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Supporting Information

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How flexible are poly(*para*-phenyleneethynylene)s?

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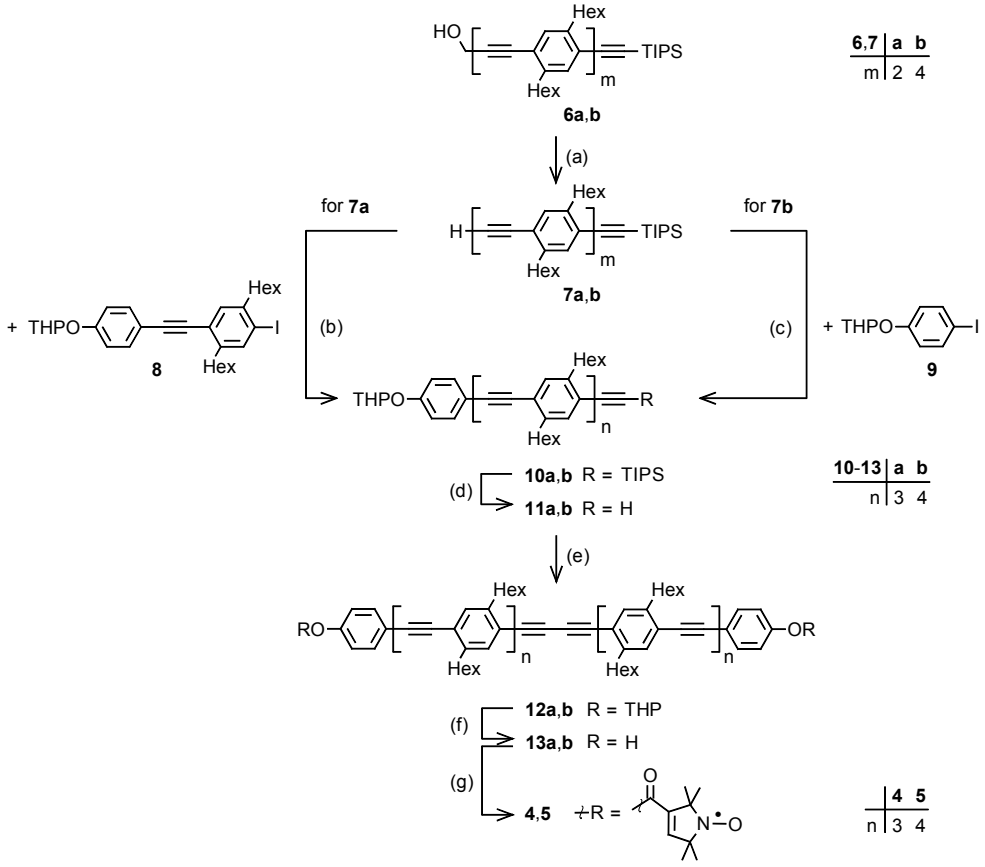
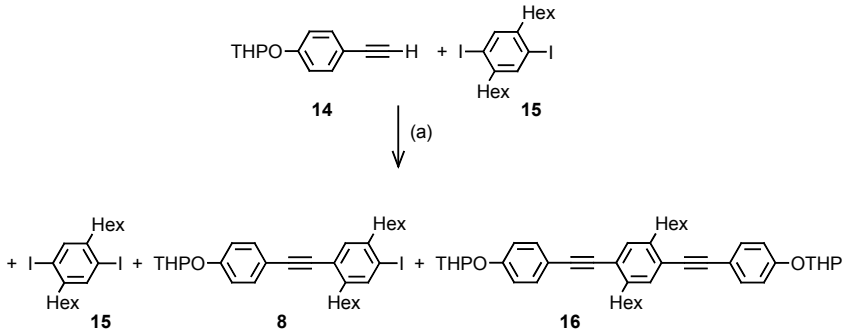
1. Synthesis

For the synthesis of compounds **4** and **5** (Scheme 1) the procedures developed for the synthesis of the shorter analogues **2** and **3** were used.[1] Starting from the readily available oligophenyleneethynylene building blocks **6a**,**b**[2] with two orthogonal protecting groups for the terminal alkyne groups, the aryl alkynes **7a**,**b** were obtained. Because of their tendency to decompose,[2] alkynes **7a**,**b** were coupled with the aryl iodides **8** or **9**, respectively, immediately after having been isolated. The alkyne protecting TIPS group of the coupling products **10a**,**b** was removed through the reaction with Bu_4NF and the thus obtained alkynes **11a**,**b** were oxidatively dimerized (Glaser coupling) in the presence of $Pd(PPh_3)_2Cl_2$ und CuI with air as the oxidant. The protected diphenols **12a**,**b** were treated with methanol in the presence of an acid to deprotect the OH groups which were used to attach finally the spin label 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic via an ester bond formation yielding the diradicals **4** and **5**.

