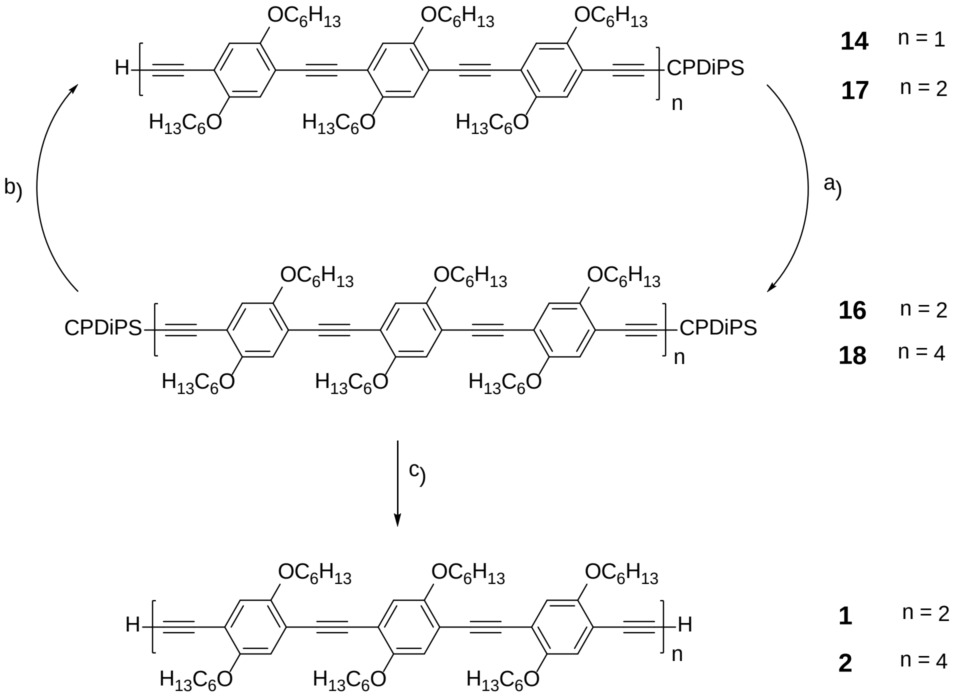
Under standard Sonogashira-Hagihara conditions, **11** and 1,4-bis(hexyloxy)-2,5-diiodobenzene are reacted to the TIPS protected *p*PE **12**, which is further treated with a 1 M solution of TBAF in THF and deprotected to give *p*PE trimer **13**. **13** is deprotonated with ethylmagnesium bromide and reacted with 3-(cyanopropyl)dimethylsilyl (CPDMS)- and 3-(cyanopropyl)diisopropylsilyl (CPD^{i}PS)-chloride in a statistical reaction to introduce the new silyl protecting group.



Scheme S2: a) 1,4-bis(hexyloxy)-2,5-diiodobenzen, Pd(PPh$_3$)Cl$_2$, CuI, PPh$_3$, piperidine, THF, r.t. 96 %, b) TBAF (1M in THF), THF, r.t., 96 %, c) ethylmagnesium bromide, CPD^{i}PS-Cl, THF, r.t., 49 %, d) ethylmagnesium bromide, CPDMS-Cl, r.t. 33 %.

The monoprotected bisacetylenes **14** and **15** are easily separated from the starting material and the doubly protected bisacetylene by column chromatogaphy.[1] The nitrile containing CPDMS and CPDiPS protecting groups offer the advantage of a higher polarity compared to their analogous TMS and TIPS groups and therefore the possibility to isolate the monoprotected compound on large scale.

Higher monodisperse oligomers can be build up from the asymmetrically substituted monomer unit **14** in a sequence of a copper(I) mediated homocoupling reaction, creating a butadiynyl bridge and a subsequent statistical deprotection.[2]

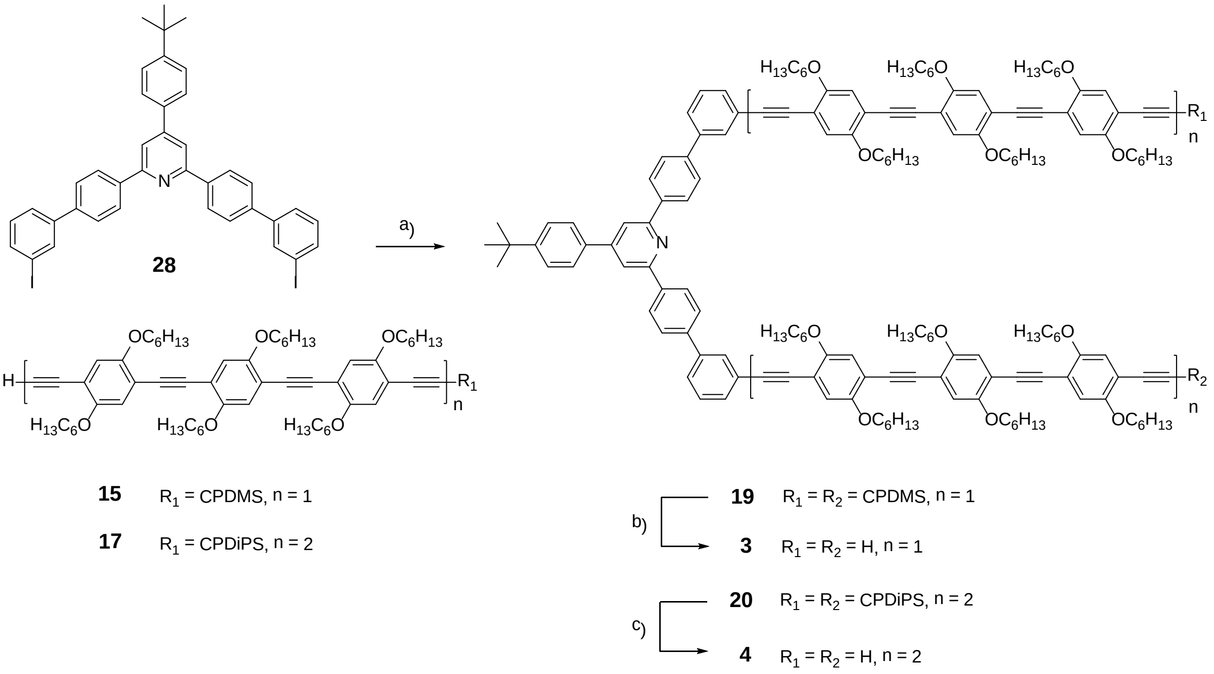


Scheme S3: a) CuCl, TMEDA, air, dichloromethane, 30 °C, **16**: 85 %, **18**: 90 %, b) TBAF, 5 vol% water, THF, r.t., 45 %, c) TBAF, THF, r.t., **1**: 90 %, **2**: 84 %.

The CPDiPS-diprotected *p*PEB **16** is build up in a homocoupling reaction under standard Hay conditions, using copper(I) chloride, TMEDA and air. **16** is treated with 1 eq of a 1 M solution of TBAF in THF in the presence of 5 vol% water to deprotect the bisacetylene in a statistical reaction. The reaction rate is significantly slowed down by the addition of water; this offers the possibility to monitor the progress of the reaction by thin layer chromatography. At the highest concentration of **17**, the reaction mixture is diluted by further addition of water. The *p*PEB **18** is prepared as well under Glaser-Hay conditions. **16** and **18** are treated with a slight excess of TBAF to obtain the deprotected oPEBs **1** and **2** in good yields.

2.2 Synthesis of “half-rings”

The so called “half-rings” are prepared in a Sonogashira-Hagihara reaction under standard conditions by coupling the molecular clamp **28** and the asymmetrically substituted bisacetylenes **14** and **17**, respectively. The synthesis of the molecular clamp is described elsewhere and will not be discussed here.[3]



Scheme S4: a) $Pd(PPh_3)Cl_2$, CuI, PPh_3, piperidine, THF, 50 °C, **19**: 94 %, **20**: 76 %, b) TBAF (1 M in THF), THF, r.t., 77 %, c) TBAF (1 M in THF), THF, r.t., 67 %.

Again, the deprotection of the silyl groups is performed in the presence of TBAF and the acetylene terminated “half-rings” are obtained in good yields.

2.3 Synthesis of the macrocycles

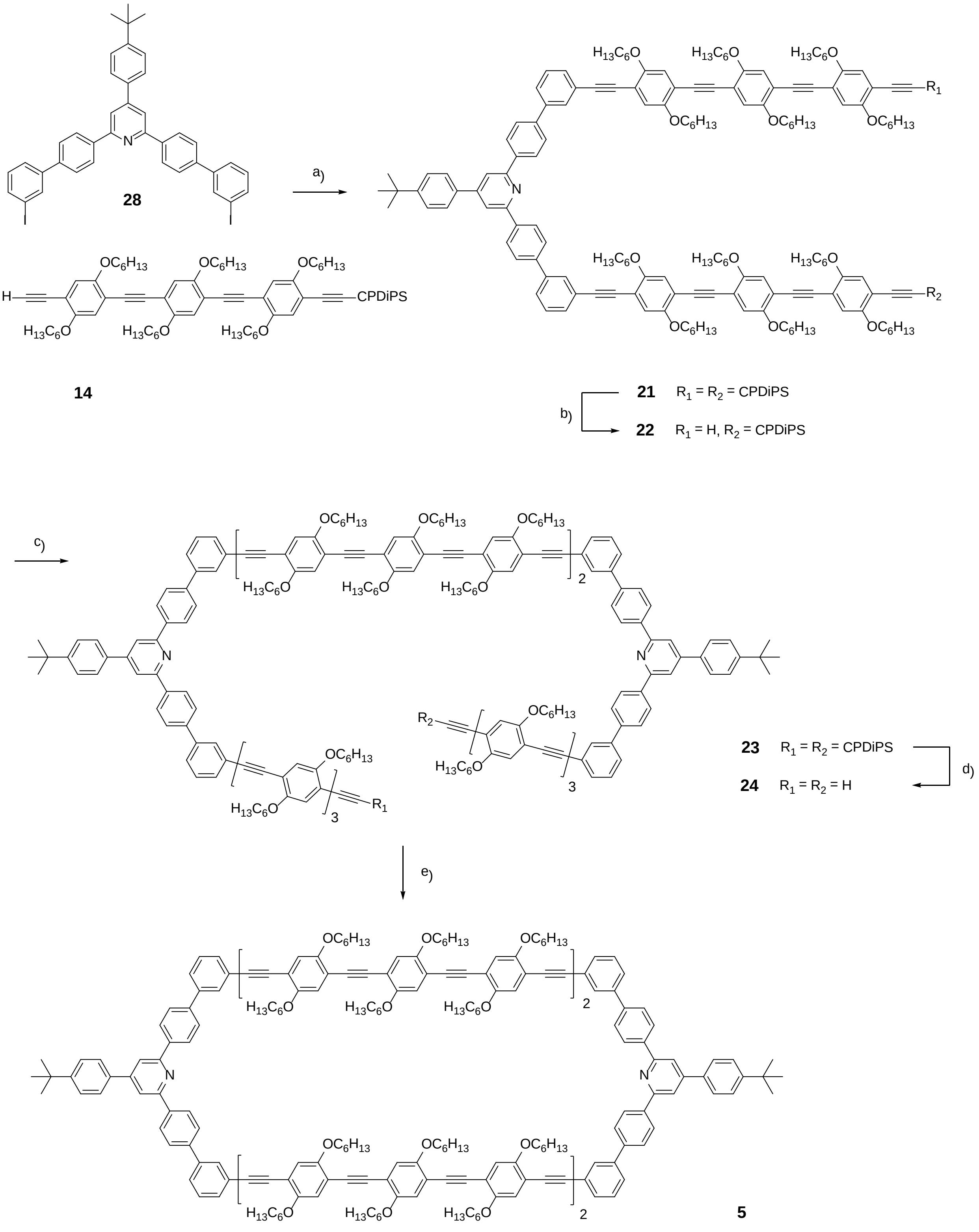
The performed syntheses towards the macrocyclic structures **5** and **6** are based on two synthetical strategies and is described in scheme S5 and S6. A final intramolecular homocoupling reaction of the acyclic dimer to the cyclic dimer is both routs in common.

Synthesis of **5**

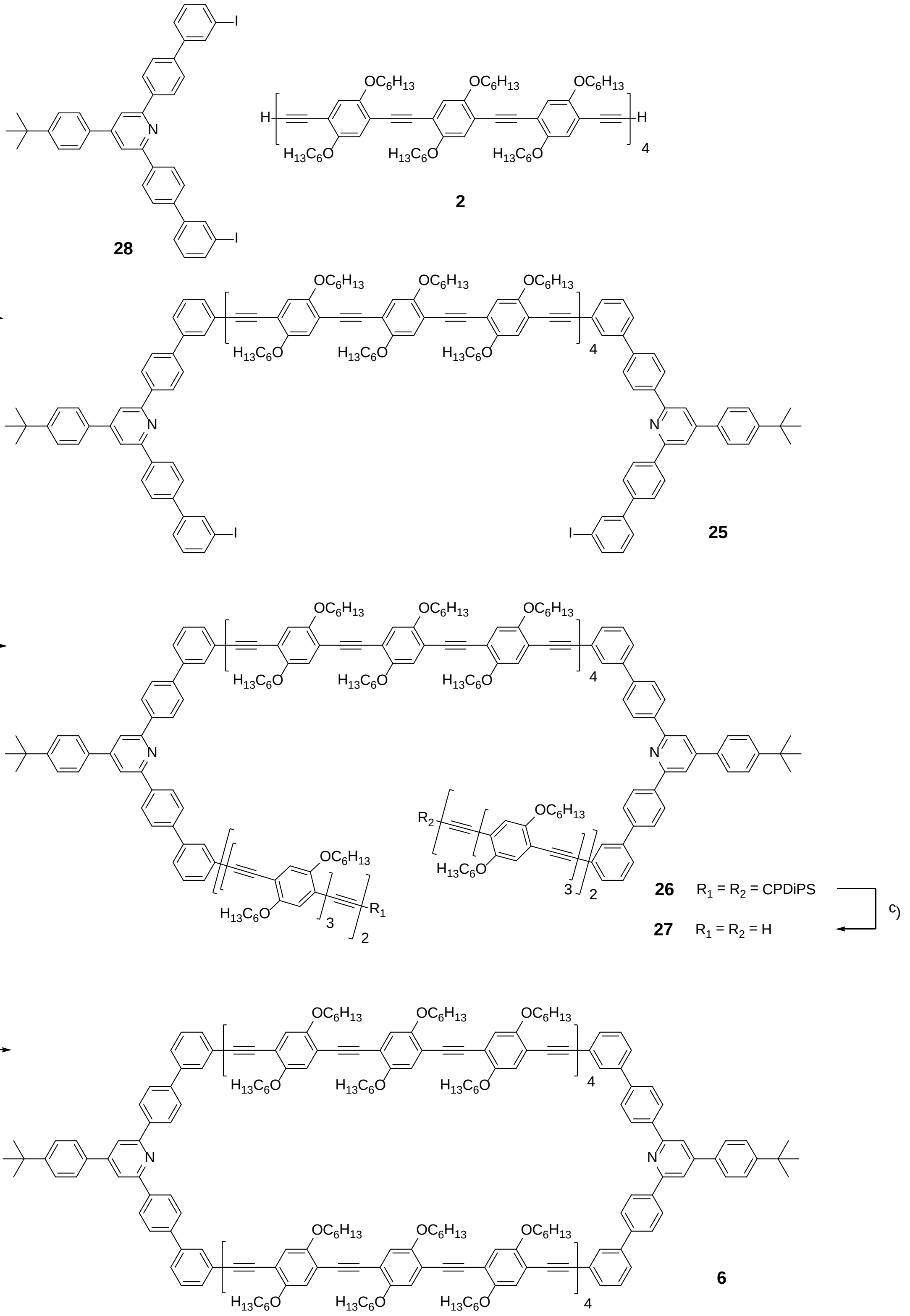
The sequence starts with the synthesis of the CPDiPS-protected "half-ring" in a Sonogashira-Hagihara reaction. Again, the CPDiPS protecting group offers the possibility to deprotect the compound in a statistical reaction in the presence of water to slow down the reaction rate. The progress of the reaction is monitored by thin layer chromatography and stopped at the highest concentration by further addition of water. After separation of the monoproteced half-ring from the sideproducts (fully deprotected half-ring and the starting material), **22** is obtained and subsequently reacted in a palladium catalyzed homocoupling reaction to the acyclic dimer **23**. After a deprotection of the CPDiPS groups in the presence of TBAF the final intramolecular ring closure reaction is performed. The bisacetylene bridge is created in a Glaser-reaction under palladium catalyzed conditions and the macrocycle **5** is obtained in 57 % yield.

