

Defined Oligo(*p*-phenylene-butadiynylene) Rods

Supporting Information

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1. General

Reagents were purchased at reagent grade from commercial sources and used without further purification. All air-sensitive reactions were carried out using standard Schlenk techniques under argon. Reaction solvents (THF, piperidine, dichloromethane) were dried, distilled, and stored under argon according to standard methods, workup solvents were either used in "p.a." quality or purified by distillation. Prior to characterization and further processing, all solids and oils were dried overnight at RT 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: DCTB, no salts added). m/z peaks smaller than 10 % (compared to the basis peak) are not reported. UV-VIS absorption spectra were either recorded on a Shimadzu UV-2100 spectrophotometer using 10 mm quartz cuvettes or during GPC analysis (diode array detection). Fluorescence experiments were run on a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer in all-transparent quartz cuvettes by monochromatic excitation at the indicated wavelength. All samples were prepared with indefinite concentration in THF. Uncorrected 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 RT. GPC analyses were run on an Agilent Technologies system at a flow rate of 1 mL/min using IsoPump G1310 A, a diode array UV detector (G1315B) and PSS columns (Polymer Standards Service, Mainz, Germany; 10^2 , 10^3 , and 10^5 Å, 5 μ , 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, 5 μ , 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). Differential Scanning Calorimetry (DSC) measurements were conducted under nitrogen on a

Mettler Toledo DSC 823^e system. An Agilent 5500 scanning probe microscope was used to investigate self-assembled monolayers of the tetramer on HOPG. **1** was dissolved in 1,2,4-trichlorobenzene (TCB) (Sigma Aldrich, $\geq 99\%$). Measurements were performed in the concentration range of 10^{-3} to 10^{-5} mol/L; the respective concentration is given in the figure caption. In a typical experiment, adlayers were prepared by dropping 8 μ L of the solution of **1** onto a piece of freshly cleaved atomically flat HOPG (SPI-2 quality, SPI Supplies, West Chester, USA). The measurements were performed in solution under ambient conditions (air, room temperature), and completed within 1-2 h. We used mechanically cut Pt/Ir (90/10) tips. All STM images shown here were recorded in constant current mode. We successfully obtained images of the adlayers in the 1-20 pA range; the respective exact value is given in the figure caption. The images were flattened by a third order line subtraction procedure.

2. Recycling GPC separation

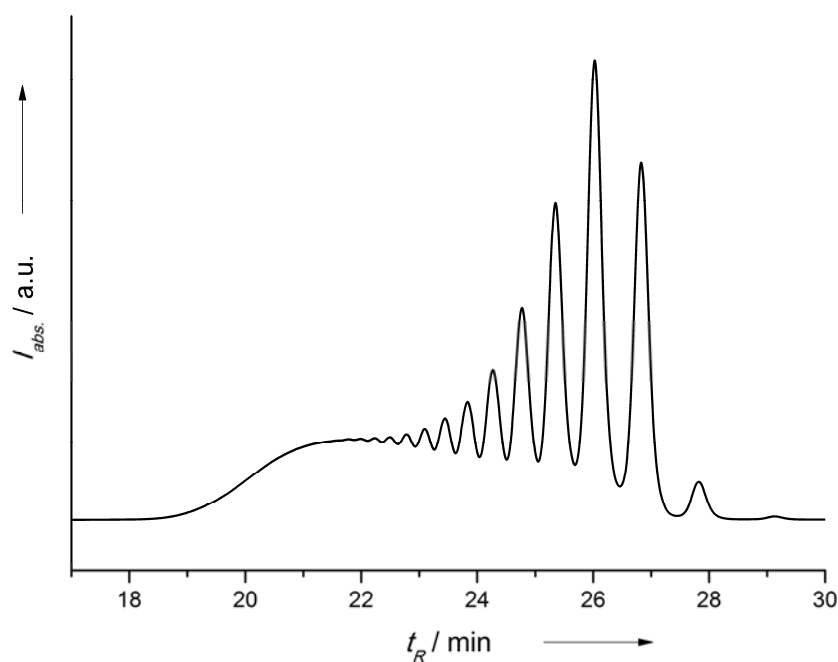


Figure S1. Recycling GPC elugram of **3** (oligomeric mixture) after one cycle.

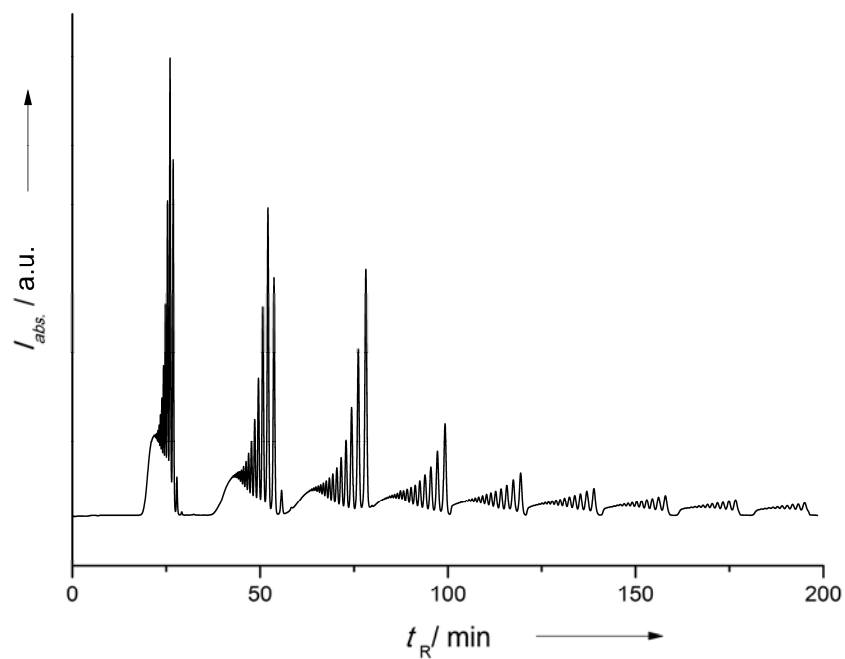


Figure S2. Recycling GPC separation of **3**: Elugrams of nine successive cycles. After each cycle, two peaks were removed from the well-resolved right margin of the signal group.