The building block **8** was obtained through a coupling of alkyne **14** with 1.5 equivalents of diiodo compound **15** (Scheme 2). The reaction mixture consisted of diiodo compound **15**, monocoupling product **8** and dicoupling product **16**[1] in a ratio of 4.7:5.0:1.0 as determined by ^1H NMR spectroscopy. These three products were separated by column chromatography.



Scheme 1. Key: (a) MnO_2, KOH, Et_2O; (b) $Pd(PPh_3)_2Cl_2$, CuI, Et_2NH; (c) $Pd_2(dba)_3$, PPh_3, CuI, piperidine, THF; (d) $n$$Bu_4NF$, THF; (e) $Pd(PPh_3)_2Cl_2$, CuI, piperidine, THF, air; (f) TsOH, methanol, THF; (g) 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid, DCC, DMAP, THF.



Scheme 2. Key: (a) $Pd(PPh_3)_2Cl_2$, CuI, Et_2NH.

General. All reactions were performed under argon. Solvents were removed under reduced pressure. THF was distilled from sodium/benzophenone. Piperidine was distilled from CaH_2. Diethylamine was used as received. The petroleum ether used had a boiling range of 30-40 °C. For flash chromatography, Merck silica gel (40-63 μm) was used. For the preparation of the chromatotron plates (centrifugal preparative thin layer chromatography) Merck silica gel 60 PF_{254} was used. Thin layer chromatography (TLC) was carried out on silica gel coated aluminum foils (Merck, 60 F_{254}). Unless otherwise specified, NMR spectra were recorded at room temperature in CD_2Cl_2 as solvent and internal standard on a 300 MHz instrument (compounds **6b**-**13b**, and **5**) or on a 250 MHz instrument (compounds **6a**-**13a**, **8**, and **4**). For signal assignment the carbon multiplicity was determined by a DEPT-135 experiment. The melting points were determined in open capillaries. The building blocks **7a**,**b**[2], 1-iodo-4-(tetrahydropyran-2-yloxy)benzene (**9**),[3] [4-(tetrahydropyran-2-yloxy)phenyl]ethyne (**14**),[3] and 1,4-dihexyl-2,5-diiodobenzene (**15**),[2] were prepared as described in the literature. 1-Oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid was purchased from Acros.

Alkynyl-Aryl-Coupling (Sonogashira-Hagihara Coupling) - General Procedure

The solution of the two coupling components in diethylamine or a mixture of dry THF and dry piperidine was degassed through several freeze-pump-thaw-cycles. The solution was still below room temperature, when a mixture of the Pd complex and CuI was added. Shortly after a second phase formed: a second liquid phase in the case of Et_2NH as the solvent and a voluminous precipitate in the case of piperidine and THF as the solvents.

Compound 8. To a solution of 1,4-dihexyl-2,5-diiodobenzene (**15**) (1.83 g, 3.67 mmol) and [4-(tetrahydropyran-2-yloxy)phenyl]ethyne (**14**) (0.495 g, 2.447 mmol) in diethylamine (8 mL) were added $Pd(PPh_3)_2Cl_2$ (17 mg, 0.02 mmol) and CuI (10 mg, 0.05 mmol). After stirring the reaction mixture for 21 h at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in a mixture of diethyl ether, CH_2Cl_2, THF[4] and water. The aqueous phase was