Synthesis of **6**

The synthesis of **6** also requires the appropriate acyclic dimer **26** as intermediate. Its synthesis can be accomplished in just two steps. The sequence begins with a Sonogashira-Hagihara reaction of the monodisperse tetrameric oPEB **2** and an excess of the molecular clamp. An excess of the clamp is applied first to ensure a complete conversion of the bisacetylene ends in the Sonogashira-reaction and second to suppress the formation of higher oligomers. In the next step **25** is reacted with the monoprotected dimeric oPEB **17** and the acyclic dimer is seperated by recycling GPC from the side products. After cleaving the CPDiPS-groups with TBAF, the final intramolecular ring closure reaction is performed under palladium catalyzed homocoupling conditions.



Scheme S5: a) $Pd(PPh_3)Cl_2$, CuI, PPh_3, piperidine, THF, r.t., 80 %, b) TBAF (1 M in THF), 5 vol% H_2O, r.t., 39 %, c) $Pd(PPh_3)Cl_2$, CuI, I_2, diisopropylamine, THF, r.t., 92 %, d) TBAF (1 M in THF), THF, r.t., 62 %, e) $Pd(PPh_3)Cl_2$, CuI, I_2, diisopropylamine, THF, 55 °C, 57 %.

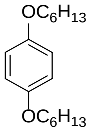


Scheme S6: $Pd(PPh_3)Cl_2$, CuI, PPh_3, piperidine, THF, r.t., 59 %, b) $Pd(PPh_3)Cl_2$, CuI, PPh_3, piperidine, THF, r.t., 46 %, c) TBAF (1 M in THF), THF, r.t. 99 %, d) $Pd(PPh_3)Cl_2$, CuI, I_2, diisopropylamine, THF, 55 °C, 20 %.

3 Synthesis

The experimental procedures are in the same order they appear in the schemes.

1,4-Bis(hexyloxy)benzene (**7**)



1-Bromohexane is added to a suspension of hydroquinone (4.00 g, 36.36 mmol), potassium carbonate (25.13 g, 181.82 mmol) and potassium iodide (0.30 g, 1.82 mmol) in DMF (70 mL). The reaction mixture is stirred over night at 70 °C and further 5 h at 80 °C. After cooling to r.t. it is diluted with water and all solids dissolved. The aqueous phase is extracted three times with dichloromethane and the combined organic phases are washed with brine and dried over magnesium sulfate. After removing the solvent under reduced pressure a dark brown solid is obtained and purified by recrystallization from methanol. 8.10 g (29.08 mmol, 80 %) of **1** are isolated as a white solid.

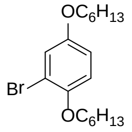
Sum formula: $C_{18}H_{30}O_2$, molecular weight: 278.43 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 6.82 (s, 4H), 3.90 (t, $^3J_{HH}$ = 6.4 Hz, 4H), 1.75 (q, $^3J_{HH}$ = 6.4 Hz, 4H), 1.48-1.41 (m, 4H), 1.35-1.31 (m, 8H), 0.92-0.89 (m, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$, RT) δ [ppm]: 153.19, 115.38, 68.66, 31.61, 29.37, 25.74, 22.61, 14.03.

MS (EI, 70 eV), m/z (%): 278.3 (30) $[M]^{+\cdot}$, 194.2 (15) $[M-C_6H_{12}]^+$, 110.1 (100) $[M-2C_6H_{12}]^{+\cdot}$.

2-Bromo-1,4-bis(hexyloxy)benzene (**8**)



7 (7.00 g, 25.14 mmol) and sodium acetate (2.00 g, 24.39 mmol) are dissolved in acetic acid (30 mL) and chloroform (5 mL) and heated to 30 °C. A solution of bromine (1.28 mL, 24.89 mmol) in acetic acid (2 mL) is slowly added and the reaction mixture is stirred over night at r.t. Water is added and the aqueous phase is extracted three times with chloroform. The combined organic layers are washed with $NaHCO_3$-solution (sat.), water and brine and dried over magnesium sulfate. The solvent is removed under reduced pressure and a brown liquid is obtained as crude product, which is purified by column chromatography (PE:DCM 5:1, R_f = 0.44). **8** (4.66 g, 13.07 mmol) is yielded as a colorless liquid in 52 % yield.

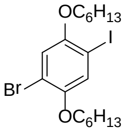
Sum formula: $C_{18}H_{29}O_2Br$, molecular weight: 357.33 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 7.11 (d, $^4J_{HH}$ = 2.8 Hz, 1H), 6.82 (d, $^3J_{HH}$ = 8.8 Hz, 1H), 6.78 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.8 Hz, 1H), 3.95 (t, $^3J_{HH}$ = 6.4 Hz, 2H), 3.88 (t, $^3J_{HH}$ = 6.4 Hz, 2H), 1.83-1.70 (m, 4H), 1.53-1.40 (m, 4H), 1.37-1.31 (m, 8H), 0.92-0.89 (m, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$, RT) δ [ppm]: 153.57, 149.75, 119.47, 114.71, 114.36, 112.77, 70.21, 68.81, 31.55, 29.23, 25.66, 22.58, 14.01.

MS (EI, 70 eV), m/z (%): 356.1 (20) $[M]^{+\cdot}$, 272.0 (25) $[M-C_6H_{12}]^+$, 187.9 (100) $[M-2C_6H_{12}]^{+\cdot}$, 110.0 (5) $[M-2C_6H_{12}-Br]^+$.

2-Bromo-5-iodo-1,4-bis(hexyloxy)benzene (**9**)



Conc. sulfuric acid (95-97 %, 0.82 mL), water (0.50 mL), potassium iodate (0.86 g, 4.02 mmol) and iodine (2.34 g, 9.21 mmol) are added to a solution of **8** (3.50 g, 9.80 mmol) in acetic acid (14 mL) and tetrachloromethane (4 mL). The reaction mixture is heated to reflux for 5.5 h, quenched with sodium hydroxide solution (10 %) after cooling to r.t. and poured onto ice. The aqueous phase is extracted four times with chloroform and the combined organic layers are washed with sodium hydroxide solution (10 %), water and brine and dried over magnesium sulfate. The solvent is removed under reduced pressure and the brown crude product is purified by column chromatography (PE:DCM 5:1, R_f = 0.38) and subsequently recrystallized from ethanol to obtain **9** (3.12 g, 6.46 mmol) as a white solid in 66 % yield.

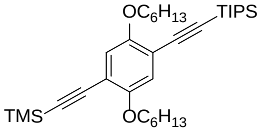
Sum formula: $C_{18}H_{28}O_2BrI$, molecular weight: 483.22 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$, RT) δ [ppm]: 7.28 (s, 1H), 7.98 (s, 1H), 3.95-3.92 (m, 4H), 1.83-1.76 (m, 4H), 1.53-1.45 (m, 4H), 1.37-1.32 (m, 8H), 0.93-0.89 (m, 6H).

^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 152.49, 150.38, 124.19, 117.03, 112.47, 84.75, 70.34, 70.28, 31.47, 31.45, 29.10, 29.06, 25.69, 25.60, 22.57, 14.03.

MS (EI, 70 eV), m/z (%): 482.0 (25) $[M]^{+\cdot}$, 397.9 (15) $[M-C_6H_{12}]^+$, 313.8 (100) $[M-2C_6H_{12}]^{+\cdot}$, 187.9 (5) $[M-2C_6H_{12}-I]^+$.

1,4-Bis(hexyloxy)-2-(2-triisopropylsilylethynyl)-5-(2-trimethylsilylethynyl)benzene (**10**)



9 (6.70 g, 13.87 mmol), $Pd(PPh_3)_2Cl_2$ (0.48 g, 0.68 mmol), copper(I) iodid (0.06 g, 0.32 mmol) and triphenylphosphine (0.13 g, 0.50 mmol) are dissolved in piperidine (30 mL) and THF (10 mL). Triisopropylsilylacetylene (2.9 mL, 12.93 mmol) is added and the mixture is stirred overnight, while a white solid is precipitating. Subsequently trimethylsilylacetylene (8.6 mL, 60.85 mmol) is added and the reaction mixture is stirred for 16 h at 50 °C. After cooling to r.t., dichloromethane is added and the organic phase is washed with water, sulfuric acid (10 %), water and brine and dried over magnesium sulfate. The solvent is removed under reduced pressure and the crude product is purified by column chromatography (PE:DCM 5:1, R_f = 0.62) to obtain **10** (5.84 g, 10.72 mmol) as slightly yellow solid in 76 % yield.

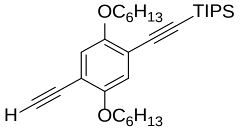
Sum formula: $C_{34}H_{58}O_2Si_2$, molecular weight: 554.99 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 6.88 (s, 1H), 6.87 (s, 1H), 3.97-3.91 (m, 4H), 1.82-1.72 (m, 4H), 1.55-1.43 (m, 4H), 1.35-1.23 (m, 8H), 1.14 (m, 21H), 0.92-0.88 (m, 6H), 0.25 (s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$, RT) δ [ppm]: 154.16, 153.90, 117.68, 116.72, 114.24, 113.77, 102.90, 101.22, 99.78, 96.45, 69.62, 69.25, 31.66, 31.62, 29.39, 29.33, 25.83, 25.70, 22.63, 18.70, 14.07, 11.38, -0.04.

MS (EI, 70 eV), m/z (%): 554.3 (100) $[M]^{+\cdot}$, 511.3 (15) $[M-C_3H_7]^+$, 469.2 (5) $[M-C_6H_{13}]^+$, 427.2 (25) $[M-C_3H_7-C_6H_{12}]^+$, 385.1 (15) $[M-C_6H_{13}-C_6H_{12}]^+$, 343.1 (30) $[M-C_3H_7-C_6H_{12}-C_6H_{12}]^+$, 73.0 (20) $[Si(CH_3)_3]^+$.

1,4-Bis(hexyloxy)-2-ethynyl-5-(2-triisopropylsilylethynyl)benzene (**11**)



Potassium carbonate (14.24 g, 102.51 mmol) is added to a solution of **10** (5.69 g, 10.25 mmol) in THF (80 mL) and methanol (40 mL) and the mixture is stirred for 3 h at r.t. The reaction mixture is diluted with water and all solids dissolved. The aqueous layer is extracted three times with dichloromethane. The combined organic layers are washed with brine and dried over magnesium sulfate. The solvent is removed under reduced pressure and a yellow crude product is obtained, which is further purified by column chromatography (PE:DCM 5:1, $R_f = 0.50$). **11** (4.14 g, 8.58 mmol) is isolated as yellow solid in 83 % yield.

Sum formula: $C_{31}H_{50}O_2Si$, molecular weight: 482.81 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 6.91 (s, 1H), 6.91 (s, 1H), 3.98 (t, $^3J_{HH}$ = 6.4 Hz, 2H), 3.93 (t, $^3J_{HH}$ = 6.4 Hz, 2H), 3.31 (s, 1H), 1.83-1.73 (m, 4H), 1.52-1.43 (m, 4H), 1.36-1.29 (m, 8H), 1.14 (m, 21H), 0.92-0.88 (m, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$, RT) δ [ppm]: 154.13, 153.90, 117.66, 117.21, 114.65, 112.60, 102.71, 96.65, 82.09, 80.07, 69.75, 69.30, 31.66, 31.53, 29.38, 29.14, 25.83, 25.58, 22.62, 22.58, 18.69, 14.07, 14.01, 11.37.

MS (EI, 70 eV), m/z (%): 482.4 (100) $[M]^{+\cdot}$, 439.3 (30) $[M-C_3H_7]^+$, 397.3 (5) $[M-C_6H_{13}]^+$, 355.2 (45) $[M-C_3H_7-C_6H_{12}]^+$, 313.2 (25) $[M-C_6H_{13}-C_6H_{12}]^+$, 271.2 (30) $[M-C_3H_7-C_6H_{12}-C_6H_{12}]^+$, 43.0 (40) $[C_3H_7]^+$.

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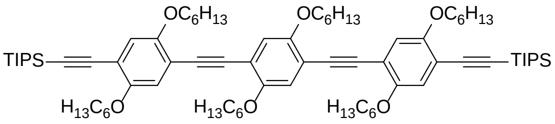


1,4-Bis(hexyloxy)-2,5-diiodobenzene[4] (1.93 g, 3.64 mmol), $Pd(PPh_3)_2Cl_2$ (0.08 g, 0.11 mmol), copper(I) iodide (0.04 g, 0.18 mmol) and triphenylphosphine (0.08 g, 0.29 mmol) are dissolved in THF (10 mL) and piperidine (20 mL). **11** (4.04 g, 8.37 mmol) is added to the reaction mixture and stirred over night at r.t. After diluting with dichloromethane, the organic layer is washed with water, sulfuric acid (10 %), water and brine and dried over magnesium sulfate. The solvent is removed under reduced pressure and the product is isolated by column chromatography (PE:DCM 2:1, $R_f = 0.62$). 4.32 g (3.48 mmol, 96 %) of **12** are obtained as a yellow solid.

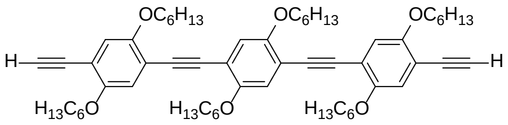
Sum formula: $C_{80}H_{126}O_6Si_2$, molecular weight: 1240.02 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 7.00 (s, 2H), 6.94 (s, 2H), 6.93 (s, 2H), 4.03 (t,$^3J_{HH}$ = 6.4 Hz, 8H), 3.95 (t, $^3J_{HH}$ = 6.4 Hz, 4H), 1.87-1.74 (m, 12H), 1.53-1.45 (m, 12H), 1.34-1.30 (m, 24H), 1.15 (m, 42H), 0.92-0.87 (m, 18H).

^{13}C-NMR (75 MHz, $CDCl_3$, RT) δ [ppm]: 154.33, 153.48, 153.24, 117.93, 117.22, 116.56, 114.38, 114.27, 113.99, 103.03, 96.49, 91.58, 91.34, 69.85, 69.66, 69.25, 31.69, 31.62, 29.44,29.30, 25.86, 25.66, 22.63, 18.71, 14.07, 14.03, 11.39.

MS (MALDI-pos, DCTB) m/z (%): 1238.9 (100) $[M]^{+\cdot}$.

13



12 (4.32 mg, 3.48 mmol) is dissolved in THF (80 mL) and a 1 M solution of TBAF in THF (8.72 mL, 8.72 mmol) is slowly added. After 2.5 h stirring at r.t. the reaction mixture is diluted with water and the aqueous phase is extracted three times with dichloromethane. The combined organic layers are washed with water and brine and dried over magnesium sulfate. The solvent is removed under reduced pressure and the crude product is precipitated as yellow solid with methanol from THF and filtered off. **13** (3.10 g, 3.34 mmol) is obtained in 96 % yield.

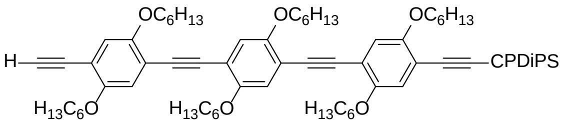
Sum formula: $C_{62}H_{86}O_6$, molecular weight: 927.34 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 7.00 (s, 2H), 6.99 (s, 2H), 6.97 (s, 2H), 4.04-3.98 (m, 12H), 3.34 (s, 2H), 1.87-1.78 (m, 12H), 1.53-1.45 (m, 12H), 1.36-1.32 (m, 24H), 0.93-0.86 (m, 18H).

^{13}C-NMR (100 MHz, $CDCl_3$, RT) δ [ppm]: 154.14, 153.51, 153.30, 117.95, 117.26, 117.05, 114.95, 114.26, 112.57, 91.54, 91.23, 82.27, 80.04, 69.73, 69.67, 69.61, 31.59, 31.53, 29.29, 29.24, 29.14, 25.66, 25.60, 22.62, 22.58, 14.02.

MS (MALDI-pos, DCTB) m/z (%): 926.6 (100) $[M]^{+\cdot}$, 1176.7 (5) $[M + DCTB]^{+\cdot}$.