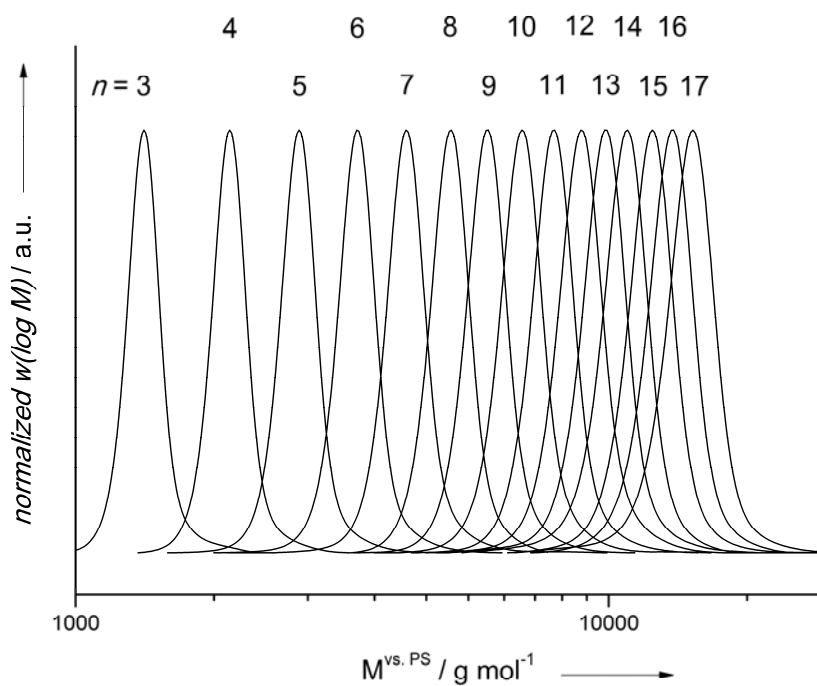


Figure S3. Normalized MWD overlay of the separated oligomers of **3** ($n = 3$ to 17).

3. PS-OPB conversion factors

Table S1. GPC peaks ($M_{p,i}$) of the separated oligomers of **3** and PS-OPB conversion factors f_i

n	$M_{abs} / \text{g mol}^{-1}$ $292.46 \cdot n + 2.016$	$\bar{M}_{p,i}^{vs. PS} / \text{D}$	f_i^{PS-OPB}
3	879.41	1350	1.54
4	1171.88	1945	1.66
5	1464.35	2620	1.79
6	1756.81	3390	1.93
7	2049.28	4180	2.04
8	2341.74	5050	2.16
9	2634.21	5910	2.24
10	2926.68	6860	2.34
11	3219.14	7890	2.45
12	3511.61	8850	2.52
13	3804.07	9880	2.60
14	4096.54	11030	2.69
15	4389.01	12060	2.75
16	4681.47	13140	2.81
17	4973.94	14320	2.88

The growth of the PS-OPB conversion factors f_{PS-OPB} plotted in Figure 2 and listed in Table S1 can be fitted and extrapolated by a limited single exponential function of the kind

$$f_{PS-OPB} = f_{\infty} - a \cdot e^{-n/b}.$$

The fit parameters are given in Table S2.

Table S2. Fit parameters for the PS-OPB correlation presented in Table S1 and Figure 2

fit parameters	scalar values
f_{∞}	3.832 ± 0.069
a	2.785 ± 0.056
b	15.879 ± 0.715

4. Calculation of Mark-Houwink parameters

The basic relation used for GPC calibration is $[\eta] \cdot M \propto V_h$, i.e. the hydrodynamic volume of a polymer sample is proportional to the product of its intrinsic viscosity and its absolute molar mass. Hence, for two polymer samples of different chemical constitution, but the same hydrodynamic volume (and elution volume), these products can be equated. In this equation, the intrinsic viscosity can be replaced according to the Mark-Houwink-Sakurada relationship.

$$[\eta_1]M_1 = [\eta_2]M_2 \quad [\eta] = K \cdot M^a \quad \Rightarrow \quad K_1 \cdot M_1^{a_1+1} = K_2 \cdot M_2^{a_2+1}$$

$$\Leftrightarrow \log K_1 = \log K_2 + (a_2 + 1) \cdot \log M_2 - (a_1 + 1) \cdot \log M_1$$

For the present case of the polystyrene (PS) – oligo(phenylene-butadiynylene) (OPB) conversion this equation becomes:

$$\log K_{OPB} = \log K_{PS} + (a_{PS} + 1) \cdot \log M_{p,i}^{vs.PS} - (a_{OPB} + 1) \cdot \log M_i$$

Average Mark-Houwink parameters a_{OPB} and K_{OPB} (highest accuracy ($\pm 2\%$) for $n = 4 - 16$) were obtained inserting pairs of oligomer data $M_{p,i}^{vs.PS}$ and M_i , into the above equation and equalisation. We used the following values of a narrow polystyrene sample: $a_{PS} = 0.714$ and $K_{PS} = 0.01363 \text{ mL g}^{-1}$.^[202] Table S3 displays the combinations of oligomer datasets **3-X / Y** inserted and equalised. The corresponding Mark-Houwink parameters obtained from five different systems of equations (lines in Table S3) have been averaged.^[306]

Table S3. Oligomer pairs used in systems of equations and Mark-Houwink parameters. The average values afford a very good reproduction of the PS-OPB correlation for $n = 4 - 16$.

oligomer pairs 3-X / Y	a_{OPB}	$10^4 K_{OPB} /$ mL g^{-1}
4 / 8	1.363	3.312
5 / 10	1.385	2.961
6 / 12	1.374	3.029
7 / 14	1.380	2.878
8 / 16	1.366	3.239
average	1.374	3.084

5. Optical properties

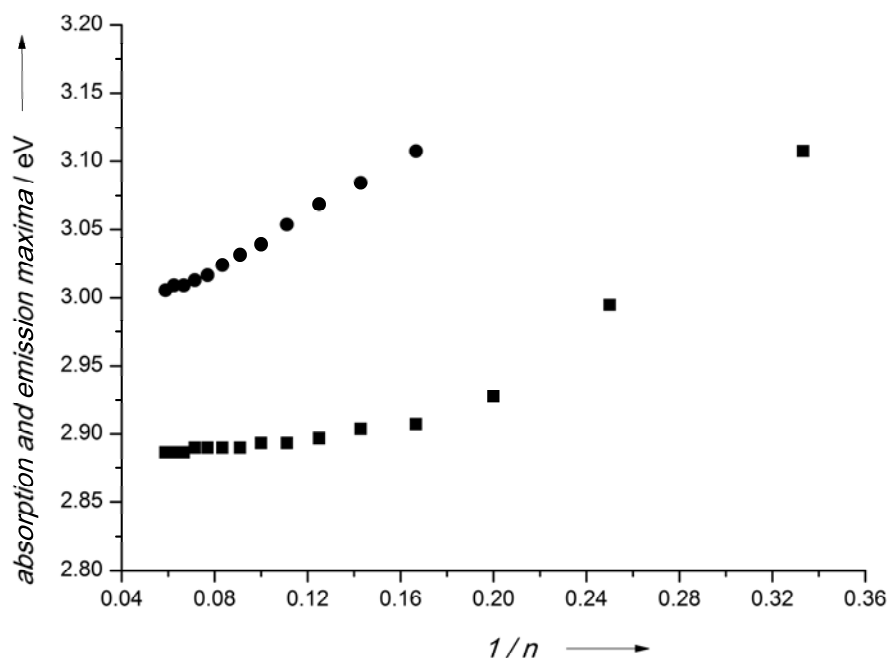


Figure S4. Alternative plot: Absorption (dots) and fluorescence (squares) maxima vs. inverse degree of polymerization $1/n$. Emission spectra measured at $\lambda_{xc} = 380 \text{ nm} = 3.26 \text{ eV}$.