extracted with diethyl ether containing a small amount of THF. The combined organic phases were washed with saturated aqueous NH_4Cl and dried (Na_2SO_4). The solvents were removed. Flash chromatography (pentane/Et_2O 20:1 v/v) gave as the first fraction starting material **15** (0.76 g, 42%; R_F = 0.7) and as a second fraction the monosubstitution product **8** (0.81 g, 58%; R_F = 0.5) as colorless solids. The disubstitution product **16** (R_F = 0.2)[1] was not isolated. Analytical data for **8**: M.p.: 51-52 °C. ^{1}H NMR: δ = 7.69 (s, 1 H, H ortho to I), 7.45 (half of AA'XX', 2 H, H meta to OTHP), 7.31 (s, 1 H, H meta to I), 7.04 (half of AA'XX', 2 H, H ortho to OTHP), 5.44 (t-shaped signal, J = 3 Hz, 1 H, O_2CH), 3.87 and 3.60 (2 m, 1 H each, OCH_2), 2.75 and 2.67 (2 t-shaped signals, J = 8 Hz, 2 H each, $ArCH_2$), 2.1 - 1.5 (m, 10 H, CH_2), 1.5 - 1.2 (m, 12 H, CH_2), 0.91 and 0.89 (2 t, J = 7 Hz, 3 H each, CH_3). ^{13}C NMR: δ = 157.8 (C_{Ar}-O), 144.4 and 143.2 (C_{Ar}-Hexyl), 140.0 (CH ortho to I), 133.1 (CH meta to OTHP), 132.5 (CH meta to I), 123.5 (C_{Ar}-C≡C of C_6H_2), 117.0 (CH ortho to OTHP), 116.6 (C_{Ar}-C≡C of C_6H_4), 100.7 (*C*-I), 96.9 (O_2CH), 93.9 and 86.8 (C≡C), 62.5 (OCH_2), 40.6, 34.2, 32.13, 32.08, 31.0, 30.68, 30.63, 29.60, 29.41, 25.6, 23.0 and 19.2 (CH_2), 14.3 (CH_3). Elemental analysis calcd (%) for $C_{31}H_{41}O_2I$ (572.572): C 65.03, H 7.22; found C 65.00, H 6.97.

Compound 10a. To a solution of alkyne **7a** (332 mg, 0.46 mmol) and iodo compound **8** (252 mg, 0.44 mmol) in THF (4 mL) and piperidine (1 mL) were added $PdCl_2(PPh_3)_2$ (3 mg, 0.004 mmol) and CuI (2 mg, 0.01 mmol). The reaction mixture was stirred at room temperature for 18 h. The suspension was cooled (ice bath) and diethyl ether and water were added. The aqueous phase was extracted with diethyl ether. The combined organic phases were washed successively with water, saturated aqueous NH_4Cl, water, and brine and dried ($MgSO_4$). The solvents were removed giving a brown, very viscous oil. Chromatography on a chromatotron plate (pentane/CH_2Cl_2 4:1 v/v, R_F = 0.27) gave impure material. A second chromatography on a chromatotron plate starting with pentane to elute a compound of unknown identity and then switching to pentane/CH_2Cl_2 4:1 → 2:1 v/v gave **10a** (400 mg, 78%) as a pale yellow oil with a blue fluorescence, that solidified slowly. ^{1}H NMR: δ = 7.47 (half of AA'XX', 2 H, H meta to OTHP), 7.393, 7.390, 7.38, 7.37, 7.35, and 7.33 (6 s, 1 H each, C_6H_2), 7.05 (half of AA'XX', 2 H, H ortho to OTHP), 5.45 (t-shaped signal, J = 3.1 Hz, 1 H, O_2CH), 3.88 and 3.61 (2 m, 1 H each, OCH_2), 2.82 (m, 12 H, $ArCH_2$), 2.1-1.6 (m, 18 H, CH_2), 1.36 (m, 36 H, CH_2), 1.17 (s, 21 H, C***H***$(CH_3)_2$), 0.89 (m, 18 H, CH_2CH_3). ^{13}C NMR: δ = 157.8 (C_{Ar}-O), 143.1, 142.6, 142.44, and 142.36 (C_{Ar}-Hex), 133.3, 133.1, 132.8, and 132.5[5] (CH of C_6H_2 and CH meta to OTHP), 123.4, 123.3, 123.25, 123.22, 123.17 and 122.8 (C_{Ar}-C≡C of C_6H_2), 117.0 (CH ortho to OTHP), 116.7 (C_{Ar}-C≡C of C_6H_4), 106.1 (*C*≡*C*-TIPS), 96.9 (O_2CH), 95.8 (*C*≡*C*-TIPS), 94.5, 93.5, 93.4, 93.3, 93.2, and 87.5 (Ar*C*≡*C*Ar), 62.5 (OCH_2), 34.8, 34.5, 32.24, 32.19, 31.3, 31.2, 31.14, 31.08, 30.7, 29.75, 29.68, 25.6, 23.1, 19.2 (CH_2), 18.9 ($CH(CH_3)_2$), 14.3 (CH_2CH_3), 11.8 (SiCH). MALDI-TOF with dithranol as the matrix: ($C_{82}H_{118}O_2Si$, 1163.930): *m/z* = 1080.3 (100%, $[M\text{-}DHP]^+$), 507.5 (45%).