14



13 (1.46 g, 1.58 mmol) is dissolved in THF (40 mL) and a 1 M solution of ethylmagnesium bromide in THF (2.20 mL, 2.20 mmol) is added. After 1 h stirring at r.t. CPDiPS-Cl (0.50 mL, 2.21 mmol) is added and the progress of the reaction is monitored by thin layer chromatography. After about 1 h the reaction is diluted with water and dichloromethane and the organic phase is extracted three times with dichloromethane. The combined organic phases are washed with sulfuric acid (10 %), water and brine and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the crude product is purified by column chromatography (PE:DCM 1:1, $R_f = 0.33$). **14** (0.86 g, 0.78 mmol) is obtained as yellow solid in 49 % yield.

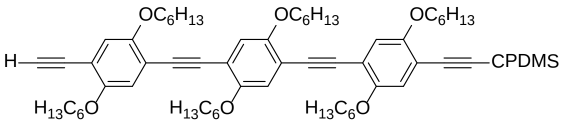
Sum formula: $C_{72}H_{105}NO_6Si$, molecular weight: 1108.69 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 7.00 (s, 1H), 7.00 (s, 1H), 6.99 (s, 1H), 6.97 (s, 1H), 6.95 (s, 1H), 6.93 (s, 1H), 4.04-3.94 (m, 12H), 3.34 (s, 1H), 2.43 (t, $^3J_{HH}$ = 6.8 Hz, 2H), 1.93-1.75 (m, 14H), 1.53-1.45 (m, 12H), 1.38-1.30 (m, 24H), 1.14-1.10 (m, 14H), 0.93-0.82 (m, 20H).

^{13}C-NMR (100 MHz, $CDCl_3$, RT) δ [ppm]: 154.28, 154.11, 153.48, 153.45, 153.27, 153.20, 119.79, 117.88, 117.70, 117.17, 116.99, 116.36, 114.91, 114.74, 114.24, 114.17, 113.21, 112.51, 103.91, 95.12, 91.54, 91.46, 91.22, 82.28, 80.03, 69.79, 69.69, 69.62, 69.58, 69.10, 31.63, 31.60, 31.53, 25.79, 25.66, 25.64, 25.60, 22.65, 22.63, 22.58, 21.28, 20.77, 18.23, 17.99, 14.07, 14.03, 11.79, 9.63.

MS (MALDI-pos, DCTB) m/z (%): 1107.8 (100) $[M]^{+\cdot}$, 1357.9 (5) $[M + DCTB]^{+\cdot}$.

15



13 (1.37 g, 1.47 mmol) is dissolved in THF (30 mL) and a 1 M solution of ethylmagnesium bromide in THF (1.47 mL, 1.47 mmol) is added. After 2 h stirring at r.t. CPDMS-Cl (0.24 mL, 1.47 mmol) is added and the reaction mixture is stirred overnight. It is diluted with water and the aqueous phase is extracted three times with dichloromethane. The combined organic phases are washed with sulfuric acid (10 %), water and brine and dried over magnesium sulfate. After removing the solvent under reduced pressure an orange oil is obtained as crude product, which is further purified by column chromatography (PE:DCM 1:1 R_f = 0.33). **15** (0.51 g, 0.49 mmol) is isolated as yellow solid in 33 % yield.

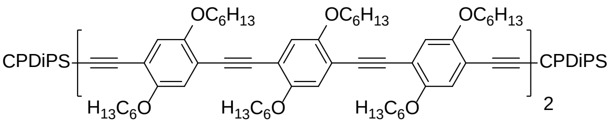
Sum formula: $C_{68}H_{97}NO_6Si$, molecular weight: 1052.59 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 7.00 (m, 2H), 6.99 (s, 1H), 6.97 (s, 1H), 6.96 (s, 1H), 6.93 (s, 1H), 4.03-3.95 (m, 12H), 3.34 (s, 1H), 2.44 (t, $^3J_{HH}$= 7.0 Hz, 2H), 1.90-1.77 (m, 14H), 1.53-1.47 (m, 12H), 1.35-1.32 (m, 24H), 0.93-0.84 (m, 20H), 0.27 (s, 6H).

^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 154.13, 154.11, 153.47, 153.46, 153.27, 153.26, 119.73, 117.88, 117.38, 117.17, 116.99, 116.70, 114.90, 114.84, 114.20, 113.04, 112.51, 102.60, 97.78, 91.67, 91.53, 91.34, 91.23, 82.29, 80.02, 69.69, 69.68, 69.62, 69.58, 69.22, 31.60, 31.52, 29.28, 29.26, 29.25, 29.22, 29.12, 25.66, 25.64, 25.60, 22.66, 22.63, 22.58, 20.65, 20.46, 15.74, 14.07, -1.79.

MS (MALDI-pos, DCTB) m/z (%): 1051.8 (100) $[M]^{+\cdot}$, 1302.0 (5) $[M + DCTB]^{+\cdot}$.

16



Copper(I) chloride (0.05 g, 0.52 mmol) and TMEDA (0.08 mL, 0.53 mmol) are added to a solution of **14** (0.57 g, 0.51 mmol) in dichloromethane. The solution is purged with an over calcium chlorid dried stream of air for 2 h at 30 °C and subsequently diluted with water and dichloromethane. The aqueous phase is extracted three times with dichloromethane and the combined organic phases are washed with ammonia solution (25 %), hydrochloric acid (10 %), water and brine and dried over magnesium sulfate. After removing the solvent under reduced pressure an orange solid is obtained which is purified by column chromatography (PE: DCM 2:3, R_f = 0.27). **16** (0.48 g, 0.21 mmol) is isolated in 85 % yield.

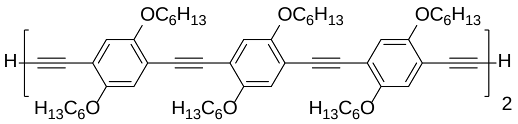
Sum formula: $C_{144}H_{208}N_2O_{12}Si_2$, molecular weight: 2215.37 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 7.00 (m, 4H), 6.99 (m, 4H), 6.96 (s, 2H), 6.93 (s, 2H), 4.04-3.94 (m, 24H), 2.43 (t, $^3J_{HH}$ = 6.8 Hz, 4H), 1.93-1.75 (m, 28H), 1.55-1.46 (m, 24H), 1.39-1.28 (m, 48H), 1.14-1.09 (m, 28H), 0.94-0.82 (m, 40H).

^{13}C-NMR (100 MHz, $CDCl_3$, RT) δ [ppm]: 154.96, 154.30, 153.53, 153.48, 153.31, 153.23, 119.77, 117.81, 117.77, 117.21, 117.07, 116.41, 115.40, 114.77, 114.36, 114.17, 113.27, 112.55, 103.93, 95.12, 92.19, 91.56, 91.53, 91.38, 79.60, 79.34, 77.20, 69.83, 69.74, 69.69, 69.65, 69.13, 31.63, 31.61, 31.53, 29.37, 29.28, 29.21, 29.12, 25.78, 25.66, 25.62, 22.63, 22.59, 21.29, 20.76, 18.23, 17.99, 14.06, 14.02, 11.80, 9.64.

MS (MALDI-pos, DCTB) m/z (%): 2213.5 (100) $[M]^{+\cdot}$, 2463.6 (35) $[M + DCTB]^{+\cdot}$.

1



16 (0.13 g, 0.06 mmol) is dissolved in THF (20 mL) and a 1 M solution of TBAF in THF (0.18 mL, 0.18 mmol) is added. The reaction mixture is stirred over night at r.t. und subsequently diluted with dichloromethane and water. The aqueous phase is extracted three times with dichloromethane and the combined organic layers are washed with brine and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the crude product is purified by column chromatography (PE:DCM 1:1, $R_f = 0.28$). **1** (0.10 g, 0.05 mmol) is isolated as yellow solid in 90 % yield.

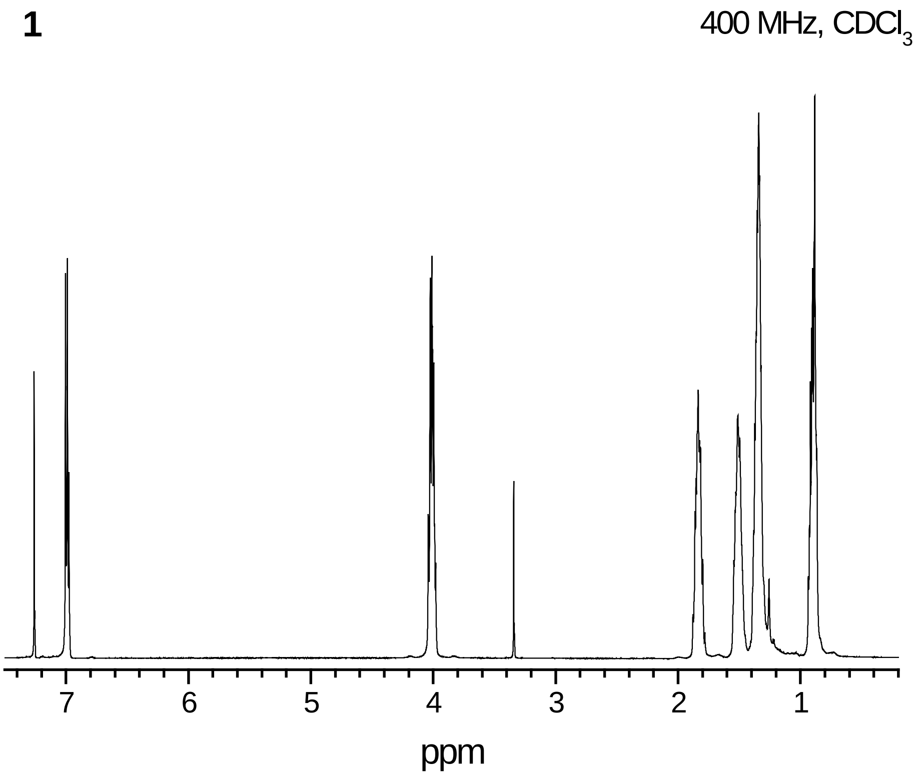
Sum formula: $C_{124}H_{170}O_{12}$, molecular weight: 1852.67 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 7.00 (m, 5H), 6.99 (m, 5H), 6.98 (m, 2H), 4.04-3.98 (m, 24H), 3.34 (s, 2H), 1.88-180 (m, 24H), 1.55-1.47 (m, 24H), 1.39-1.30 (m, 48H), 0.94-0.87 (m, 36H).

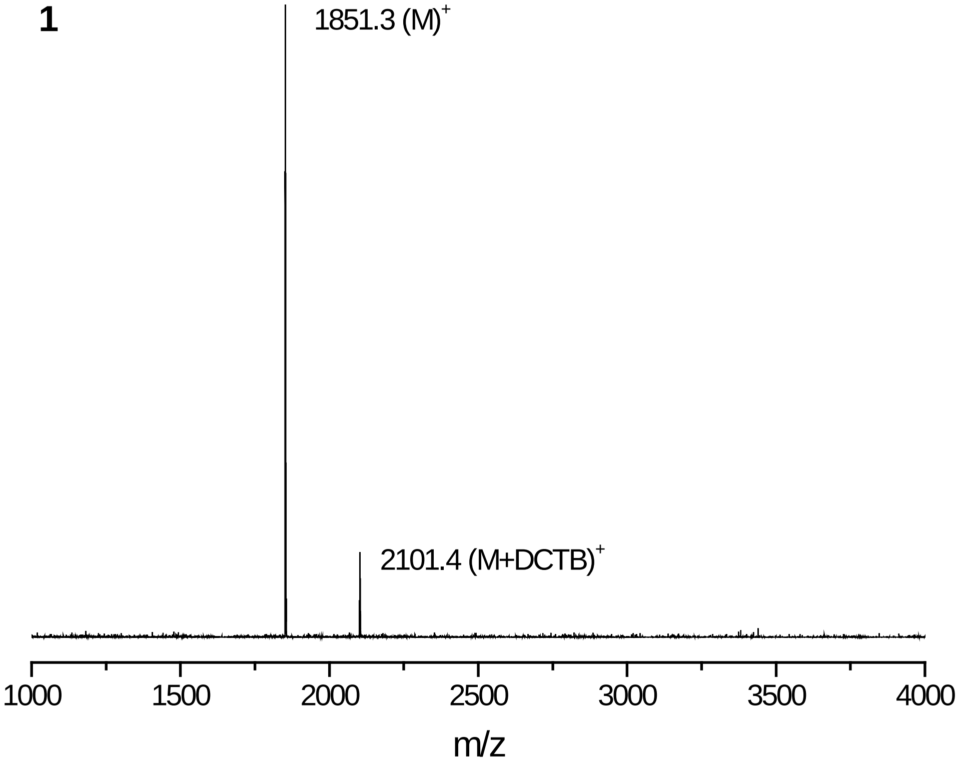
^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 154.94, 154.11, 153.50, 153.48, 153.27, 117.87, 117.75, 117.17, 117.01, 116.98, 115.34, 114.88, 114.28, 114.16, 112.52, 92.17, 91.53, 91.37, 91.28, 82.30, 80.03, 79.59, 79.33, 69.71, 69.69, 69.65, 69.63, 69.57, 31.61, 31.60, 31.53, 29.27, 29.22, 29.20, 29.12, 29.11, 25.66, 25.64, 25.61, 25.60, 22.63, 22.60, 14.03.

MS (MALDI-pos, DCTB) m/z (%): 1851.3 (100) $[M]^{+\cdot}$, 2101.4 (10) $[M + DCTB]^{+\cdot}$.

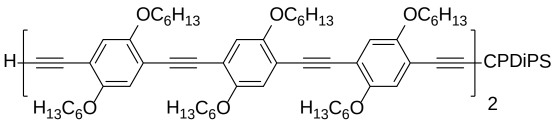
1


400 MHz, $CDCl_3$
7
6
5
4
3
2
1
ppm

1


1851.3 $(M)^+$
2101.4 $(M+DCTB)^+$
1000
1500
2000
2500
3000
3500
4000
m/z

17



16 (0.47 g, 0.21 mmol) is dissolved in THF (5.9 mL), water (0.31 mL, 5 vol%) is added and then a 1 M solution of TBAF in THF (0.19 mL, 0.19 mmol). The progress of the reaction is monitored every hour by thin layer chromatography. After 8 h stirring at r.t. the reaction mixture is diluted with water and the aqueous layer is extracted three times with dichloromethane. The combined organic phases are washed with brine and dried over magnesium sulfate. After removing the solvent under reduced pressure the crude product is purified by column chromatography (PE:DCM 2:3, $R_f = 0.66$) and subsequently by radial chromatography. **17** (0.19 g, 0.09 mmol) is obtained as yellow solid in 45 % yield.

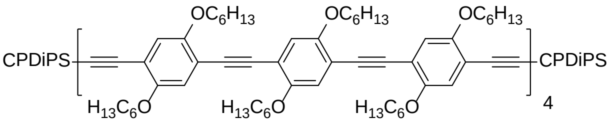
Sum formula: $C_{134}H_{189}NO_{12}Si$, Molecular weight: 2034.02 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$, RT) δ [ppm]: 7.00 (m, 4H), 6.99 (m, 5H), 6.98 (s, 1H), 6.96 (s, 1H), 6.93 (s, 1H), 4.04-3.98 (m, 22H), 3.96 (t, $^3J_{HH} = 6.5$ Hz, 2H), 3.35 (s, 1H), 2.44 (t, $^3J_{HH} = 7.0$ Hz, 2H), 1.91-1.77 (m, 26H), 1.57-1.47 (m, 24H), 1.39-1.30 (m, 48H), 1.14-1.10 (m, 14H), 0.93-0.82 (m, 38H).

^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 154.94, 154.28, 154.11, 153.51, 153.48, 153.46, 153.29, 153.21, 119.78, 117.88, 117.76, 117.70, 117.19, 117.16, 117.02, 116.99, 116.36, 115.36, 114.89, 114.73, 114.32, 114.29, 114.17, 114.12, 113.23, 112.53, 112.51, 103.91, 95.12, 92.17, 91.55, 91.53, 91.37, 91.28, 82.29, 80.02, 79.59, 79.33, 69.79, 69.71, 69.69, 69.65, 69.62, 69.58, 69.10, 31.63, 31.61, 31.59, 31.53, 29.37, 29.27, 29.22, 29.20, 29.11, 25.78, 25.66, 25.64, 25.61, 22.65, 22.63, 22.60, 22.58, 21.29, 20.77, 18.23, 17.99, 14.07, 14.03, 14.01, 11.79, 9.62.