In principle, any exponential fit can be applied to determine the saturation wavelengths λ_{∞} of the absorption and fluorescence maxima. Meier et al.¹ used the exponential equation

$$\lambda(n) = \lambda_{\infty} - (\lambda_{\infty} - \lambda_1) \cdot \exp(-b(n-1)) \quad (1)$$

requiring n as the number of repeating units (degree of polymerization) and λ_1 as the absorption / fluorescence maximum of the monomer ($n = 1$). Parameter b allows an estimation of the effective conjugation length n_{ECL} according to²

$$n_{ECL} = \frac{\ln(\lambda_{\infty} - \lambda_1)}{b} + 1. \quad (2)$$

Sometimes, the absorption maximum of the monomer λ_1 cannot be used because the main bands transform with increasing chain length (as they do in our case). In these cases, virtual values λ_1^* can be calculated (fitted) with equation (1). Tables S4 and S5 show the data obtained from absorption and fluorescence measurements on our OPB systems as well as the respective fit parameters to determine the effective conjugation length n_{ECL} .

Table S4. UV-Vis data of the separated oligomers of **3** ($n = 3$ to 17). Emission spectra measured at $\lambda_{\text{exc}} = 380 \text{ nm} = 3.26 \text{ eV}$.

n	$1/n$	absorption		emission	
		$\lambda_{\text{max}} / \text{nm}$	$E_{\text{max}} / \text{eV}$	$\lambda_{\text{max}} / \text{nm}$	$E_{\text{max}} / \text{eV}$
3	0.333	-	-	399	3.11
4	0.250	-	-	414	2.99
5	0.200	-	-	423.5	2.93
6	0.167	399	3.11	426.5	2.91
7	0.143	402	3.08	427	2.90
8	0.125	404	3.07	428	2.90
9	0.111	406	3.05	428.5	2.89
10	0.100	408	3.04	428.5	2.89
11	0.091	409	3.03	429	2.89
12	0.083	410	3.02	429	2.89
13	0.077	411	3.02	429	2.89
14	0.071	411.5	3.01	429	2.89
15	0.067	412	3.01	429.5	2.89
16	0.063	412	3.01	429.5	2.89
17	0.059	412	3.01	430	2.88

Table S5. Fit parameters obtained for absorption and fluorescence maxima series.

fit parameters	absorption	fluorescence
χ^2	$4.46 \cdot 10^{-2}$	0.2997
$\lambda_{\infty} / \text{nm}$	414 ± 2	429 ± 2
λ_1^* / nm	368 ± 3	291 ± 10
b	0.224 ± 0.011	0.757 ± 0.031
n_{ECL}	18	8

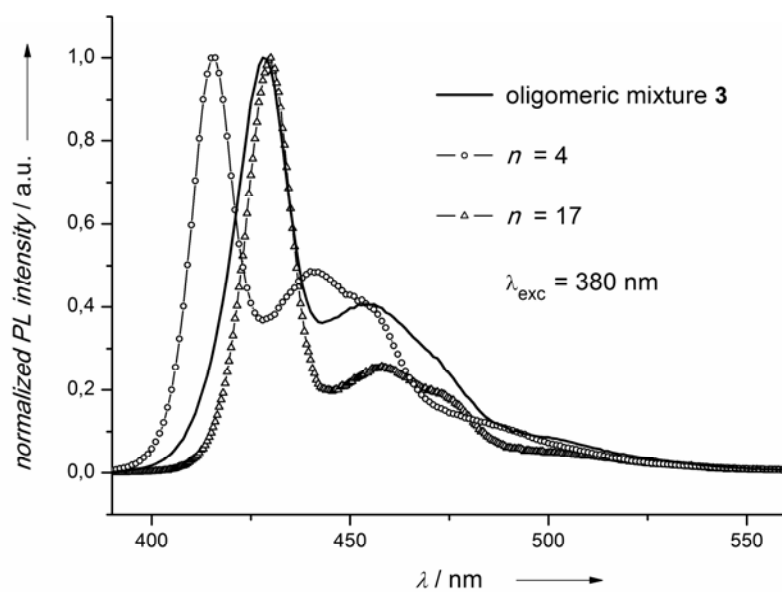


Figure S5. Emission spectra of the oligomeric mixture **3** (black curve) and some separated oligomers (symbols).

6. ^1H NMR end group analysis

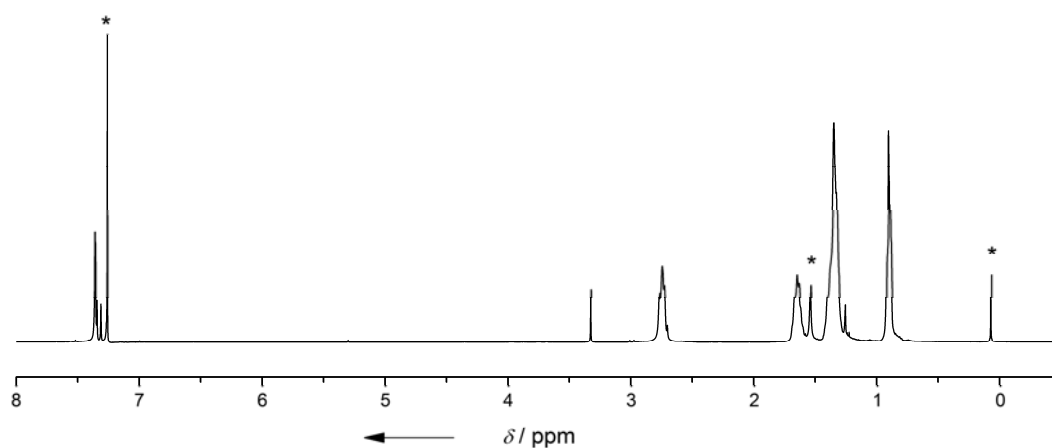


Figure S6. Full ^1H NMR spectrum of oligomeric mixture **3**. Asterisked peaks can be ascribed to residual solvents and impurities.