Alkyne 11a. To a solution of **10a** (377 mg, 0.32 mmol) in THF (8 mL) was added 1M *n*-Bu_4NF (0.6 mL, 0.6 mmol) in THF at room temperature. The color of the reaction mixture turned instantaneously orange. After 4 h, diethyl ether and subsequently water was added. The aqueous phase was extracted

with diethyl ether. The combined organic phases were washed with brine and dried (Na_2SO_4). The solvents were removed. The yellow solid was suspended in methanol (2 mL). Removal of the methanolic solution with a pipette and drying of the solid residue under reduced pressure gave a pale yellow solid (330 mg) consisting of **11a** which was contaminated with a small amount of silyl containing products of the reaction. ^{1}H NMR: δ = 7.46 (half of AA'XX', 2 H, H meta to OTHP), 7.39 (s, 2 H , C_6H_2), 7.38, 7.37, 7.36 and 7.35 (4 s, 1 H each, C_6H_2), 7.05 (half of AA'XX', 2 H, H ortho to OTHP), 5.45 (t-shaped signal, J = 3.1 Hz, 1 H, O_2CH), 3.88 and 3.60 (2 m, 1 H each, OCH_2), 3.37 (s, 1 H, C≡CH), 2.88-2.73 (m, 12 H, $ArCH_2$), 2.1-1.6 (m, 18 H, CH_2), 1.5 -1.2 (m, 36 H, CH_2), 0.89 (m, 18 H, CH_3). Additional signals due to residual silyl byproduct: δ = 1.07 (s), 1.053 (s), 1.048 (s).

Protected Diphenol 12a. To a solution of **11a** (318 mg, 0.32 mmol) in THF (5 mL) and piperidine (1.5 mL) were added $PdCl_2(PPh_3)_2$ (4 mg, 0.006 mmol) and CuI (2 mg, 0.01 mmol) at room temperature. The reaction mixture was stirred under air for 2.3 h. The reaction was monitored by TLC [pentane/diethyl ether 5:1 v/v, R_F(**11a**) = 0.63, R_F(**12a**) = 0.55]. Diethyl ether and then water were added. The aqueous phase was extracted with Et_2O. The organic phase was washed with saturated aqueous NH_4Cl and brine. After drying (Na_2SO_4) the solvents were removed. Filtration through a short column with silica gel (CH_2Cl_2) gave **12a** (289 mg, 91%) as a yellow colored solid. ^{1}H NMR: δ = 7.47 (half of AA'XX', 4 H, H meta to OTHP), 7.42 (s, 2 H, C_6H_2), 7.41 (s, 4 H , C_6H_2), 7.40, 7.39, and 7.38 (3 s, 2 H each, C_6H_2), 7.06 (half of AA'XX', 4 H, H ortho to OTHP), 5.45 (t-shaped signal, J = 3.0 Hz, 2 H, O_2CH), 3.88 and 3.60 (2 m, 2 H each, OCH_2), 2.84 (m, 24 H, $ArCH_2$), 2.1-1.6 (m, 36 H, CH_2), 1.5 -1.2 (m, 72 H, CH_2), 0.90 (m, 36 H, CH_3).