MS (MALDI-pos, DCTB) m/z (%): 2032.4 (100) $[M]^{+\cdot}$, 2282.5 (10) $[M + DCTB]^{+\cdot}$.

18



17 (98 mg, 48.1 µmol), copper(I) chloride (5 mg, 48.1 µmol) and TMEDA (8 µL, 48.1 µmol) are dissolved in dichloromethane (5 mL) and purged with an over calcium chloride dried stream of air for 3 h at 30 °C. The reaction mixture is stirred over night at r.t and subsequently diluted with water and dichloromethane. The aqueous phase is extracted three times with dichloromethane and the combined organic phases are washed with ammonia solution (25 %), hydrochloric acid (10 %), water and brine and dried over magnesium sulfate. After removing the solvent under reduced pressure a yellow solid is obtained which is further purified by column chromatography (PE: DCM 2:5, $R_f = 0.43$) and finally precipitated as yellow solid with methanol from dichloromethane. **18** (88 mg, 21.6 µmol) is isolated in 90 % yield.

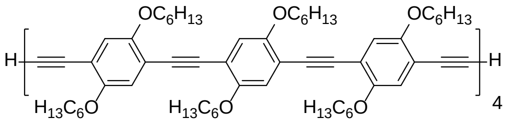
Sum formula: $C_{268}H_{376}N_2O_{24}Si_2$, molecular weight: 4066.13 g/mol.

^{1}**H-NMR** (500 MHz, $CDCl_3$, RT) δ [ppm]: 7.01-7.00 (m, 8H), 7.00-6.98 (m, 12H), 6.95 (s, 2H), 6.93 (s, 2H), 4.06-3.98 (m, 44H), 3.96 (t, $^3J_{HH}$ = 6.5 Hz, 4H), 2.44 (t, $^3J_{HH}$ = 7.0 Hz, 4H), 1.96-1.75 (m, 52H), 1.55-1.44 (m, 48H), 1.40-1.30 (m, 96H), 1.19-1.04 (m, 28H), 0.93-0.82 (m, 76H).

^{13}**C-NMR** (125 MHz, $CDCl_3$, RT) δ [ppm]: 154.95, 154.29, 153.53, 153.47, 153.31, 153.22, 119.78, 117.79, 117.73, 117.19, 117.05, 116.39, 115.37, 114.75, 114.34, 114.26, 114.14, 113.25, 112.55, 103.93, 95.13, 92.19, 91.56, 91.53, 91.435, 91.38, 79.61, 79.34, 69.81, 69.73, 69.67, 69.65, 69.12, 31.61, 31.54, 29.38, 29.29, 29.21, 29.12, 25.79, 25.67, 25.65, 25.62, 22.64, 22.60, 21.29, 20.77, 18.24, 17.99, 14.07, 14.04, 11.80, 9.64.

MS (MALDI-pos, DCTB) m/z (%): 4066.0 (100) $[M]^{+\cdot}$, 4316.4 (55) $[M + DCTB]^{+\cdot}$, 4566.6 (20) $[M + 2\ DCTB]^{+\cdot}$, 4817.6 (5) $[M + 3\ DCTB]^{+\cdot}$.

2



18 (88 mg, 21.6 µmol) is dissolved in THF (15 mL), degassed with argon for 30 min and a 1 M solution of TBAF in THF (0.07 mL, 0.07 mmol) is added. The reaction mixture is stirred for 3 h at r.t. and diluted with dichloromethane and water. The aqueous phase is extracted three times with dichloromethane and the combined organic layers are washed with brine and dried over magnesium sulfate. After removal of the solvent under reduced pressure the crude product is purified by column chromatography (PE:DCM 1:1, $R_f = 0.13$). **2** (69 mg, 18.7 µmol) is isolated as yellow solid in 84 % yield.

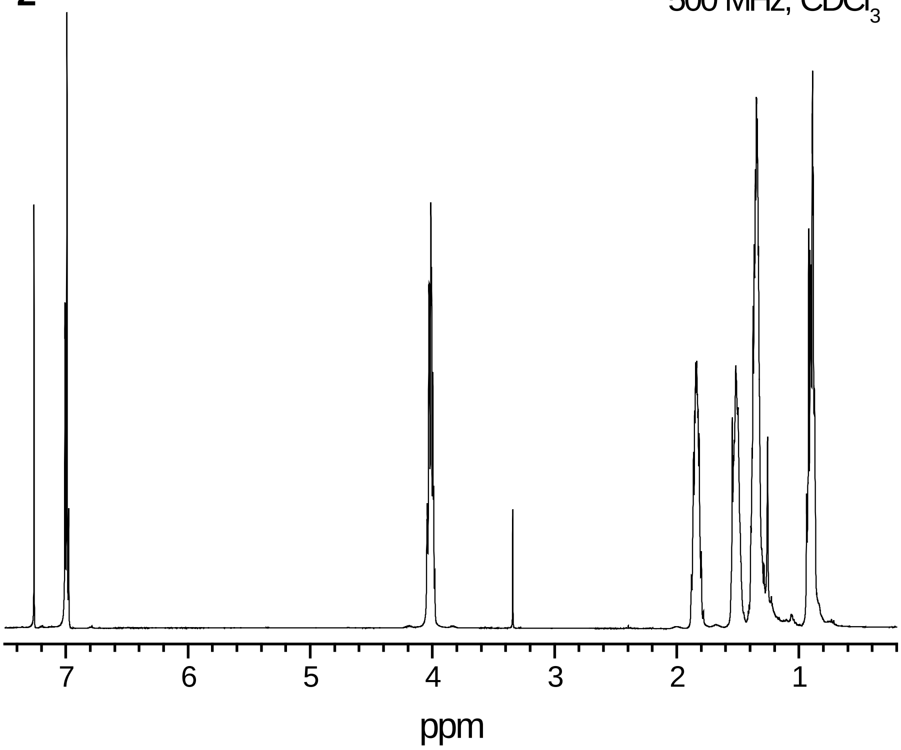
Sum formula: $C_{248}H_{338}O_{24}$, molecular weight: 3703.32 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$, RT) δ [ppm]: 7.01-7.00 (m, 8H), 7.00-6.99 (m, 14H), 6.98 (s, 2H), 4.07-3.96 (m, 48H), 3.35 (s, 2H), 1.91-1.76 (m, 48H), 1.55-1.46 (m, 48H), 1.44-1.28 (m, 96H), 0.93-0.87 (m, 72H).

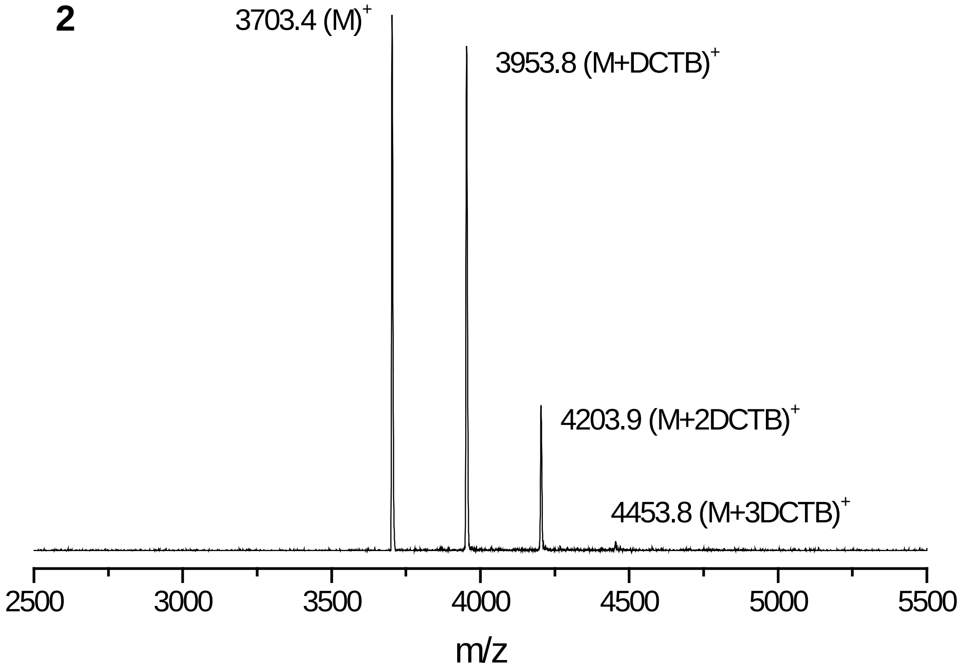
^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 154.95, 154.12, 153.52, 153.49, 153.30, 117.89, 117.78, 117.19, 117.03, 117.00, 115.36, 114.90, 114.30, 114.25, 114.18, 112.54, 92.18, 91.53, 91.43, 91.37, 91.28, 82.29, 80.03, 79.59, 79.34, 77.00, 69.72, 69.66, 69.64, 69.58, 31.61, 31.54, 29.28, 29.23, 29.20, 29.11, 25.67, 25.64, 25.62, 22.63, 22.60, 14.03.

MS (MALDI-pos, DCTB) m/z (%): 3703.4 (100) $[M]^{+\cdot}$, 3953.8 (95) $[M + DCTB]^{+\cdot}$, 4203.9 (30) $[M + 2\ DCTB]^{+\cdot}$, 4453.8 (5) $[M + 3\ DCTB]^{+\cdot}$.

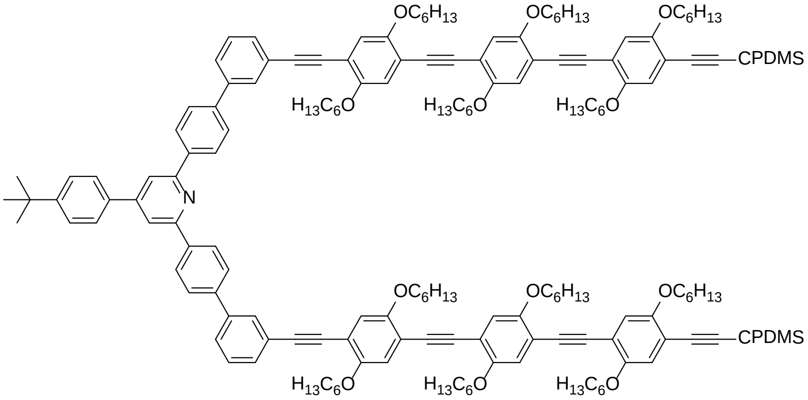
2


500 MHz, $CDCl_3$
7
6
5
4
3
2
1
ppm

2


3703.4 $(M)^+$
3953.8 $(M+DCTB)^+$
4203.9 $(M+2DCTB)^+$
4453.8 $(M+3DCTB)^+$
2500
3000
3500
4000
4500
5000
5500
m/z

19



28 (0.14 g, 0.19 mmol), **15** (0.45 g, 0.43 mmol), $Pd(PPh_3)_2Cl_2$ (8 mg, 11 µmol), copper(I) iodide (3 mg, 19 µmol) and triphenylphosphine (8 mg, 30 µmol) are dissolved in THF (2 mL) and piperidine (5 mL). After stirring the reaction mixture for 16 h at 50 °C it is diluted with dichloromethane and the organic layer is washed with water, sulfuric acid (10 %), water and brine and dried over magnesium sulfate. The solvent is removed under reduced pressure and the product is isolated by column chromatography (PE:DCM 1:2, $R_f = 0.16$). 0.46 g (0.18 mmol, 94 %) of **19** are obtained as yellow solid.

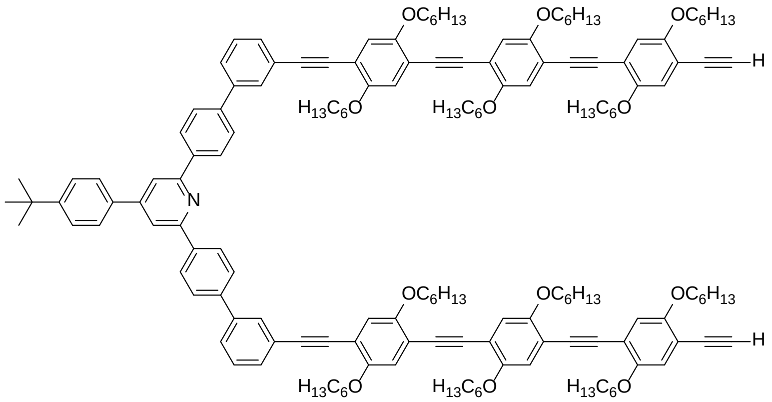
Sum formula: $C_{175}H_{223}N_3O_{12}Si_2$, molecular weight: 2616.8 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 8.33 (d, $^3J_{HH} = 8.4$ Hz, 4H), 7.97 (s, 2H), 7.88 (m, 2H), 7.78 (d, $^3J_{HH} = 8.4$ Hz, 4H), 7.75 (d, $^3J_{HH} = 8.4$ Hz, 2H), 7.66 (m, 2H), 7.59 (d, $^3J_{HH} = 8.4$ Hz, 2H), 7.56 (m, 2H), 7.47 (dd, $^3J_{HH} = 7.8$ Hz, 2H), 7.07 (s, 2H), 7.04 (s, 2H), 7.03 (s, 2H), 7.02 (s, 2H), 6.98 (s, 2H), 6.95 (s, 2H), 4.09-4.00 (m, 20H), 3.98 (t, $^3J_{HH} = 6.4$ Hz, 4H), 2.44 (t, $^3J_{HH} = 7.0$ Hz, 4H), 1.91-1.79 (m, 28H), 1.60-1.48 (m, 24H), 1.42 (s, 9H), 1.37-1.34 (m, 48H), 0.94-0.84 (m, 40H), 0.28 (s, 12H).

^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 156.92, 154.12, 153.66, 153.48, 153.46, 153.24, 152.39, 150.17, 140.93, 140.83, 138.74, 135.97, 130.54, 130.18, 128.84, 127.58, 127.38, 126.87, 126.11, 123.99, 119.71, 117.38, 117.19, 117.15, 117.08, 117.04, 116.68, 114.86, 114.34, 114.31, 114.10, 113.87, 113.01, 102.60, 97.76, 94.83, 91.71, 91.55, 91.52, 91.31, 86.25, 69.67, 69.63, 69.60, 69.20, 34.74, 31.63, 31.59, 31.56, 31.29, 29.34, 29.26, 29.23, 25.79, 25.67, 25.65, 25.63, 22.65, 22.63, 22.62, 20.63, 20.44, 15.73, 14.06, 14.03, -1.81.

MS (MALDI-pos, DCTB) m/z (%): 2614.6 (100) $[M]^{+\cdot}$, 2865.7 (10) $[M + DCTB]^{+\cdot}$.

3



19 (0.45 g, 0.17 mmol) is dissolved in THF (80 mL) and a 1 M solution of TBAF in THF (0.60 mL, 0.60 mmol) is added. After stirring the reaction mixture for 2.5 h at r.t. it is diluted with dichloromethane and water. The aqueous phase is extracted three times with dichloromethane and the combined organic layers are washed with water and brine and dried over magnesium sulfate. The solvent is removed under reduced pressure and the crude product is further purified by column chromatography (PE:DCM 1:1, $R_f = 0.42$). **3** (0.32 g, 0.14 mmol) is isolated as yellow solid in 77 % yield.