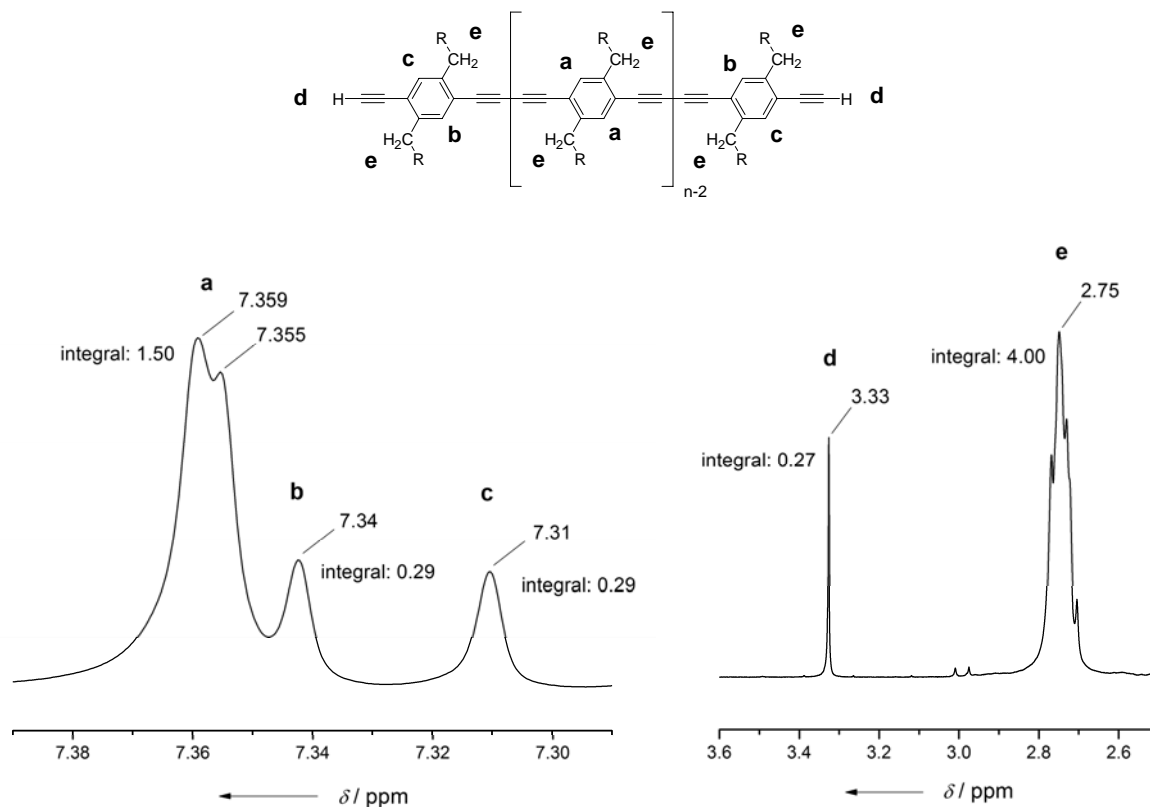


Figure S7. ¹H NMR spectra of **3**: aromatic (**a-c**), terminal alkyne (**d**) and aryl-CH₂ (**e**) signals of the oligomeric mixture.

Figure S7 displays two ¹H NMR spectra of **3** which have been integrated for end group analysis. Signal group **a** comprises all internal aromatic signals; the alkyl signal **e** consists of end group signals as well as internal signals and can be set as integration standard (4 H per repeating unit). Usually, terminal alkyne hydrogens are discriminated by the standard “zg” pulse sequences, resulting in insufficient integrals. If the “zg30” pulse sequence is applied, their signal intensity becomes comparable to aromatic signals. We know from comparison with the defined oligomers (e.g. **1**, **2** or **10**) that the integral of the terminal alkyne signal (**d**) relates to approximately 92 % of each integral of the aromatic end group signals (**b** and **c**). Hence, the integral of **d** can also be set as 0.29 ($\approx 0.27 / 0.92$). However, for the monomer one expects two acetylenic protons, resulting in a conversion ratio of $p = 1 - 0.29 / 2 = 0.855$ for the acetylene dimerization. Since the poly-Glaser reaction can be regarded as a polycondensation reaction with a single monomer, the simplified Carothers equation can be applied to determine the average degree of polymerization. We find

$$\bar{P}_n^{end\ group} = \frac{1}{1 - p} = 7 \pm 0.5.$$

7. MALDI-MS spectra

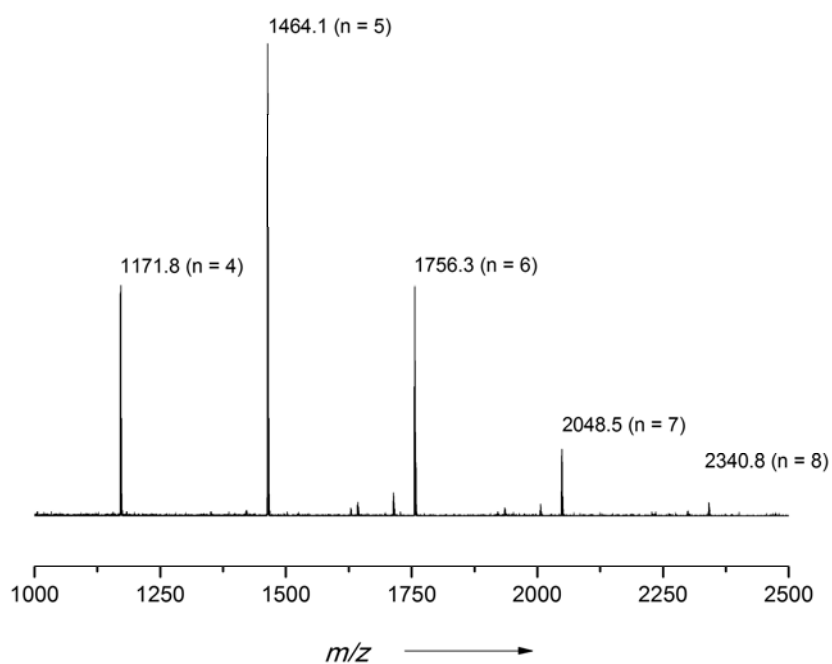


Figure S8. MALDI-MS spectrum of **3** (low mass method, matrix: DCTB).

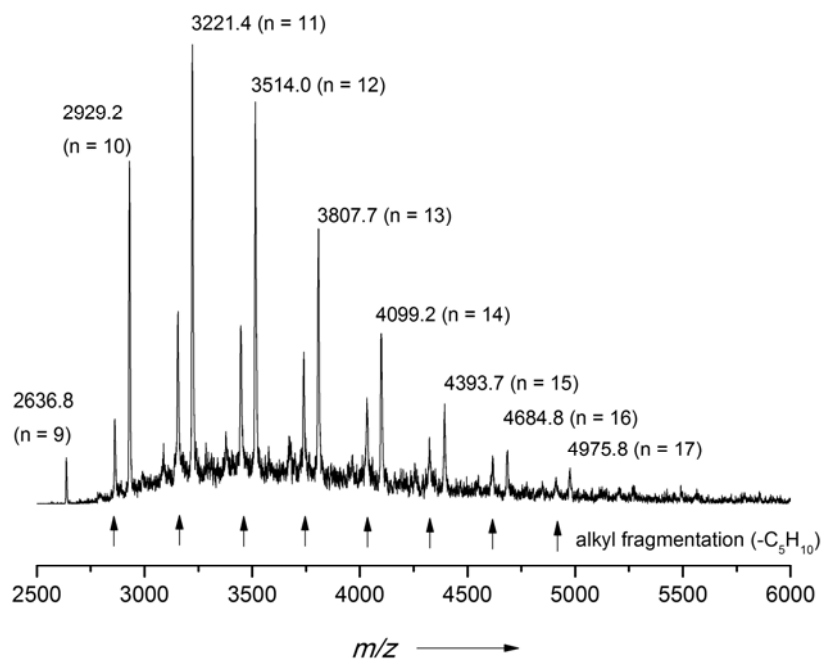


Figure S9. MALDI-MS spectrum of **3** (high mass method, matrix: dithranol).