Diphenol 13a. To a solution of **12a** (259 mg, 0.13 mmol) in methanol (4 mL) and THF (10 mL) was added *p*-toluenesulphonic acid monohydrate (24 mg, 0.13 mmol). The reaction was monitored by TLC [CH_2Cl_2, R_F(**13a**) = 0.2, R_F(**12a**) = 0.8], After 5h at room temperature, methanol was added. The precipitate was isolated and washed with methanol and finally dried in vacuo to give **13a** (185 mg, 78 %) as a yellow solid. ^{1}H NMR: δ = 7.44 (half of AA'XX', 4 H, H meta to OH), 7.42 (s, 2 H, C_6H_2), 7.41 (s, 4 H, C_6H_2), 7.40, 7.39, and 7.38 (3 s, 2 H each, C_6H_2), 6.85 (half of AA'XX', 4 H, H ortho to OH), 5.26 (s, 2H, OH), 2.85 (m, 24 H, $ArCH_2$), 1.72 (m, 24 H, CH_2), 1.37 (m, 72 H, CH_2), 0.91 (m, 36 H, CH_3). ^{13}C NMR: δ = 156.5 (C_{Ar}-O), 144.3, 142.6, 142.5, and 142.4 (***C***$_{Ar}$-Hex), 133.7, 133.6, and 133.5[5] (CH of C_6H_2, CH meta to OH), 132.8 and 132.5[5] (CH of C_6H_2), 124.3 (***C***$_{Ar}$-C≡C-C≡C), 123.5, 123.4, 123.0, 122.8 and 121.5 (***C***$_{Ar}$-C≡CAr of C_6H_2), 116.1 (***C***$_{Ar}$-C≡C of C_6H_4), 116.0 (CH ortho to OH), 94.4, 94.2, 93.6, 93.2 (signal intensity suggests 2C), and 87.4 (Ar***C***≡***C***Ar), 82.2 (***C***≡C-C≡***C***), 78.6 (C≡***C***-***C***≡C), 34.6, 34.4, 32.3, 32.2, 32.1, 31.14, 31.07, 31.0, 29.7, 29.6, 29.5, 23.1 (CH_2), 14.3 (CH_3). MALDI-TOF with dithranol as the matrix ($C_{136}H_{178}O_2$, 1844.918): *m/z* = 1846.1 (100%, M^+).

Diradical 4. To a solution of diphenol **13a** (96 mg, 0.052 mmol), 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid (38 mg, 0.21 mmol) and DMAP (25 mg, 0.21 mmol) in THF (3 mL) was added N,N'-dicyclohexylcarbodiimide (42 mg, 0.21 mmol). The reaction mixture was stirred at room

temperature for 3 d. The precipitate was filtered off and washed with THF until the solid was colorless. The solvent of the filtrate was removed. In order to get rid of trapped THF, the crude product was dissolved in CH_2Cl_2 and the solvent was removed . The crude product was suspended in a small amount of CH_2Cl_2 containing some pentane (the colorless insoluble material is most probably the urea compound) and applied to a chromatotron plate. Elution with pentane/CH_2Cl_2 1:1 v/v gave a first fraction containing unidentified compounds. Then the solvent was changed to pentane/CH_2Cl_2/Et_2O 15:15:1 to give diradical **4** (63 mg, 56%) as a yellow solid which was freeze-dried from benzene. M.p: 162-163 °C. ^{1}H NMR: All signals are broad and structureless. δ = 7.63 (br s, 4 H, H meta to OR), 7.42 (s, 12 H, C_6H_2),[6] 2.85 (m, 24 H, $ArCH_2$), 1.74 (m, 24 H, CH_2), 1.38 (m, 72 H, CH_2), 0.91 (m, 36 H, CH_3). ^{13}C NMR:[7] δ = 143.7, 142.3, 142.04, and 142.01 (***C***$_{Ar}$-Hex), 133.2 (br, $C_{Ar}H$), 132.4 (br and very intense, $C_{Ar}H$)[5], 123.7, 122.9, 122.6, and 122.3 (***C***$_{Ar}$-C≡C), 121.3 (broad, CH ortho to OR), 121.0 (***C***$_{Ar}$-C≡C), 93.7, 93.0, 92.9, 92.7 and 88.6 (Ar***C***≡***C***Ar), 81.7 (***C***≡C-C≡***C***), 78.1 (C≡***C***-***C***≡C), 34.1, 34.0, 33.9, 31.8, 31.7, 31.6, 30.63, 30.57, 30.50, 29.2, 29.1, 29.0, and 22.6 (CH_2), 13.8 (CH_3). Elemental analysis calcd (%) for $C_{154}H_{202}O_6N_2$ (2177.318): C 84.95, H 9.35, N 1.29; found C 85.05, H 9.21, N 1.29. MALDI-TOF with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malonitrile as the matrix: *m/z* = 2178.0 (25%, M^+), 2162.8 (0.6%, $[M-CH_3]^+$), 2147.5 (0.2%, $[M-2CH_3]^+$).