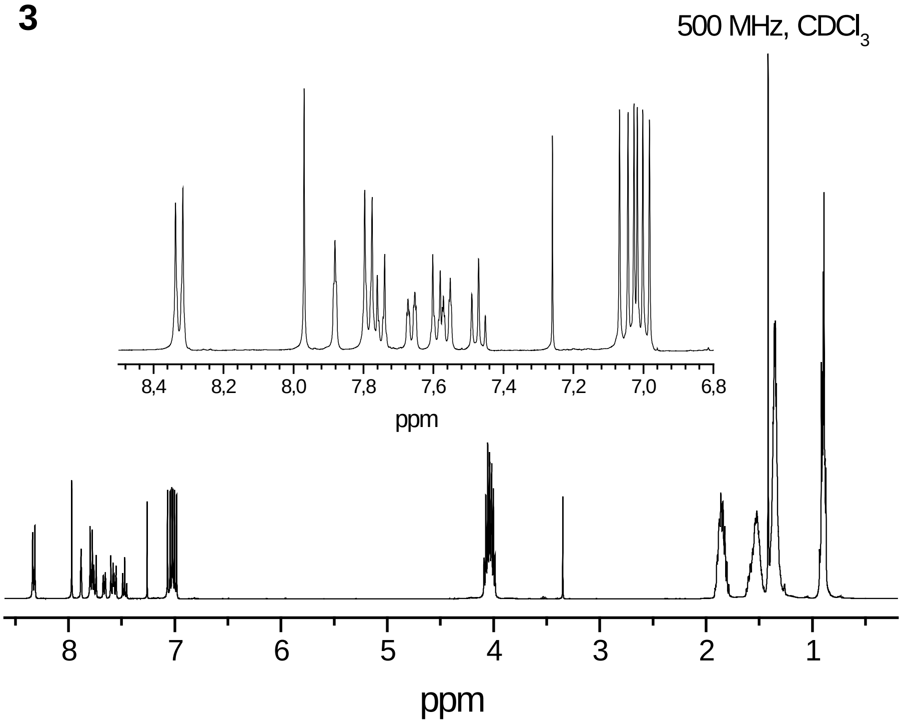
Sum formula: $C_{163}H_{201}NO_{12}$, molecular weight: 2366.3 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$, RT) δ [ppm]: 8.33 (d, $^{3}J_{HH} = 8.5$ Hz, 4H), 7.97 (s, 2H), 7.88 (m, 2H), 7.78 (d, $^{3}J_{HH} = 8.5$ Hz, 4H), 7.75 (d, $^{3}J_{HH} = 8.5$ Hz, 2H), 7.66 (m, 2H), 7.59 (d, $^{3}J_{HH} = 8.5$ Hz, 2H), 7.56 (m, 2H), 7.47 (dd, $^{3}J_{HH} = 7.8$ Hz, 2H), 7.07 (s, 2H), 7.04 (s, 2H), 7.03 (s, 2H), 7.02 (s, 2H), 7.00 (s, 2H), 6.98 (s, 2H), 4.08-3.99 (m, 20H), 3.35 (s, 2H), 1.91-1.79 (m, 24H), 1.61-1.46 (m, 24H), 1.42 (s, 9H), 1.35-1.32 (m, 48H), 0.93-0.87 (m, 36H).

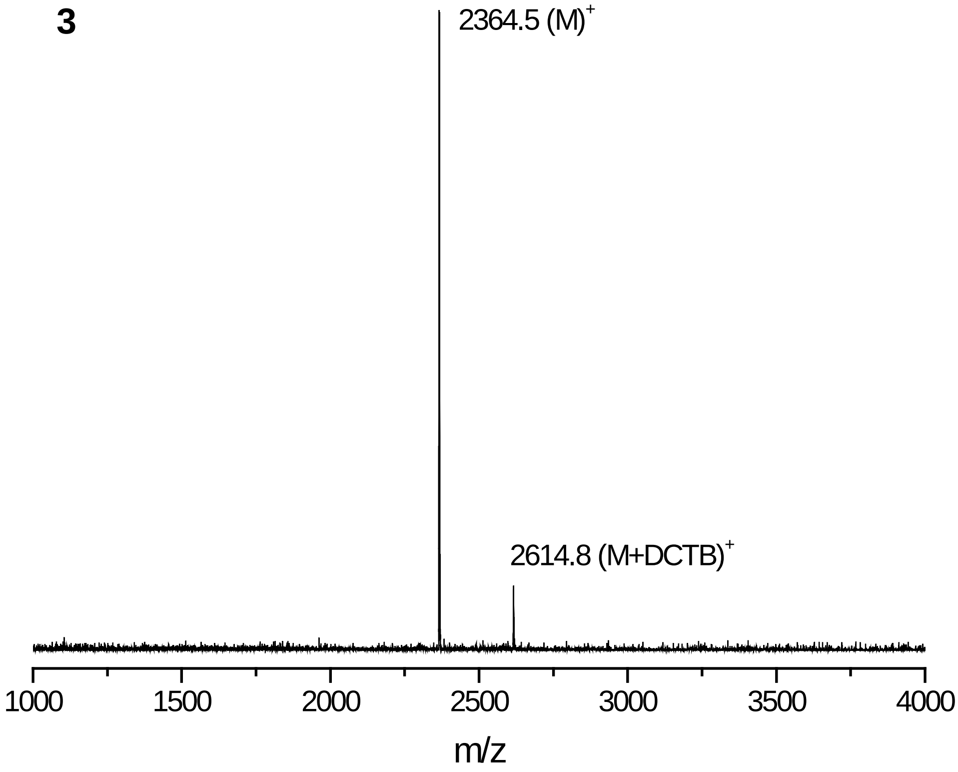
^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 156.95, 154.11, 153.68, 153.50, 153.47, 153.27, 152.39, 150.18, 140.94, 140.85, 138.94, 140.85, 138.78, 136.00, 130.55, 130.20, 128.85, 127.59, 127.40, 127.08, 126.88, 126.12, 124.01, 117.89, 117.22, 117.20, 117.10, 117.06, 116.99, 114.93, 114.36, 114.33, 114.12, 113.88, 112.50, 94.84, 91.58, 91.53, 91.19, 86.26, 82.28, 80.04, 69.70, 69.66, 69.63, 69.57, 34.76, 31.64, 31.61, 31.59, 31.52, 31.31, 29.36, 29.29, 29.27, 29.23, 29.12, 25.81, 25.67, 25.60, 22.66, 22.64, 22.58, 14.07, 14.05, 14.03, 14.01.

MS (MALDI-pos, DCTB) m/z (%): 2364.5 (100) $[M]^{+\cdot}$, 2614.8 (10) $[M + DCTB]^{+\cdot}$.

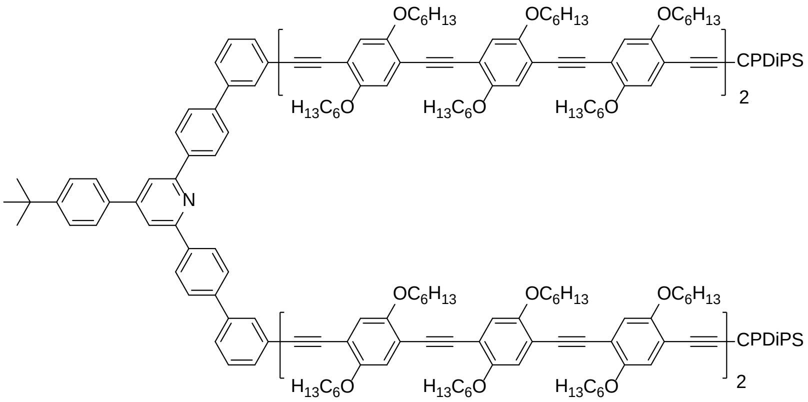
3


500 MHz, $CDCl_3$
8,4
8,2
8,0
7,8
7,6
7,4
7,2
7,0
6,8
ppm
8
7
6
5
4
3
2
1
ppm

3


2364.5 $(M)^+$
2614.8 $(M+DCTB)^+$
1000
1500
2000
2500
3000
3500
4000
m/z

20



28 (25 mg, 0.03 mmol), **17** (0.15 g, 0.07 mmol), $Pd(PPh_3)_2Cl_2$ (1 mg, 2 µmol), copper(I) iodide (1 mg, 3 µmol) and triphenylphosphine (1 mg, 5 µmol) are dissolved in THF (1 mL) and piperidine (2 mL). After stirring the reaction mixture for 16 h at 50 °C it is diluted with dichloromethane and the organic layer is washed with water, sulfuric acid (10 %), water and brine and dried over magnesium sulfate. The solvent is removed under reduced pressure and the product is purified by column chromatography (PE:DCM 1:1 … 2:3) and subsequently by radial chromatography (PE:DCM 3:2, $R_f = 0.07$). 0.11 g (0.02 mmol, 76 %) of **20** are obtained as orange solid.

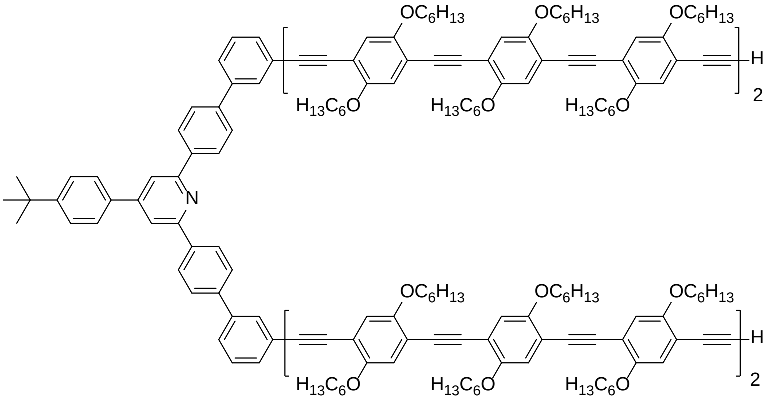
Sum formula: $C_{307}H_{407}N_3O_{24}Si_2$, molecular weight: 4579.7 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$, RT) δ [ppm]: 8.32 (d, $^3J_{HH} = 8.5$ Hz, 4H), 7.97 (s, 2H), 7.88 (m, 2H), 7.78 (d, $^3J_{HH} = 8.5$ Hz, 4H), 7.75 (d, $^3J_{HH} = 8.0$ Hz, 2H), 7.66 (m, 2H), 7.59 (d, $^3J_{HH} = 8.0$ Hz, 2H), 7.56 (m, 2H), 7.47 (dd, $^3J_{HH} = 7.5$ Hz, 2H), 7.06 (s, 2H), 7.04 (s, 2H), 7.02 (s, 2H), 7.01-6.99 (m, 14H), 6.96 (s, 2H), 6.93 (s, 2H), 4.08-3.99 (m, 44H), 3.96 (t, $^3J_{HH} = 6.5$ Hz, 4H), 2.44 (t, $^3J_{HH} = 7.0$ Hz, 4H), 1.93-1.76 (m, 52H), 1.59-1.47 (m, 48H), 1.41 (s, 9H), 1.39-1.31 (m, 96H), 1.17-1.10 (m, 28H), 0.93-0.82 (m, 76H).

^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 156.98, 154.95, 154.29, 153.69, 153.52, 153.48, 153.47, 153.30, 153.21, 152.38, 150.14, 140.93, 140.88, 138.87. 136.05, 130.56, 130.21, 128.86, 127.57, 127.41, 127.09, 126.89, 126.12, 124.02, 119.79, 117.78, 117.71, 117.21, 117.17, 117.11, 117.07, 117.03, 116.37, 115.40, 115.36, 114.74, 114.44, 114.33, 114.14, 114.08, 113.90, 113.23, 112.53, 112.50, 103.91, 95.13, 94.86, 92.23, 92.19, 91.61, 91.55, 91.53, 91.38, 91.35, 86.26, 79.60, 79.34, 69.80, 69.72, 69.67, 69.63, 69.11, 34.77, 31.65, 31.63, 31.61, 31.54, 31.32, 29.41, 29.37, 29.28, 29.20, 29.11, 25.81, 25.79, 25.67, 25.64, 25.62, 22.67, 22.64, 22.60, 21.29, 20.77, 18.24, 17.99, 14.07, 14.04, 11.79, 9.63.

MS (MALDI-pos, Dithranol) m/z (%): 4580.5 (100) $[M]^{+\cdot}$, 4720.8 (10) $[M + \text{Dithranol} - C_6H_{12}]^{+\cdot}$, 4805.4 (3) $[M + \text{Ditranol}]^{+\cdot}$.

4

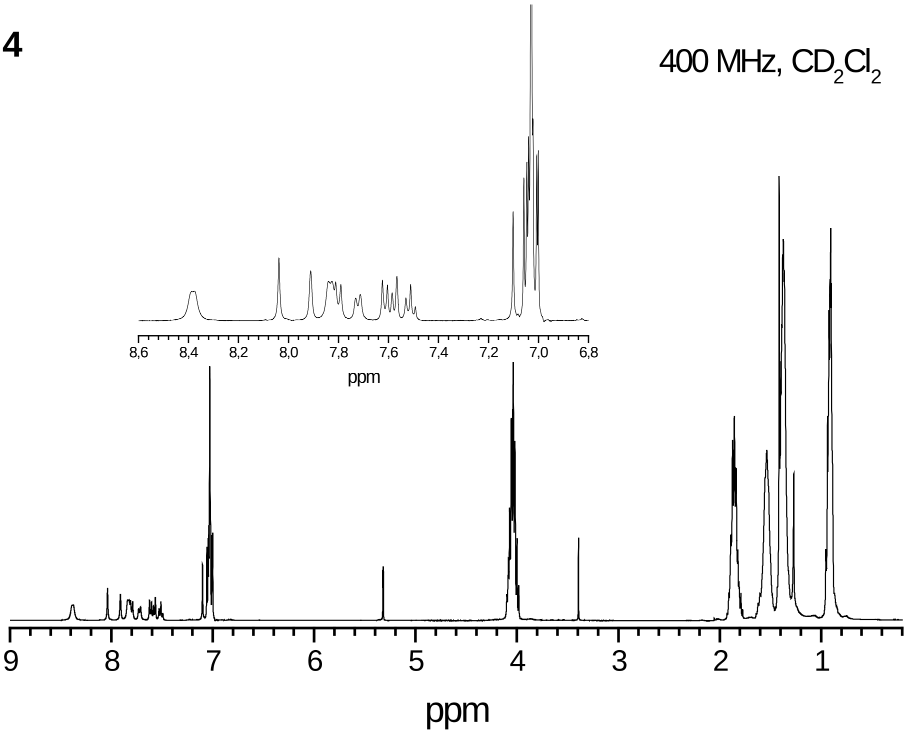


20 (0.10 g, 22 µmol) is dissolved in THF (10 mL), degassed with argon for 1 h and a 1 M solution of TBAF (0.06 mL, 0.06 mmol) in THF is added. After 1.5 h stirring at r.t. the reaction mixture is diluted with dichloromethane and the organic phase is washed with water and brine and dried over magnesium sulfate. The solvent is removed under reduced pressure and the crude product is purified by column chromatography (CH:DCM 1:1 *(R_f = 0.20)* … 2:3). **4** (62 mg, 14.7 µmol) is obtained as orange solid in 67 % yield.
Sum formula: $C_{287}H_{367}NO_{24}$, molecular weight: 4216.99 g/mol.

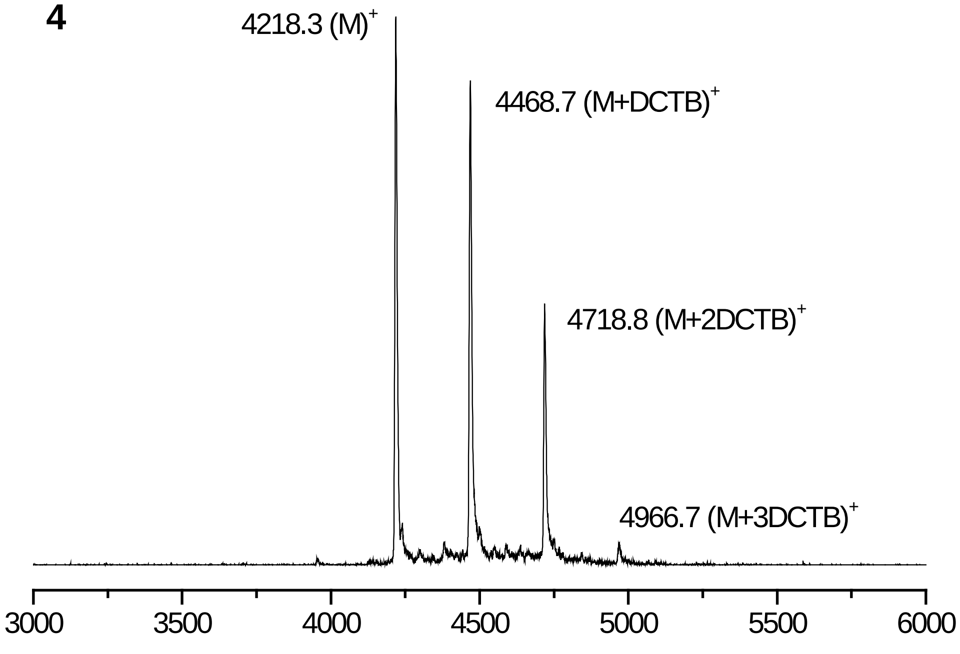
^{1}H-NMR (400 MHz, CD_2Cl_2 RT) δ [ppm]: 8.43-8.33 (m, 4H), 8.04 (s, 2H), 7.91 (m, 2H), 7.87-7.77 (m, 6H), 7.75-7.70 (m, 2H), 7.64-7.55 (m, 4H), 7.51 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.10 (s, 2H), 7.06-6.99 (m, 22H), 4.14-3.96 (m, 48H), 3.39 (s, 2H), 1.96-1.76 (m, 48H), 1.66-1.45 (m, 48H), 1.44-1.31 (m, 105H), 0.95-0.87 (m, 72H).
^{13}C-NMR (100 MHz, CD_2Cl_2, RT) δ [ppm]: 156.82, 155.10, 154.23, 153.81, 153.63, 153.60, 153.57, 153.37, 140.94, 140.90, 135.88, 130.59, 130.12, 129.09, 127.69, 127.41, 126.91, 126.23, 124.05, 117.91, 117.73, 117.13, 117.05, 116.94, 116.85, 115.46, 115.44, 115.41, 114.74, 114.41, 114.28, 114.24, 114.10, 114.03, 113.97, 112.66, 112.25, 112.23, 110.06, 94.79, 92.32, 92.28, 91.70, 91.57, 91.53, 91.42, 91.38, 86.45, 86.37, 83.06, 82.33, 80.03, 79.80, 79.01, 69.76, 69.73, 69.65, 34.74, 31.75, 31.71, 31.69, 31.63, 31.12, 29.47, 29.37, 29.33, 29.30, 29.25, 29.20, 25.92, 25.75, 25.73, 25.69, 22.78, 22.74, 22.70, 22.68, 13.95, 13.90.