8. DSC measurements

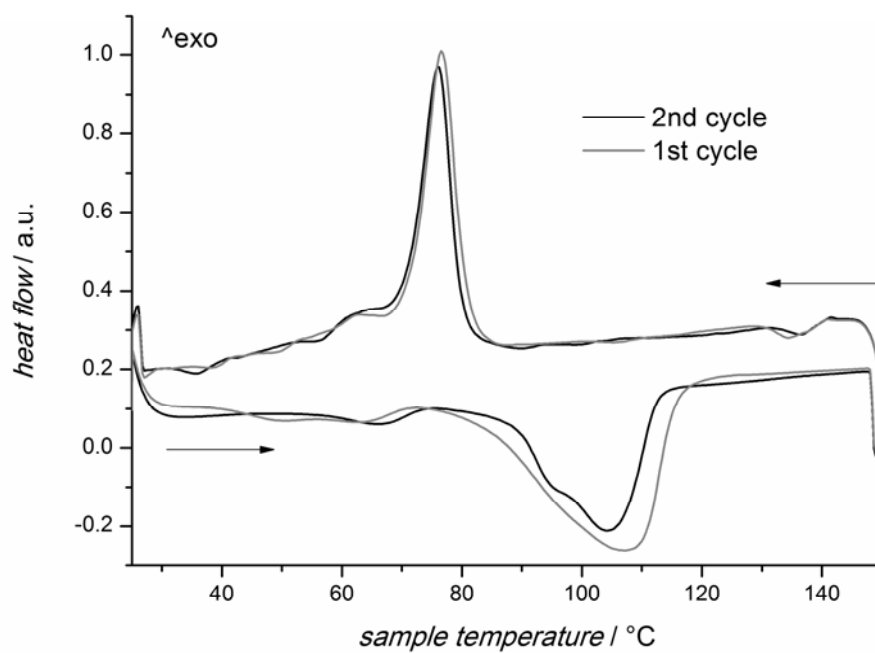


Figure S10. DSC thermogram of **3** measured at a heating/cooling rate of $\pm 10 \text{ K min}^{-1}$ (as obtained from precipitation with MeOH and drying in vacuo)

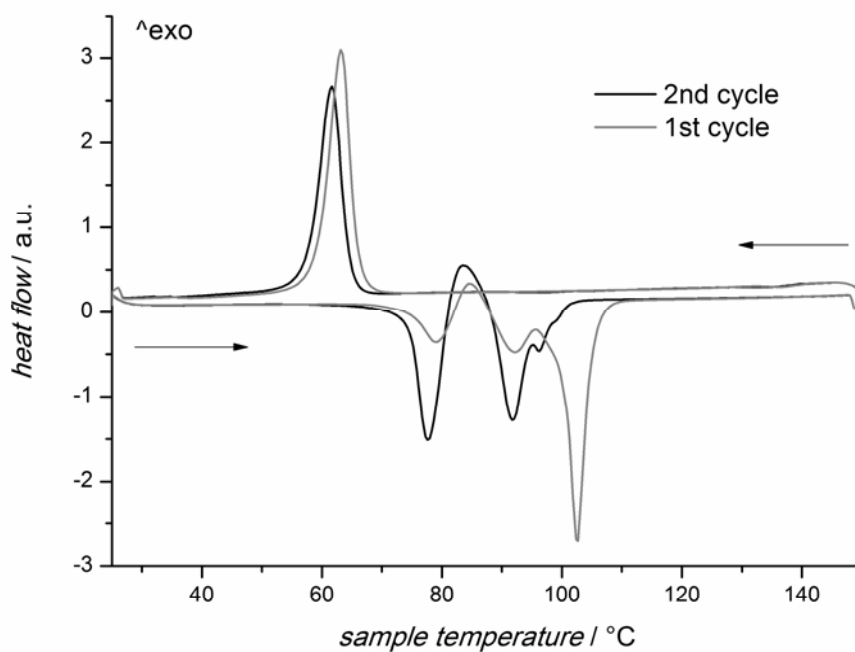
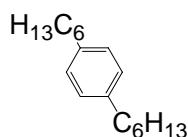


Figure S11. DSC thermogram of **1** measured at a heating/cooling rate of $\pm 10 \text{ K min}^{-1}$.

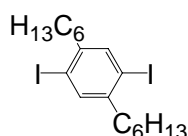
9. Synthesis

5 1,4-Dihexylbenzene



10.39 g (0.427 mol) Mg swarf was placed in a dry three-neck flask, which was then evacuated, heated and cooled down in a flow of Ar. The metal was suspended in dry (molecular sieve) Et₂O (180 mL) and 5 mL of 1-bromohexane were added via dropping funnel to start the reaction (turbid suspension). The reaction flask was cooled down to 0 °C and 1-bromohexane was added over 30 min (total 70.35 g, 0.426 mol). After 2 h of reflux heating (50 °C), the suspension was transferred into a dropping funnel. At 0 °C, the Grignard reagent was added dropwise to a solution of 25.06 g (0.170 mol) 1,4-dichlorobenzene (**4**) and 138.5 mg (0.256 mmol) NiCl₂(dppp) in 65 mL of Et₂O. The dropping funnel was rinsed with another 65 mL of Et₂O, then the reaction mixture was refluxed at 50 °C bath temperature for 5 h, cooled to RT and stirred overnight. The reaction was carefully quenched by addition of water (80 mL) and 400 mL of 1 mol/L HCl. The aqueous layer was separated and extracted several times with Et₂O, the combined organic layers were washed with water and brine and dried over MgSO₄. After removing the solvent at reduced pressure, the liquid residue was distilled in vacuo. The product was obtained as a colorless liquid (35.55 g, 0.144 mol, 85 %). B.p. 122 °C / 1.5 mbar; ¹H-NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.09 (s, 4 H), 2.57 ("t", ³J(H,H) ≈ 7.8 Hz, 4 H), 1.64-1.53 (m, 4 H), 1.38-1.27 (m, 12 H), 0.88 (t, ³J(H,H) ≈ 6.8 Hz, 6 H) ppm; ¹³C-NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 140.06, 128.20, 35.57, 31.75, 31.56, 29.06, 22.61, 14.09 ppm; MS (EI) C₁₈H₃₀ (246.23): *m/z* (%) 246.2 (30) [M]⁺, 175.1 (100) [M - C₅H₁₁]⁺, 117.0 (10), 105.0 (10) [M - C₁₀H₂₁]⁺, 91.0 (15).