Compound 10b. To a solution of alkyne **7b** (363 mg, 0.29 mmol) and 1-iodo-4-(tetrahydropyran-2-yloxy)benzene (**9**) (76 mg, 0.25 mmol) in THF (6 mL) and piperidine (2.5 mL) were added $Pd_2(dba)_3$ (14.0 mg, 0.015 mmol), CuI (5.1 mg, 0.027 mmol), and triphenylphosphane (16.0 mg, 0.06 mmol) at room temperature. The reaction was stirred at room temperature for 14 h. The suspension was cooled (ice bath) and diethyl ether and water were added. The aqueous phase was extracted with diethyl ether. The combined organic phases were washed successively with water, saturated aqueous NH_4Cl, water, and brine and dried (Na_2SO_4). The solvent was removed. Flash chromatography (petroleum ether/CH_2Cl_2 4:1 v/v; The crude product was applied as a solution in petroleum ether/CH_2Cl_2 2:1 v/v) gave **10b** (326 g, 91%, R_F = 48) as a dark yellow, slowly solidifying oil. M.p: 83-85 °C. ^{1}H NMR: δ = 7.47 (half of AA'XX', 2 H, H meta to OTHP), 7.41 (s, 3 H, C_6H_2), 7.40, 7.39, 7.38, 7.36, and 7.34 (5 s, 1 H each, C_6H_2), 7.06 (half of AA'XX', 2 H, H ortho to OTHP), 5.46 (t-shaped signal, J = 3.1 Hz, 1 H, O_2CH), 3.88 and 3.61 (2 m, 1 H each, OCH_2), 2.84 (m, 16 H, $ArCH_2$), 2.1-1.5 (m, 22 H, CH_2), 1.5-1.2 (m, 48 H, CH_2), 1.17 (s, 21 H, C***H***($C***H***_3$)$_2$), 0.90 (m, 24 H, $CH_2C***H***_3$). ^{13}C NMR: δ = 157.7 (C_{Ar}-O), 143.1, 142.6, 142.44, 142.42, and 142.3 (***C***$_{Ar}$-Hex), 133.2, 133.1, 132.79, 132.75 and 132.4 (CH of C_6H_2 and CH meta to OTHP), 123.33, 123.26, 123.22, 123.19, 123.14 and 122.8 (***C***$_{Ar}$-C≡C of C_6H_2), 116.9 (CH ortho to OTHP), 116.7 (***C***$_{Ar}$-C≡C of C_6H_4), 106.1 (***C***≡***C***-TIPS), 96.8 (O_2CH), 95.8 (***C***≡***C***-TIPS), 94.5, 93.52, 93.46, 93.42, 93.39, 93.30, 93.2, and 87.5 (Ar***C***≡***C***Ar), 62.5 (OCH_2), 34.8, 34.5, 32.24, 32.18, 31.3, 31.2, 31.14, 31.08, 30.7, 29.75, 29.68, 25.6, 23.1, and 19.2 (CH_2), 18.9

($CH(\boldsymbol{C}H_3)_2$), 14.3 ($CH_2\boldsymbol{C}H_3$), 11.8 (SiCH). Elemental analysis calcd (%) for $C_{102}H_{146}O_2Si$ (1432.374): C 85.53, H 10.27; found C 85.17, H 9.93.