MS (MALDI-pos, DCTB) m/z (%): 4218.3 (100) $[M]^{+\cdot}$, 4468.7 (90) $[M + DCTB]^{+\cdot}$, 4718.8 (45) $[M + 2\ DCTB]^{+\cdot}$, 4966.7 (5) $[M + 3\ DCTB]^{+\cdot}$.

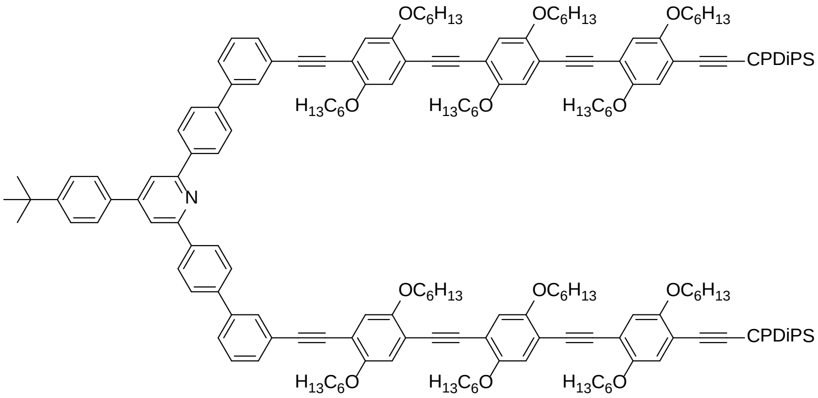
4


400 MHz, CD_2Cl_2
8,6
8,4
8,2
8,0
7,8
7,6
7,4
7,2
7,0
6,8
ppm
9
8
7
6
5
4
3
2
1
ppm

4


4218.3 (M)$^+$
4468.7 (M+DCTB)$^+$
4718.8 (M+2DCTB)$^+$
4966.7 (M+3DCTB)$^+$
3000
3500
4000
4500
5000
5500
6000
m/z

21



28 (0.11 g, 0.14 mmol) and **14** (0.35 g, 0.32 mmol) are dissolved in THF (2 mL) and piperidine (5 mL) and $Pd(PPh_3)_2Cl_2$ (6 mg, 8 µmol), copper(I) iodide (3 mg, 14 µmol) and triphenylphosphine (4 mg, 22 µmol) are added. After stirring the reaction mixture for 3 d at r.t. it is diluted with dichloromethane and the organic layer is washed with water, sulfuric acid (10 %), water and brine and dried over magnesium sulfate. The solvent is removed under reduced pressure and the crude product is purified by column chromatography (PE:DCM 1:1 ... 0:1) and subsequently by radial chromatography (PE:DCM 1:1, $R_f = 0.07$). 0.30 g (0.11 mmol, 80 %) of **21** are obtained as yellow film.

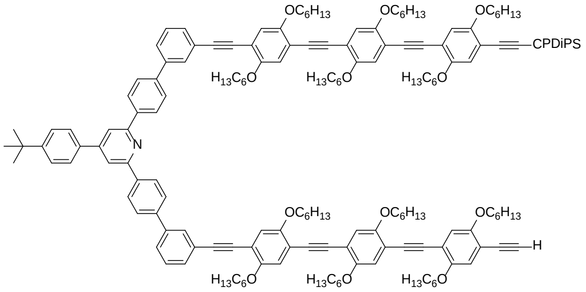
Sum formula: $C_{183}H_{239}N_3O_{12}Si_2$, molecular weight: 2729.04 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$, RT) δ [ppm]: 8.32 (d, $^3J_{HH}$ = 8.5 Hz, 4H), 7.97 (s, 2H), 7.88 (m, 2H), 7.78 (d, $^3J_{HH}$ = 8.5 Hz, 4H), 7.75 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.66 (m, 2H), 7.59 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.56 (m, 2H), 7.47 (dd, $^3J_{HH}$ = 7.8 Hz, 2H), 7.06 (s, 2H), 7.04 (s, 2H), 7.02 (s, 2H), 7.01 (s, 2H), 6.96 (s, 2H), 6.93 (s, 2H), 4.08-4.02 (m, 20H), 3.96 (t, $^3J_{HH}$ = 6.3 Hz, 4H), 2.44 (t, $^3J_{HH}$ = 7.0 Hz, 4H), 1.93-1.76 (m, 28H), 1.59-1.47 (m, 24H), 1.41 (s, 9H), 1.37-1.32 (m, 48H), 1.14-1.07 (m, 28H), 0.92-0.82 (m, 40H).

^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 156.95, 154.29, 153.68, 153.50, 153.47, 153.20, 152.42, 150.23, 140.97, 140.85, 138.75, 135.60, 130.56, 130.20, 128.85, 127.61, 127.41, 127.09, 126.89, 126.13, 124.02, 119.79, 117.72, 117.20, 117.17, 117.11, 117.07, 116.37, 114.78, 114.35, 114.32, 114.16, 113.88, 113.20, 103.93, 95.10, 94.84, 91.60, 91.55, 91.44, 86.26, 69.81, 69.70, 69.65, 69.62, 69.10, 34.77, 31.62, 31.32, 29.37, 29.29, 29.28, 25.81, 25.79, 25.66, 22.67, 22.65, 21.29, 20.77, 18.24, 17.99, 14.07, 14.05, 11.80, 9.63.

MS (MALDI-pos, DCTB) m/z (%): 2726.8 (100) $[M]^{+\cdot}$, 2979.0 (30) $[M + DCTB]^{+\cdot}$.

22



21 (0.22 g, 0.08 mmol) is dissolved in THF (2.2 mL) and water (0.12 mL, 5 vol%) and a 1 M solution of TBAF in THF (0.07 mL, 0.07 mmol) is added. The progress of the reaction is monitored every hour by thin layer chromatography. The reaction mixture is stirred for 6 h at r.t. and subsequently diluted with water. The aqueous layer is extracted three times with dichloromethane and the combined organic phases are washed with brine and dried over magnesium sulfate. After removing the solvent under reduced pressure the crude product is purified by column chromatography (PE:DCM 1:1) and subsequently by radial chromatography (PE:DCM 1:1, $R_f = 0.09$). **22** (79 mg, 0.03 mmol) is obtained as yellow solid in 39 % yield.

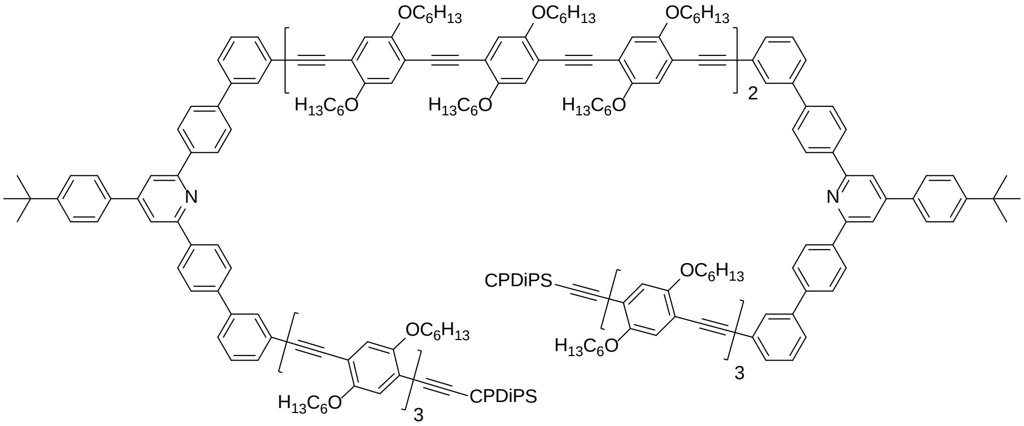
Sum formula: $C_{173}H_{220}N_2O_{12}Si$, molecular weight: 2547.7 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 8.33 (d, $^3J_{HH}$ = 8.8 Hz, 4H), 7.97 (s, 2H), 7.88 (m, 2H), 7.78 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 7.75 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.66 (m, 2H), 7.59 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.56 (m, 2H), 7.47 (dd, $^3J_{HH}$ = 8.0 Hz, 2H), 7.06 (s, 2H), 7.04 (s, 2H), 7.03 (s, 2H), 7.02 (s, 2H), 7.00 (s, 1H), 6.98 (s, 1H), 6.97 (s, 1H), 6.94 (s, 1H), 4.09-3.99 (m, 22H), 3.96 (t, $^3J_{HH}$ = 6.5 Hz, 2H), 3.35 (s, 1H), 2.44 (t, $^3J_{HH}$ = 7.0 Hz, 2H), 1.92-1.77 (m, 26H), 1.60-1.47 (m, 24H), 1.42 (s, 9H), 1.39-1.30 (m, 48H), 1.15-1.10 (m, 14H), 0.93-0.82 (m, 38H).

^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 156.96, 154.28, 154.11, 153.68, 153.50, 153.47, 153.27, 153.20, 152.36, 150.12, 140.91, 140.86, 138.85, 136.03, 130.89, 130.54, 130.19, 128.84, 127.56, 127.39, 127.07, 126.87, 126.11, 124.01, 119.78, 117.89, 117.71, 117.21, 117.19, 117.16, 117.10, 117.05, 117.02, 116.99, 116.36, 114.93, 114.77, 114.36, 114.33, 114.31, 114.15, 114.12, 113.88, 113.19, 112.49, 103.92, 95.09, 94.84, 91.59, 91.57, 91.54, 91.43, 91.19, 86.26, 82.28, 80.03, 69.80, 69.69, 69.64, 69.61, 69.57, 69.09, 34.75, 31.64, 31.62, 31.61, 31.59, 31.52, 31.31, 29.35, 29.29, 29.27, 29.22, 29.12, 25.81, 25.78, 25.68, 25.66, 25.63, 25.61, 25.59, 22.66, 22.64, 22.63, 22.58, 21.28, 20.76, 18.23, 17.99, 14.07, 14.04, 11.79, 9.62.

MS (MALDI-pos, DCTB) m/z (%): 2545.6 (100) $[M]^{+\cdot}$, 2795.8 (5) $[M + DCTB]^{+\cdot}$.

23



22 (43 mg, 17 µmol), $Pd(PPh_3)_2Cl_2$ (1 mg, 0.2 µmol), copper(I) iodide (1 mg, 0.2 µmol) and iodine (2 mg, 8 µmol) are dissolved in THF (6 mL) and diisopropylamine (4 mL). The reaction mixture is stirred over night at r.t. and diluted with dichloromethane. The organic phase is washed with water, sulfuric acid (10 %), water and brine and dried over magnesium sulfate. After removing the solvent under reduced pressure the crude product is purified by column chromatography (PE:DCM 2:3, R_f = 0.19). **23** (40 mg, 8 µmol) is isolated as orange film in 92 % yield.

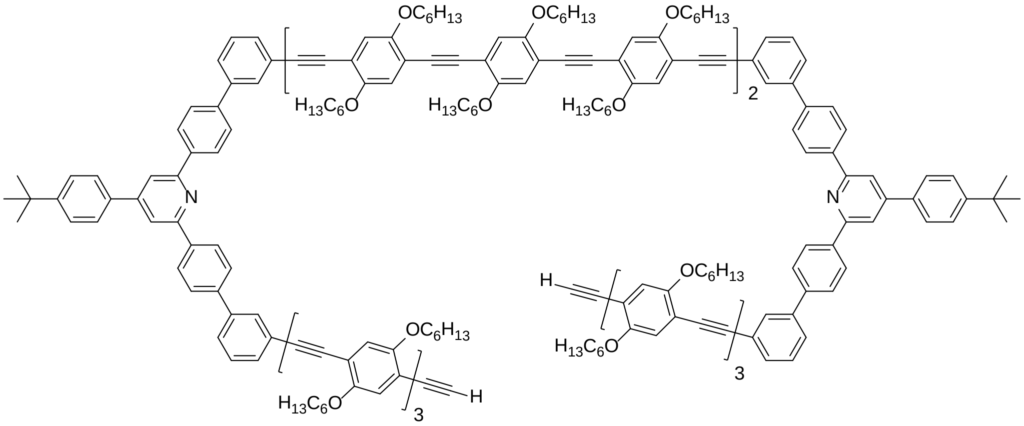
Sum formula: $C_{346}H_{438}N_4O_{24}Si_2$, molecular weight: 5093.36 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$, RT) δ [ppm]: 8.33 (d, $^3J_{HH}$ = 8.5 Hz, 8H), 7.97 (s, 4H), 7.88 (m, 4H), 7.78 (d, $^3J_{HH}$ = 8.5 Hz, 8H), 7.75 (d, $^3J_{HH}$ = 8.5 Hz, 4H), 7.66 (m, 4H), 7.59 (d, $^3J_{HH}$ = 8.5 Hz, 4H), 7.56 (m, 4H), 7.47 (dd, $^3J_{HH}$ = 7.5 Hz, 4H), 7.07 (m, 4H), 7.04 (m, 4H), 7.03 (s, 2H), 7.02 (m, 6H), 7.00 (m, 4H), 6.96 (s, 2H), 6.94 (s, 2H), 4.08-4.00 (m, 44H), 3.96 (t, $^3J_{HH}$ = 6.5 Hz, 4H), 2.44 (t, $^3J_{HH}$ = 7.0 Hz, 4H), 1.91-1.77 (m, 52H), 1.60-1.49 (m, 48H), 1.42 (s, 18H), 1.38-1.31 (m, 96H), 1.16-1.10 (m, 28H), 0.93-0.82 (m, 76H).

^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 156.97, 154.95, 154.29, 153.68, 153.53, 153.50, 153.47, 153.29, 153.20, 152.37, 150.13, 140.92, 140.87, 138.86, 136.04, 130.55, 130.20, 128.85, 127.57, 127.40, 127.08, 126.88, 126.12, 124.01, 119.79, 117.78, 117.72, 117.19, 117.17, 117.11, 117.06, 117.03, 116.37, 115.39, 114.78, 114.44, 114.34, 114.32, 114.15, 114.08, 113.90, 113.88, 113.20, 112.50, 103.92, 95.10, 94.84, 92.23, 92.22, 91.60, 91.55, 91.44, 86.26, 79.61, 79.33, 69.81, 69.72, 69.70, 69.66, 69.61, 69.10, 34.76, 31.64, 31.61, 31.54, 31.31, 29.36, 29.29, 29.27, 29.20, 29.11, 25.81, 25.78, 25.74, 25.67, 25.64, 25.62, 23.80, 22.66, 22.64, 22.60, 21.28, 20.76, 18.23, 17.99, 14.07, 14.04, 11.79, 9.62.

MS (MALDI-pos, Dithranol) m/z (%): 5094.4 (100) $[M]^{+\cdot}$, 5233.9 (5) $[M + Dithranol - C_6H_{12}]^{+\cdot}$.