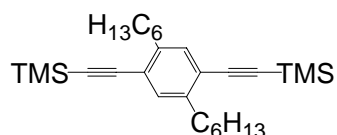
6 1,4-Dihexyl-2,5-diiodobenzene



5 (7.40 g, 30.0 mmol), I₂ (8.38 g, 33.0 mmol) and HIO₃ (2.64 g, 15.0 mmol) were placed in a round flask without the use of inert gas. The solids were suspended in HOAc (90 mL), H₂SO₄ (6 mL), CCl₄ (20 mL) and water (1.0 mL) and refluxed for 5 h at 115 °C oil bath temperature. The reaction mixture was cooled down to RT, stirred overnight, then poured on crushed ice

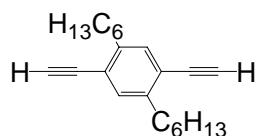
(200 mL). Phases were separated after addition of CHCl_3 (200 mL). The aqueous layer was extracted several times with CHCl_3 , the dark purple organic layer was washed with 10 % NaOH (until a yellow solution was obtained), water and brine. After drying over Na_2SO_4 , the solvents were removed in vacuo. The crude product was filtered through a short silica gel column (PE as eluent), recrystallized from EtOH (60 mL) and dried in vacuo. The product was received as a white powder (12.21 g, 24.5 mmol, 82 %). M.p. 50 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): δ = 7.59 (s, 2 H), 2.59 ("t", $^3J(\text{H,H}) = 7.8$ Hz, 4 H), 1.58-1.46 (m, 4 H), 1.37-1.28 (m, 12 H), 0.90 (t, $^3J(\text{H,H}) = 6.8$ Hz, 6 H) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C, TMS): δ = 144.69, 139.15, 100.18, 39.70, 31.46, 30.03, 28.85, 22.45, 13.94 ppm; MS (EI) $\text{C}_{18}\text{H}_{28}\text{I}_2$ (498.03): m/z (%) 498.0 (100) $[\text{M}]^+$, 427.0 (40) $[\text{M} - \text{C}_5\text{H}_{11}]^+$, 342.9 (10), 301.0 (30) $[\text{M} - \text{C}_5\text{H}_{11}\text{I}]^+$, 215.2 (20), 201.2 (15).

7 1,4-Dihexyl-2,5-bis(2-trimethylsilyl)ethynyl-benzene



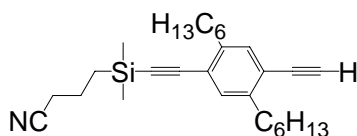
6 (3.74 g, 7.5 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.158 g, 0.225 mmol), anhydrous CuI (71 mg, 0.375 mmol) and PPh_3 (0.158 g, 0.60 mmol) were placed in a dry Schlenk tube, which was evacuated and purged with Ar. The solids were suspended in 20 mL of piperidine and dissolved by stirring at RT. 2.5 equivalents of trimethylsilyl acetylene (TMSA) (1.84 g, 18.75 mmol) were added, the reaction mixture was cooled with a water bath. Upon cooling to RT, another 0.5 equiv. of TMSA (0.37 g, 3.75 mmol) were added, the turbid mixture was diluted with 10 mL of THF and stirred overnight at RT. The reaction was diluted with distilled water (100 mL), phases were separated by adding the same amount of Et_2O . The aqueous phase was extracted several times with the Et_2O , the combined organic layers were washed with diluted HOAc (10 %), water and brine. After drying over Na_2SO_4 , the solvents were removed. The residue was purified by column chromatography (PE, $R_f = 0.72$) to yield 3.12 g of a white solid (7.11 mmol, 95 %). M.p. 44 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): δ = 7.24 (s, 2 H), 2.68 ("t", $^3J(\text{H,H}) \approx 7.8$ Hz, 4 H), 1.63-1.54 (m, 4 H), 1.39-1.25 (m, 12 H), 0.89 (t, $^3J(\text{H,H}) \approx 6.8$ Hz, 6 H), 0.25 (s, 18 H) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C, TMS): δ = 142.63, 132.43, 122.53, 103.93, 98.87, 34.11, 31.71, 30.57, 29.26, 22.62, 14.10, -0.30 ppm; MS (EI) $\text{C}_{28}\text{H}_{46}\text{Si}_2$ (438.31): m/z (%) 438.3 (100) $[\text{M}]^+$, 423.3 (30) $[\text{M} - \text{CH}_3]^+$, 367.2 (10) $[\text{M} - \text{C}_5\text{H}_{11}]^+$, 293.2 (30), 73.1 (35).

2 1,4-Diethynyl-2,5-dihexylbenzene



7 (3.10 g, 7.07 mmol) was dissolved in THF/MeOH (2:1, 150 mL, purged for 15 min with Ar). In a flow of Ar, anhydrous K_2CO_3 powder (9.77 g, 70.7 mmol) was added in small portions and the resulting white suspension was vigorously stirred overnight. The reaction was diluted with water (100 mL) and Et_2O (100 mL). The aqueous phase was extracted with Et_2O , the combined organic layers were washed with diluted HOAc (5 %, w/w), water and brine and dried over Na_2SO_4 . After removing the solvents, the crude product was purified by column chromatography (PE, $R_f = 0.80$). The product was received as a colorless oil (1.97 g, 6.70 mmol, 95 %). 1H -NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.30$ (s, 2 H), 3.28 (s, 2 H), 2.71 (“t”, $^3J(H,H) = 7.8$ Hz, 4 H), 1.65-1.55 (m, 4 H), 1.39-1.26 (m, 12 H), 0.89 (t, $^3J(H,H) = 6.9$ Hz, 6 H) ppm; ^{13}C -NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 142.67$, 132.92, 121.90, 82.24, 81.50, 33.76, 31.63, 30.42, 29.08, 22.58, 14.07 ppm; MS (EI) $C_{22}H_{30}$ (294.236): m/z (%) 294.2 (80) $[M]^+$, 279.2 (10), 265.2 (15), 251.2 (30), 237.2 (10), 223.2 (100) $[M - C_5H_{11}]^+$, 195.1 (15), 181.1 (25), 165.1 (30), 153.1 (40), 139.1 (45). GPC (PS calibration): $M_w = 510$ g mol^{-1} .

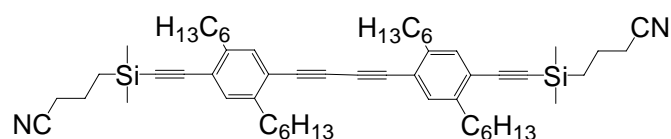
8 4-[(4-Ethynyl-2,5-dihexylphenylethynyl)dimethylsilyl]butyronitrile



To a stirred solution of **2** (1.96 g, 6.67 mmol) in dry THF (25 mL) was added dropwise $EtMgBr$ (6.7 mL, 1.0 mol/L solution in THF) via syringe and septum. The slightly warming mixture was stirred for 2 h at ambient conditions (no more ethane developing). (3-Cyanopropyl)dimethylsilyl chloride (1.08 g, 6.67 mmol) was then added slowly in a flow of Ar. After 3 h, the reaction was quenched by diluting with water and Et_2O . After phase separation, the aqueous layer was extracted several times with Et_2O , the combined organic layers were washed with diluted HOAc (5 %, w/w), water and brine. After drying over Na_2SO_4 , the solvents were removed in vacuo. The crude product was purified by column chromatography (PE/ $CH_2Cl_2 = 3:1 - 1:1$, $R_f(3:1) = 0.34$) to give 1.72 g (4.10 mmol, 61 %) of a yellow resin. 1H -NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.28$ (s, 1 H), 7.26 (s, 1 H), 3.29 (s, 1 H), 2.69 (2”t”, $^3J(H,H) \approx 6.3$ Hz, 4 H), 2.43 (t, $^3J(H,H) = 7.0$ Hz, 2 H), 1.89-1.77 (m, 2 H), 1.66-1.53 (m, 4 H), 1.41-1.23 (m, 12 H), 0.92-0.82 (m, 8 H), 0.26 (s, 6 H) ppm; ^{13}C -