Alkyne 11b. To a solution of **10b** (317 g, 0.22 mmol) in THF (8 mL) was added 1M Bu_4NF (0.5 mL, 0.5 mmol) in THF at room temperature. The reaction mixture turned instantaneously reddish brown and became intensively fluorescent. After 3.5 h, diethyl ether and subsequently water was added. The aqueous phase was extracted with diethyl ether. The combined organic phases were washed first with water and then brine, and dried ($MgSO_4$). The solvent was removed. The residue, a green solid, was suspended in methanol (10 mL). Heating of this suspension resulted in a melting of **11b** and a mixture of two liquid phases. After cooling to room temperature, the solid was isolated and treated once again, as described above, with methanol (15 mL) to yield **11b** (262 mg, 93%) as a green solid containing traces of the silyl byproduct formed upon desilylation. ^{1}H NMR: δ = 7.47 (half of AA'XX', 2 H, H meta to OTHP), 7.40 (s, 3 H, C_6H_2), 7.39, 7.382, 7.375, 7.366 and 7.35 (5 s, 1 H each, C_6H_2), 7.05 (half of AA'XX', 2 H, H ortho to OTHP), 5.45 (t-shaped signal, J = 3.2 Hz, 1 H, O_2CH), 3.88 and 3.61 (2 m, 1 H each, OCH_2), 3.37 (s, 1 H, C≡CH), 2.88-2.73 (m, 16 H, $ArCH_2$), 2.1-1.6 (m, 22 H, CH_2), 1.5 -1.2 (m, 48 H, CH_2), 0.90 (m, 24 H, CH_3). Additional signals due to residual silyl byproduct: δ = 1.08 (s), 1.048 (s), 1.053 (s). FD-MS ($C_{93}H_{126}O_2$, 1276.029): *m/z* = 1276.5 (100%, M^+), 1232.4 (15%), 1190.7 (84%, $[M\text{-}DHP]^+$), 637.9 (97%, M^{2+}), 595.7 (66%, $[M\text{-}DHP]^{2+}$).

Protected Diphenol 12b. To a solution of **11b** (244 mg, 0.19 mmol) in THF (4 mL) and piperidine (1 mL) were added $PdCl_2(PPh_3)_2$ (2.8 mg, 0.004 mmol) and CuI (1.5 mg, 0.008 mmol) at room temperature. After stirring the reaction mixture for 2 h under air at room temperature, water (10 mL) was added. The green precipitate was isolated, washed with water and finally with methanol, and dried at reduced pressure. Chromatography (petroleum ether/CH_2Cl_2 4:1 v/v; The compound was applied to the column as a solution in petroleum ether/CH_2Cl_2 1:1.) gave **12b** (205 mg, 84%) as a greenish yellow solid. ^{1}H NMR: δ = 7.46 (half of AA'XX', 4 H, H meta to OTHP), 7.41 (s, 2 H, C_6H_2), 7.40 (s, 8 H, C_6H_2), 7.39, 7.38, and 7.37 (3 s, 2 H each, C_6H_2), 7.05 (half of AA'XX', 4 H, H ortho to OTHP), 5.45 (t-shaped signal, J = 3.1 Hz, 2 H, O_2CH), 3.87 and 3.61 (2 m, 2 H each, OCH_2), 2.84 (m, 32 H, $ArCH_2$), 2.1-1.6 (m, 44 H, CH_2), 1.5 -1.2 (m, 96 H, CH_2), 0.89 (m, 48 H, CH_3).

Diphenol 13b. Compound **12b** (186 mg, 0.07 mmol) was dissolved in THF (8 mL) and methanol (1.5 mL) under very mild heating. *P*-toluenesulphonic acid monohydrate (6.6 mg, 0.04 mmol) was added to this solution at room temperature. The reaction was monitored by TLC [CH_2Cl_2, R_F(**13b**) = 0.3; R_F(**12b**) = 0.9; R_F(most probably of monodeprotected **12b**) = 0.6]. After 1 h methanol (0.2 mL) was added. The reaction was still incomplete after 3 h. Therefore more of *p*-toluenesulphonic acid monohydrate (7.7 mg, 0.04 mmol) was added. Because 4 h later, the TLC still showed a trace of monodeprotected **12b**, once again *p*-toluenesulphonic acid monohydrate (6.5 mg, 0.04 mmol) was added. After stirring the reaction mixture for another 1 h, methanol was added. The yellow-green precipitate was isolated, washed with methanol and ethanol and finally dried in vacuo to give **13b** (167 mg, 96 %) as a green-yellow waxy solid which showed a low solubility in CH_2Cl_2. M.p.: 173-174 ^{o}C.