24



23 (40 mg, 8 µmol) is dissolved in THF (8 mL) and a 1 M solution of TBAF in THF (0.02 mL, 0.02 mmol) is added. The reaction mixture is stirred for 6 h at r.t. und diluted with dichloromethane and water. The aqueous phase is extracted three times with dichloromethane and the combined organic phases are washed with brine and dried over magnesium sulfate. After removing the solvent under reduced pressure the crude product is purified by radial chromatography (PE:DCM 3:2, $R_f = 0.08$). **24** (23 mg, 5 µmol) is obtained as yellow film in 62 % yield.

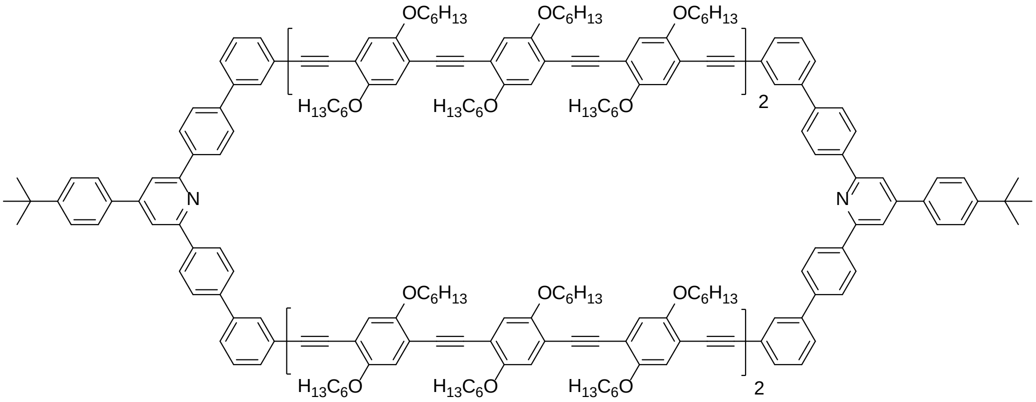
Sum formula: $C_{326}H_{400}N_2O_{24}$, Molecular weight: 4730.66 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$, RT) δ [ppm]: 8.32 (d, $^3J_{HH}$ = 8.5 Hz, 8H), 7.97 (s, 4H), 7.88 (m, 4H), 7.78 (d, $^3J_{HH}$ = 8.5 Hz, 8H), 7.75 (d, $^3J_{HH}$ = 8.5 Hz, 4H), 7.66 (m, 4H), 7.59 (d, $^3J_{HH}$ = 8.5 Hz, 4H), 7.56 (m, 4H), 7.47 (dd, $^3J_{HH}$ = 7.5 Hz, 4H), 7.07 (m, 4H), 7.04 (m, 4H), 7.02 (m, 4H), 7.01 (m, 4H) 7.00 (m, 4H), 6.99 (m, 2H), 6.98 (s, 2H), 4.08-3.99 (m, 48H), 3.35 (s, 2H), 1.91-1.79 (m, 48H), 1.61-1.49 (m, 48H), 1.41 (s, 18H), 1.40-1.29 (m, 96H), 0.93-0.87 (m, 72H).

^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 156.98, 154.95, 154.12, 153.69, 153.53, 153.51, 153.48, 153.30, 153.28, 152.38, 150.14, 142.16, 140.93, 140.87, 138.87, 136.04, 130.56, 130.20, 128.85, 127.57, 127.41, 127.09, 126.88, 126.12, 124.02, 117.90, 117.78, 117.21, 117.11, 117.07, 117.04, 117.00, 115.39, 114.94, 114.44, 114.36, 114.34, 114.13, 114.09, 113.89, 112.50, 94.84, 92.22, 91.58, 91.55, 91.20, 86.26, 82.28, 80.04, 79.61, 79.34, 69.71, 69.67, 69.63, 69.58, 34.77, 31.65, 31.62, 31.54, 31.32, 29.41, 29.36, 29.28, 29.23, 29.21, 29.13, 29.11, 25.81, 25.67, 25.64, 25.62, 25.60, 22.67, 22.64, 22.60, 22.58, 14.07, 14.05.

MS (MALDI-pos, Dithranol) m/z (%): 4731.6 (100) $[M]^{+\cdot}$, 4872.4 (5) $[M + \text{Dithranol} - C_6H_{12}]^{+\cdot}$, 4956.1 (10) $[M + \text{Ditranol}]^{+\cdot}$.

5



$Pd(PPh_3)_2Cl_2$ (3 mg, 4 µmol), copper(I) iodide (1 mg, 3 µmol) and iodine (1 mg, 3 µmol) are suspended in THF (15 mL) and diisopropylamine (15 mL) and heated to 55 °C. A solution of **24** (23 mg, 5 µmol) in THF (20 mL) is slowly added to the catalyst system over 48 h and further 2 d stirred at this temperature. The reaction mixture is diluted with dichloromethane and water and the aqueous phase is extracted three times with dichloromethane. The combined organic phases are washed with sulfuric acid (10 %), water and brine and dried over magnesium sulfate. After removal of the solvent the crude product is purified by flash chromatography and subsequently by recGPC. **5** (13 mg, 3 µmol) is isolated as yellow solid in 57 % yield.

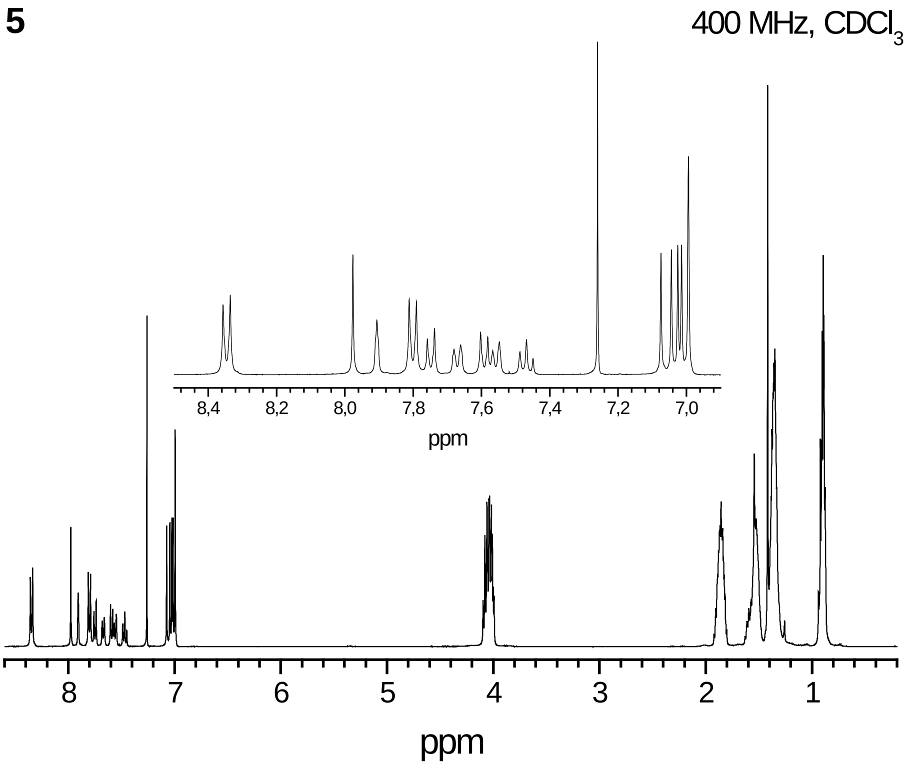
Sum formula: $C_{326}H_{398}N_2O_{24}$, molecular weight: 4728.65 g/mol.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 8.34 (d, $^3J_{HH}$ = 8.4 Hz, 8H), 7.98 (s, 4H), 7.90 (m, 4H), 7.80 (d, $^3J_{HH}$ = 8.4 Hz, 8H), 7.75 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 7.67 (m, 4H), 7.59 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 7.56 (m, 4H), 7.47 (dd, $^3J_{HH}$ = 7.6 Hz, 4H), 7.07 (s, 4H), 7.04 (s, 4H), 7.02 (s, 4H), 7.01 (s, 4H), 6.99 (m, 8H), 4.09-3.99 (m, 48H), 1.92-1.80 (m, 48H), 1.61-1.49 (m, 48H), 1.42 (s, 18H), 1.38-1.33 (m, 96H), 0.96-0.84 (m, 72H).

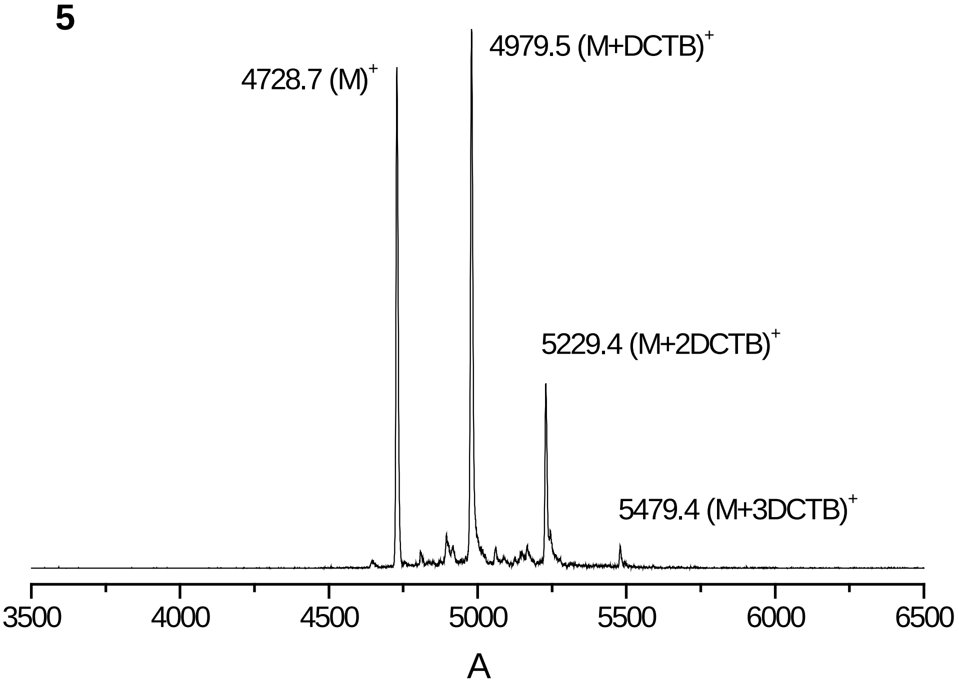
^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 156.82, 154.96, 153.70, 153.54, 153.49, 153.31, 152.38, 150.15, 140.80, 140.71, 138.78, 136.08, 130.53, 130.19, 128.85, 127.54, 127.32, 126.97, 126.89, 126.13, 124.07, 117.79, 117.21, 117.11, 117.04, 116.97, 115.40, 114.45, 114.36, 114.10, 113.91, 112.53, 94.81, 92.19, 91.57, 91.53, 91.33, 86.24, 79.55, 79.33, 69.73, 69.71, 69.67, 69.64, 34.77, 31.66, 31.62, 31.54, 31.33, 29.37, 29.28, 29.21, 29.12, 25.83, 25.68, 25.65, 25.62, 22.69, 22.64, 22.60, 14.09, 14.04.

MS (MALDI-pos, DCTB) m/z (%): 4728.7 (90) $[M]^{+\cdot}$, 4979.5 (100) $[M + DCTB]^{+\cdot}$, 5229.4 [M + 2 DCTB]$^{+\cdot}$, 5229.4 (35) [M + 3 DCTB]$^{+\cdot}$, 5479.4 (5) [M + 4 DCTB]$^{+\cdot}$.

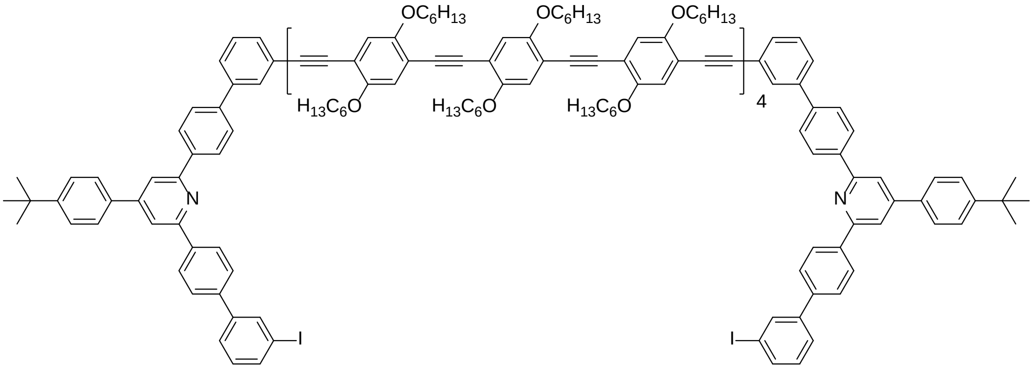
5


400 MHz, CDCl$_3$
8,4
8,2
8,0
7,8
7,6
7,4
7,2
7,0
ppm
8
7
6
5
4
3
2
1
ppm

5


4728.7 (M)$^+$
4979.5 (M+DCTB)$^+$
5229.4 (M+2DCTB)$^+$
5479.4 (M+3DCTB)$^+$
3500
4000
4500
5000
5500
6000
6500
A

25



28 (62 mg, 0.08 mmol), $Pd(PPh_3)_2Cl_2$ (1 mg, 2 µmol), copper(I) iodide (1 mg, 3 µmol) and triphenylphosphine (1 mg, 5 µmol) are dissolved in piperidine (1.5 mL) and degassed with argon for 30 min. **2** (27 mg, 7.2 µmol) and THF (2 mL) is added to the solution. The reaction mixture is stirred over night at r.t. and subsequently diluted with dichloromethane. The organic phase is washed with water, sulfuric acid (10 %), water and brine and dried over magnesium sulfate. After removing the solvent under reduced pressure the crude product is purified by column chromatography (PE:DCM 1:1 ($R_f = 0.34$) … 2:3). **25** (21 mg, 4.2 µmol) is obtained as orange film in 59 % yield.

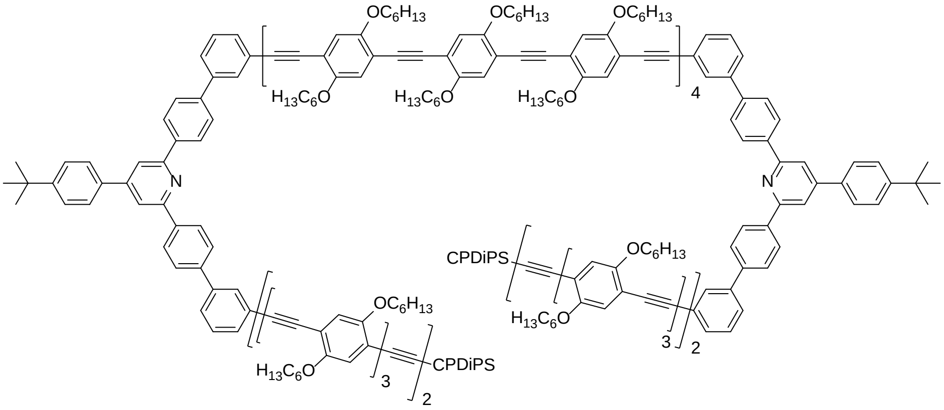
Sum formula: $C_{326}H_{400}N_2O_{24}I_2$, molecular weight: 4984.59 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$, RT) δ [ppm]: 8.37-8.21 (m, 8H), 8.04 (dd, $^4J_{HH}$ = 1.7 Hz, 2H), 7.96 (d, $^3J_{HH}$ = 6.7 Hz, 4H), 7.89-7.87 (m, 2H), 7.80-7.76 (m, 4H), 7.76-7.70 (m, 10H), 7.69-7.61 (m, 4H), 7.61-7.53 (m, 6H), 7.47 (dd, $^3J_{HH}$ = 7.7 Hz, 2H), 7.21 (dd, $^3J_{HH}$ = 7.8 Hz, 2H), 7.07 (s, 2H), 7.04 (s, 2H), 7.03 (s, 2H), 7.02-7.01 (m, 6H), 7.01-6.98 (m, 12H), 4.15-3.94 (m, 48H), 1.92-1.80 (m, 48H), 1.63-1.47 (m, 48H), 1.41 (s, 18H), 1.40-1.30 (m, 96H), 0.94-0.87 (m, 72H).