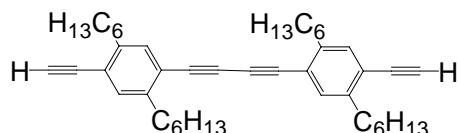
NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 142.77, 142.59, 132.98, 132.55, 122.48, 121.85, 119.60, 105.08, 96.74, 82.29, 81.60, 34.08, 33.81, 31.72, 31.63, 30.51, 30.49, 29.23, 29.12, 22.62, 22.58, 20.68, 20.52, 15.78, 14.10, 14.09, -1.80 ppm; MS (EI) C₂₈H₄₁NSi (419.30): *m/z* (%) 419.3 (100) [M]⁺, 404.2 (24) [M - CH₃]⁺, 351.3 (55) [M - C₄H₆N]⁺, 349.2 (25) [M - C₅H₁₀]⁺, 281.2 (16), 209.1 (14), 126.1 (73) [C₆H₁₁NSi]⁺, 98.0 (28).

9



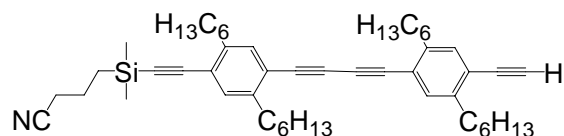
8 (1.00 g, 2.38 mmol) was dissolved in CH₂Cl₂ (75 mL, freshly distilled over CaH₂). Anhydrous CuCl (0.236 g, 2.38 mmol) and TMEDA (0.213 mL, 0.280 g, 2.38 mmol) were added to the vigorously stirred solution, which was kept in an oil bath at 30 °C. With a small membrane pump, a steady flow of air was piped through the suspension for 2 h. The reaction mixture was diluted with water, the layers were separated and the aqueous phase was extracted several times with CH₂Cl₂. The combined organic layers were washed with aqueous NH₃ solution (25 %), water, diluted HCl (0.5 M), water and brine. After drying over Na₂SO₄ the solvent was removed in vacuo. The crude product was purified by column chromatography (PE/CH₂Cl₂ = 1:1, *R_f* = 0.45) giving 1.00 g (1.19 mmol, quant.) of a yellow to orange solid. M.p. 63 °C; ¹H-NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.32 (s, 2 H), 7.27 (s, 2 H), 2.73 (“t”, ³*J* (H,H) \approx 7.8 Hz, 4 H), 2.69 (“t”, ³*J* (H,H) \approx 7.8 Hz, 4 H), 2.43 (t, ³*J* (H,H) = 7.0 Hz, 4 H), 1.87-1.79 (m, 4 H), 1.67-1.52 (m, 8 H), 1.41-1.27 (m, 24 H), 0.92-0.83 (m, 16 H), 0.27 (s, 12 H) ppm; ¹³C-NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 143.65, 142.71, 133.25, 132.63, 122.87, 121.59, 119.61, 105.02, 97.48, 81.55, 78.31, 34.07, 33.89, 31.72, 31.62, 30.58, 30.45, 29.21, 29.03, 22.62, 22.59, 20.66, 20.53, 15.74, 14.11, -1.82 ppm; MS (MALDI-TOF) C₅₆H₈₀N₂Si₂ (836.59): *m/z* 836.6 [M]⁺; GPC (PS calibration): *M_w* = 1310 g mol⁻¹.

10



9 (1.00 g, 1.19 mmol) was dissolved in THF/MeOH (2:1, 30 mL, purged with Ar for 15 min) In a flow of Ar, anhydrous powdered K_2CO_3 (1.81 g, 33.1 mmol) was added in small portions and the resulting white suspension was vigorously stirred overnight. The reaction mixture was diluted with Et_2O and water and the layers were separated. The aqueous layer was extracted several times with Et_2O , the combined organic layers were washed with water and brine and dried over Na_2SO_4 . After removal of the solvents in vacuo, the crude product was purified by column chromatography (PE, $R_f = 0.46$). The main fraction contained 0.64 g (1.09 mmol, 92 %) of a slightly yellow solid. M.p. 58 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.34$ (s, 2 H), 7.31 (s, 2 H), 3.32 (s, 2 H), 2.77-2.69 (m [2t], 8 H), 1.69-1.57 (m, 8 H), 1.41-1.28 (m, 24 H), 0.88 (m [2t], 12 H) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C, TMS): $\delta = 143.57$, 142.82, 133.21, 133.01, 122.33, 121.66, 82.24, 82.10, 81.43, 78.21, 33.86, 33.77, 31.64, 31.62, 30.52, 30.35, 29.07, 29.00, 22.58, 14.11, 14.08 ppm; MS (EI) $\text{C}_{44}\text{H}_{58}$ (586.45): m/z (%) 586.4 (100) $[\text{M}]^+$. GPC (PS calibration): $M_w = 850 \text{ g mol}^{-1}$.

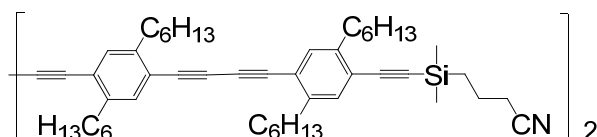
11



To a stirred solution of **10** (0.621 g, 1.06 mmol) in dry THF (5 mL), EtMgBr (1.2 mL, 1.0 mol/L solution in THF) was added dropwise over 15 min at RT. After 2 h, (3-cyanopropyl)dimethylsilylchloride (0.171 g, 1.06 mmol) was slowly added in a flow of Ar (15 min). After stirring overnight, the opaque reaction mixture was diluted with water and Et_2O . The aqueous layer was extracted several times with Et_2O , the combined organic layers were washed with water and brine and dried over Na_2SO_4 . After removal of the solvents in vacuo, the crude product was purified by column chromatography (PE/ $\text{CH}_2\text{Cl}_2 = 2:1$, $R_f = 0.46$) to give 0.387 g (0.543 mmol, 51 %) of an orange solid. M.p. 45 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.33$ (s, 1 H), 7.32 (s, 1 H), 7.30 (s, 1 H), 7.27 (s, 1 H), 3.32 (s, 1 H), 2.76-2.66 (m, 8 H), 2.43 (t, $^3J(\text{H,H}) = 6.9 \text{ Hz}$, 2 H), 1.87-1.79 (m, 2 H), 1.67-1.56 (m, 8 H), 1.41-1.27 (m, 24 H), 0.92-0.83 (m, 14 H), 0.27 (s, 6 H) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C, TMS): $\delta = 143.65$, 143.57, 142.82, 142.71, 133.26, 133.21, 133.01, 132.64, 122.88, 122.32,

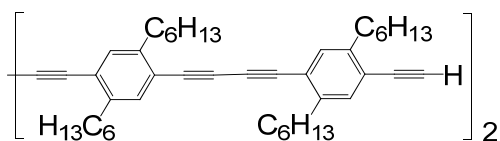
121.65, 121.61, 119.59, 105.04, 97.48, 82.23, 82.11, 81.51, 81.48, 78.32, 78.21, 34.08, 33.90, 33.86, 33.72, 31.62, 30.59, 30.51, 30.45, 30.35, 29.21, 29.06, 29.04, 28.99, 22.62, 22.58, 20.67, 20.53, 15.76, 14.11, -1.82 ppm; MS (EI) C₅₀H₆₉NSi (711.52): *m/z* (%) 711.5 (100) [M]⁺, 126.1 (25) [C₆H₁₁NSi]⁺, 98.0 (20).