^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 156.96, 156.82, 154.94, 153.68, 153.51, 153.47, 153.29, 152.39, 150.17, 142.92, 140.93, 140.83, 140.11, 139.08, 138.79, 136.36, 136.06, 135.99, 130.54, 130.47, 130.21, 128.85, 127.60, 127.56, 127.38, 126.87, 126.36, 126.12, 124.01, 117.77, 117.18, 117.09, 117.03, 115.39, 115.34, 114.44, 114.33, 114.25, 114.08, 113.89, 112.53, 112.49, 94.85, 92.21, 91.60, 91.55, 91.43, 91.35, 86.26, 79.62, 79.60, 79.57, 79.33, 69.71, 69.66, 69.63, 34.76, 31.61, 31.53, 31.31, 29.36, 29.28, 29.20, 29.11, 25.81, 25.67, 25.64, 25.61, 22.63, 22.60, 14.04.

MS (MALDI-pos, DCTB) m/z (%): 4984.5 (30) $[M]^{+\cdot}$, 5235.0 (100) $[M + DCTB]^{+\cdot}$, 5485.0 (85) $[M + 2\ DCTB]^{+\cdot}$, 5735.8 (40) $[M + 3\ DCTB]^{+\cdot}$, 5984.8 (10) $[M + 4\ DCTB]^{+\cdot}$.

26



25 (20 mg, 4 µmol) is purged with argon for 1.5 h and **17** (28 mg, 14 µmol), $Pd(PPh_3)_2Cl_2$ (1 mg, 2 µmol), copper(I) iodide (1 mg, 3 µmol) and triphenylphosphine (1 mg, 5 µmol) are added and further purged with argon for 1 h. The starting materials are dissolved in THF (5 mL) and piperidine (3 mL) and the reaction mixture is stirred over night at r.t. It is diluted with water and dichloromethane and the aqueous phase is extracted three times with dichloromethane. The combined organic layers are washed with sulfuric acid (10 %), water and brine and dried over magnesium sulfate. After removal of the solvent the crude product is purified by flash chromatography and subsequently by recGPC. 16 mg of **26** (2 µmol, 46 %) are isolated as yellow solid.

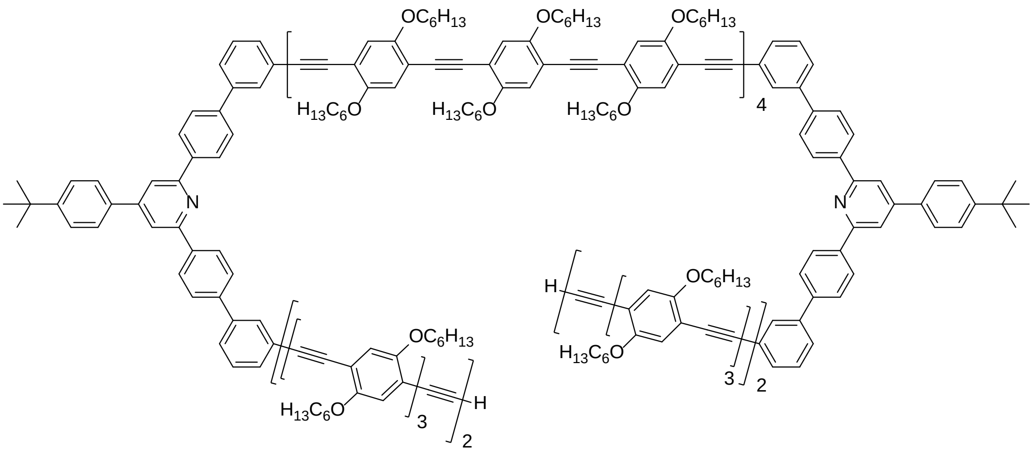
Sum formula: $C_{594}H_{776}N_4O_{48}Si_2$, Molecular weight: 8796.91 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$, RT) δ [ppm]: 8.37-8.28 (m, 8H), 7.97 (s, 4H), 7.89-7.86 (m, 4H), 7.81-7.73 (m, 12H), 7.69-7.63 (m, 4H), 7.62-7.53 (m, 8H), 7.47 (dd, $^3J_{HH}$ = 7.6 Hz, 4H), 7.07 (s, 4H), 7.04 (s, 4H), 7.03-6.98 (m, 36H), 6.96 (s, 2H), 6.93 (s, 2H), 4.10-3.98 (m, 92H), 3.96 (t, $^3J_{HH}$ = 6.5 Hz, 4H), 2.44 (t, $^3J_{HH}$ = 7.0 Hz, 4H), 1.94-1.71 (m, 100H), 1.63-1.44 (m, 96H), 1.41 (s, 18H), 1.41-1.27 (m, 192H), 1.15-1.06 (m, 28H), 0.94-0.82 (m, 148H).

^{13}C-NMR (125 MHz, $CDCl_3$, RT) δ [ppm]: 156.93, 154.94, 154.28, 153.68, 153.51, 153.47, 153.29, 153.21, 152.46, 150.31, 150.29, 150.27, 141.01, 140.85, 138.67, 135.95, 130.57, 130.21, 128.85, 127.66, 127.42, 127.11, 126.90, 126.14, 124.02, 119.78, 117.77, 117.71, 117.19, 117.11, 117.07, 117.03, 116.37, 115.40, 115.36, 114.74, 114.44, 114.33, 114.25, 114.13, 114.08, 113.90, 113.23, 112.52, 112.50, 103.91, 95.12, 94.84, 92.22, 92.18, 91.60, 91.55, 91.37, 91.35, 86.26, 79.59, 79.33, 69.80, 69.72, 69.66, 69.62, 69.10, 34.77, 31.64, 31.61, 31.53, 31.31, 29.36, 29.28, 29.20, 29.11, 25.81, 25.78, 25.66, 25.64, 25.61, 22.66, 22.63, 22.59, 21.28, 20.76, 18.23, 17.99, 14.07, 14.03, 11.79, 9.62.

MS (MALDI-pos, Dithranol) m/z (%): 8710.9 (5) $[M – C_6H_{12}]^{+\cdot}$, 8794.7 (100) $[M]^{+\cdot}$, 8935.0 (35) $[M + \text{Dithranol} - C_6H_{12}]^{+\cdot}$, 9020.6 (10) $[M + \text{Ditranol}]^{+\cdot}$, 9160.3 (5) $[M + 2\ \text{Dithranol} - C_6H_{12}]^{+\cdot}$.

27

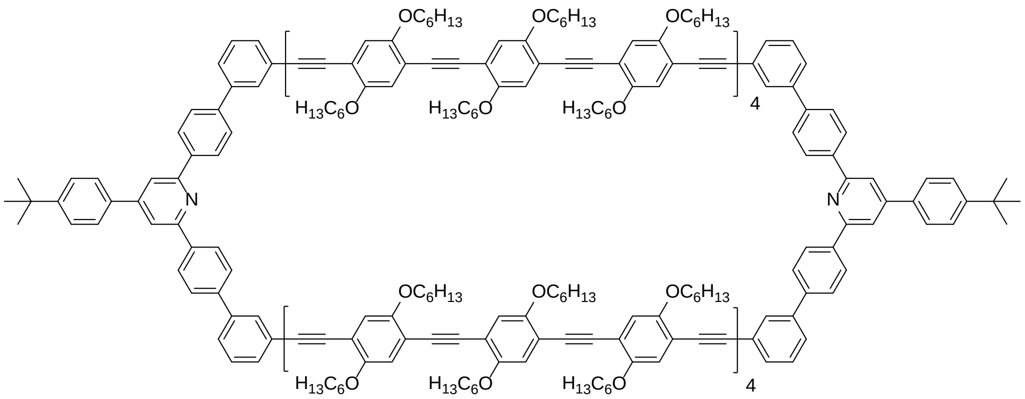


26 (16 mg, 2 µmol) is purged with argon for 1 h, dissolved in THF (20 mL) and a 1 M solution of TBAF in THF (5 µL, 5 µmol) is added. The reaction mixture is stirred for 6 h at r.t. and subsequently diluted with dichloromethane and water. The aqueous phase is extracted three times with dichloromethane and the combined organic phases are washed with brine and dried over magnesium sulfate. After removing the solvent under reduced pressure the crude product is further purified by column chromatography. **27** (15 mg, 1.8 µmol) is obtained as yellow film in 99 % yield.

^{1}H-NMR (400 MHz, $CDCl_3$, RT) δ [ppm]: 8.32 (d, $^3J_{HH}$ = 7.1 Hz, 8H), 7.97 (s, 4H), 7.91-7.84 (m, 4H), 7.84-7.71 (m, 12H), 7.66 (d, $^3J_{HH}$ = 7.5 Hz, 4H), 7.63-7.53 (m, 8H), 7.47 (dd, $^3J_{HH}$ = 7.7 Hz, 4H), 7.09-6.96 (m, 48H), 4.14-3.93 (m, 96H), 3.34 (s, 2H), 1.98-1.74 (m, 96H), 1.64-1.46 (m, 96H), 1.42-1.34 (m, 210H), 0.94-0.88 (m, 144H).

MS (MALDI-pos, Dithranol) m/z (%): 8432.1 (100) $[M]^{+\cdot}$, 8572.7 (10) $[M + Dithranol - C_6H_{12}]^{+\cdot}$, 8657.3 (5) $[M + Ditranol]^{+\cdot}$.

6



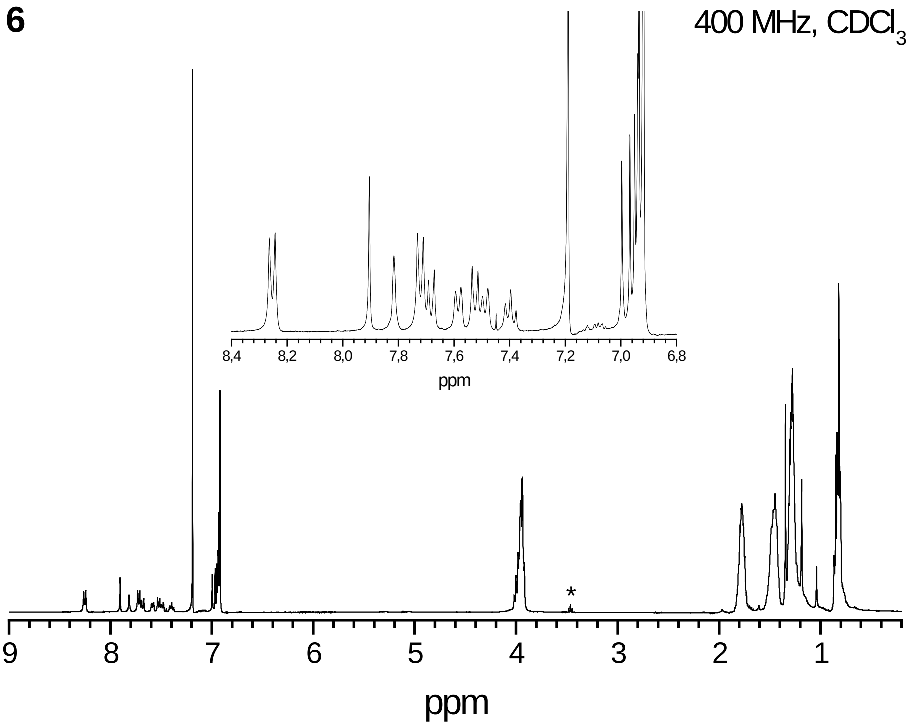
Pd(PPh$_3$)$_2$Cl$_2$ (6 mg, 9 µmol), copper(I) iodide (1 mg, 5 µmol) and iodine (2 mg, 9 µmol) are suspended in THF (15 mL) and diisopropylamine (15 mL) and heated to 50 °C. A solution of **27** (15 mg, 2 µmol) in THF (30 mL) is slowly added to the catalyst system over 60 h and further 8 h stirred at this temperature. The reaction mixture is diluted with dichloromethane and water and the aqueous phase is extracted three times with dichloromethane. The combined organic phases are washed with sulfuric acid (10 %), water and brine and dried over magnesium sulfate. After removal of the solvent the crude product is purified by flash chromatography and subsequently by recGPC. **6** (3 mg, 0.4 µmol) is isolated as yellow solid in 20 % yield.

Sum formula: $C_{574}H_{734}N_2O_{48}$, molecular weight: 8430.17 g/mol.

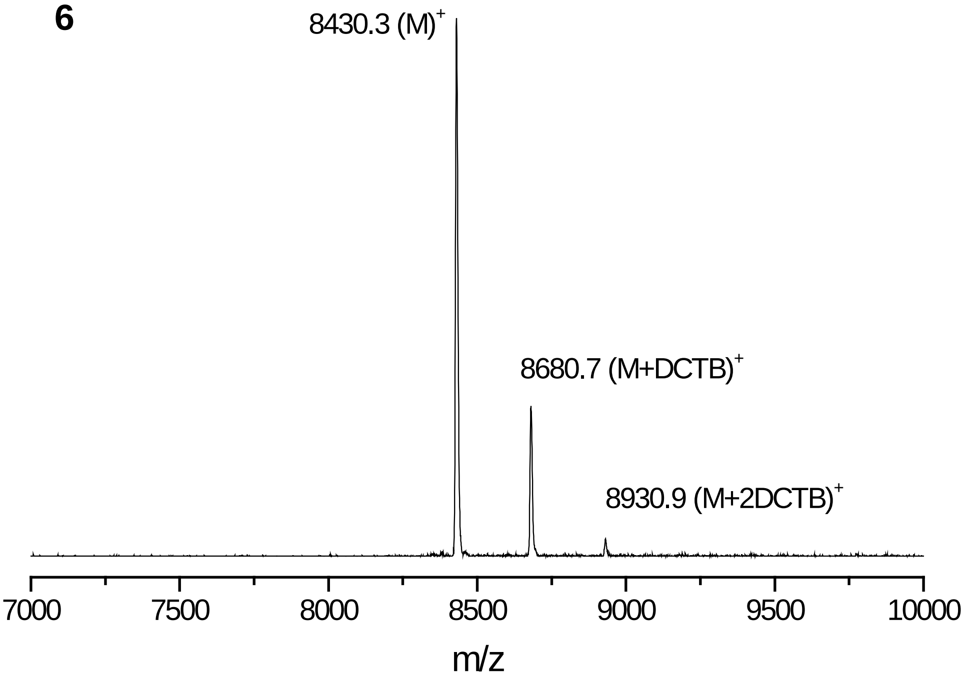
^{1}H-NMR (400 MHz, CD$_2$Cl$_2$, RT) δ [ppm]: 8.39 (d, *J* = 8.37 Hz, 8H), 8.04 (s, 4H), 7.94-7.88 (m, 4H), 7.87-7.77 (m, 12H), 7.75-7.68 (m, 4H), 7.66-7.47 (m, 12H), 7.14-6.98 (m, 48H), 4.12-3.99 (m, 96H), 1.98-1.73 (m, 96H), 1.66-1.47 (m, 96H), 1.47-1.29 (m, 210H), 1.00-0.81 (m, 144H).

MS (MALDI-pos, DCTB) m/z (%): 8430.3 (100) $[M]^{+\cdot}$, 8680.7 (30) $[M + DCTB]^{+\cdot}$, 8930.9 (5) $[M + 2\ DCTB]^{+\cdot}$.

6


400 MHz, CDCl$_3$
*
9
8
7
6
5
4
3
2
1
ppm
8,4
8,2
8,0
7,8
7,6
7,4
7,2
7,0
6,8
ppm

6


8430.3 (M)$^+$
8680.7 (M+DCTB)$^+$
8930.9 (M+2DCTB)$^+$
7000
7500
8000
8500
9000
9500
10000
m/z

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[1] a) S. Höger, K. Bonrad, *J. Org. Chem.* **2000**, *65*, 2243-2245. b) G. Gaefke, S. Höger, *Synthesis* **2006**, *114*, 2155-2157.

[2] D. Mössinger, S.-S. Jester, E. Sigmund, U. Müller, S. Höger, *Macromolecules* **2009**, *42*, 7974-7978.

[3] S.-S. Jester, N. Shabelina, S. M. Le Blanc, S. Höger, *Angew. Chem.* 2010, **122**, 6237; *Angew. Chem. Int. Ed.* 2010, **49**, 6101.

[4] C.- Z. Zhou, T. Liu, J.- M. Xu, Z.- K. Chen, *Macromolecules* **2003**, *36*, 1457-1464.