12



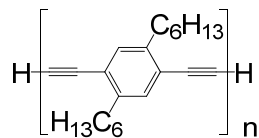
11 (0.100 g, 0.14 mmol) was dissolved in CH₂Cl₂ (10 mL, freshly distilled over CaH₂). Anhydrous CuCl (14 mg, 0.14 mmol) and TMEDA (16 mg, 0.14 mmol) were added to the vigorously stirred solution, which was kept in an oil bath at 30 °C. With a small membrane pump, a steady flow of air was piped through the suspension for 4 h. In between, after 2 h, 5 mL of CH₂Cl₂ were refilled. The reaction mixture was diluted with water, the layers were separated and the aqueous phase was extracted several times with CH₂Cl₂. The combined organic layers were washed with aqueous NH₃ solution (25 %), water, diluted H₂SO₄ (10 %, w/w), water and brine. After drying over MgSO₄ the solvent was removed in vacuo. The crude product was purified by repeated column chromatography (PE/CH₂Cl₂ = 1:1, *R_f* = 0.30) giving 82.4 mg (0.58 mmol, 83 %) of a bright yellow solid. M.p. 115 °C; ¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 7.35 (s, 4 H), 7.33 (s, 2 H), 7.27 (s, 2 H), 2.77-2.67 (m, 12 H), 2.43 (t, ³*J* (H,H) = 7.0 Hz, 4 H), 1.87-1.80 (m, 4 H), 1.68-1.57 (m, 16 H), 1.42-1.28 (m, 48 H), 0.93-0.84 (m, 28 H), 0.27 (s, 12 H) ppm; ¹³C-NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 143.69, 143.68, 142.73, 133.28, 133.26, 132.64, 122.93, 122.11, 122.01, 121.54, 119.61, 105.01, 97.53, 81.90, 81.82, 81.48, 78.87, 78.82, 78.29, 34.08, 33.90, 33.86, 31.72, 31.62, 30.60, 30.46, 29.22, 29.04, 28.98, 22.63, 22.58, 20.66, 20.53, 15.75, 14.12, -1.82 ppm; MS (MALDI-TOF) C₁₀₀H₁₃₆N₂Si₂ (1421.02): *m/z* 1672.0 [M + DCTB]⁺, 1422.0 [M]⁺; GPC (PS calibration): *M_w* = 2570 g mol⁻¹.

1



12 (78.5 mg, 55.0 μmol) was dissolved in THF/MeOH (5:2, 35 mL, purged with Ar for 15 min). In a flow of Ar, anhydrous powdered K_2CO_3 (76 mg, 0.55 mmol) was added and the resulting suspension was vigorously stirred for 2.5 hours. The reaction mixture was diluted with CH_2Cl_2 and water and the layers were separated. The aqueous layer was extracted several times with CH_2Cl_2 , the combined organic layers were washed with water and brine, and dried over MgSO_4 . After removal of the solvent in vacuo, the crude product was purified by column chromatography (PE/ CH_2Cl_2 = 4:1, R_f (10:1) = 0.74) and precipitation with methanol, giving 60.2 mg (51.4 μmol , 93%) of a yellow solid. M.p. 106 $^\circ\text{C}$; $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ = 7.36 (s, 4 H), 7.34 (s, 2 H), 7.31 (s, 2 H), 3.33 (s, 2 H), 2.81-2.67 (m, 16 H), 1.72-1.56 (m, 16 H), 1.45-1.22 (m, 48 H), 0.95-0.83 (m, 24 H) ppm; $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ = 143.70, 143.60, 142.84, 133.29, 133.22, 133.03, 122.39, 122.14, 122.03, 121.61, 82.23, 82.15, 81.86, 81.83, 81.41, 78.89, 78.83, 78.20, 33.87, 33.77, 31.63, 30.52, 30.46, 30.36, 29.07, 28.99, 22.59, 14.11, 14.08 ppm; MS (MALDI-TOF) $\text{C}_{88}\text{H}_{114}$ (1170.89): m/z 1170.9 $[\text{M}]^+$; GPC (PS calibration): M_w = 1970 g mol^{-1} .

3 Poly(1,4-(2,5-dihexyl)phenylene-butadiynylene)



2 (0.100 g, 0.34 mmol) was dissolved in CH₂Cl₂ (10 mL, freshly distilled over CaH₂). TMEDA (40 mg, 0.34 mmol) and anhydrous CuCl (34 mg, 0.34 mmol) were added to the vigorously stirred solution, which was kept in an oil bath at 30 °C. With a small membrane pump, a steady flow of air was piped through the suspension. In between, CH₂Cl₂ was refilled (5 mL per hour). After 6 h, the reaction mixture was poured into methanol (25 mL) and filtrated through a PTFE filter. The blue filtrate was discarded; the greenish filter cake was dissolved in THF and filtered through a short silica gel column (5 cm) to remove the copper salts. The turbid solution (silica gel particles) was again filtered through a PTFE filter. Finally, the solution was concentrated and the oligomer precipitated with methanol. 76.2 mg (73 %) of **3** as a bright yellow solid were received. ¹H-NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.38-7.34 (m, internal Ar-H), 7.34 (s, terminal Ar-H), 7.31 (s, terminal Ar-H), 3.33 (s, terminal alkyne), 2.79-2.69 (m, Ar-CH₂), 1.70-1.57 (m, Ar-CH₂-CH₂), 1.42-1.28 (m), 0.93-0.86 (m, CH₃) ppm; ¹³C-NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 143.72, 143.70, 143.60, 142.84, 133.30, 133.22, 133.03, 122.39, 122.14, 122.08, 122.02, 121.61, 83.23, 82.15, 81.86, 81.85, 81.83, 81.80, 81.41, 78.87, 78.83, 78.19, 33.87, 33.78, 31.63, 30.53, 30.46, 30.36, 29.72, 29.07, 28.99, 22.59, 14.12, 14.09 ppm; MS (MALDI-TOF): see SI; DSC (25 - 150 °C): see SI; GPC (PS calibration): <M_w> = 7600 g mol⁻¹; <P_n> (end group analysis) = 7 ± 0.5.

(1) Meier, H.; Stalmach, U.; Kolshorn, H. *Acta Polym.* **1997**, *48*, 379-384.

(2) Ickenroth, D.; Weissmann, S.; Rumpf, N.; Meier, H. *Eur. J. Org. Chem.* **2002**, 2808-2814.