^{1}H NMR ($CDCl_3$): δ = 7.41 (half of AA'XX', 4 H, H meta to OH), 7.37 (s, 2 H, C_6H_2), 7.36 (s, 8 H, C_6H_2), 7.34 (s, 6 H, C_6H_2), 6.81 (half of AA'XX', 4 H, H ortho to OH), 4.88 (br s, 2H, OH), 2.81 (m, 32 H, $ArCH_2$), 1.69 (m, 32 H, CH_2), 1.33 (m, 96 H, CH_2), 0.87 (m, 48 H, CH_3). ^{13}C NMR: δ = 156.5 (C_{Ar}-O), 144.2, 142.52, 142.49, 142.47, 142.45, and 142.43 (***C***$_{Ar}$-Hex), 133.7 and 133.5 (CH of C_6H_2, CH meta to OH), 132.84, 132.80, and 132.4 (CH of C_6H_2), 124.2 (***C***$_{Ar}$-C≡C-C≡C), 123.4, 123.31, 123.28, 123.1, 123.0, 122.8 and 121.5 (***C***$_{Ar}$-C≡CAr of C_6H_2), 116.01 (***C***$_{Ar}$-C≡C of C_6H_4), 115.95 (CH ortho to OH), 94.3, 94.2, 93.6, 93.5, 93.4, 93.2 (signal intensity suggests 2C), and 87.3 (Ar***C***≡***C***Ar), 82.1 (***C***≡C-C≡***C***), 78.6 (C≡***C***-***C***≡C), 34.5, 34.3, 32.20, 32.17, 32.1, 31.14, 31.06, 30.99, 29.7, 29.6, 29.5, 23.1 (CH_2), 14.3 (CH_3). Elemental analysis calcd (%) for $C_{176}H_{234}O_2$(2381.806): C 88.75, H 9.90; found C 88.65, H 9.87. FD-MS: *m/z* = 2382.8 (72%, M^+), 1786.7 (14%) 1588.8 (23%), 1226.3 (15%), 1191.0 (100%, M^{2+}), 952.3 (17%), 794.0 (55%, M^{3+}).

Diradical 5. To a solution of diphenol **13b** (60 mg, 0.025 mmol), 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid (18.3 mg, 0.10 mmol) and DMAP (12.9 mg, 0.11 mmol) in THF (4 mL) was added N,N'-dicyclohexylcarbodiimide (20 mg, 0.10 mmol). The reaction mixture was stirred at room temperature for 3 d. The precipitate was filtered off and washed with THF until the solid was colorless. The filtrate was concentrated to dryness. To remove residual THF, the residue was dissolved in CH_2Cl_2 and the solvent was removed. The crude product was suspended (the colorless insoluble material is most probably the urea compound) in a small amount of CH_2Cl_2 containing petroleum ether and applied to a chromatotron plate. Elution with pentane/CH_2Cl_2 1:1 v/v gave a first fraction containing unidentified compounds. Then the solvent was changed to petroleum ether/CH_2Cl_2/Et_2O 15:15:2 to give diradical **5** (55 mg, 80%) as a yellow solid. M.p.: 195-197 °C. ^{1}H NMR ($CDCl_3$): All signals are broad and structureless. δ = 7.6 (very br s, 4 H, H meta to OR), 7.41 (s, 4 H, C_6H_2), 7.42, 7.39 and 7.38 (3 s, together 16 H, C_6H_2),[8] 2.82 (m, 32 H, $ArCH_2$), 1.72 (m, 32 H, CH_2), 1.36 (m, 96 H, CH_2), 0.90 (m, 48 H, CH_3). Elemental analysis calcd (%) for $C_{194}H_{258}O_6N_2$ (2714.206): C 85.85, H 9.58, N 1.03; found C 85.80, H 9.62, N 0.96. MALDI-TOF with dithranol as the matrix: *m/z* = 2715 (100%, $[M]^+$), 2701 (18 %, $[M\text{-}CH_3]^+$), 2687 (6%, $[M\text{-}2CH_3]^+$), 2547 (28%, [M-spin label]$^+$), 2535 (6%).

2. EPR spectroscopy

EPR samples were prepared by dissolving 0.5 mg of compounds **1** or **2** or 0.1 mg of compounds **3**, **4**, or **5** in the appropriate amount of perdeuterated *o*-terphenyl, synthesized according to standard procedures,[9] to obtain concentrations of 1.5 mmol L^{-1} (**1**, **2**) or 0.4 mmol L^{-1} (**3**, **4**, **5**). An industrial heat gun GHG 660 LCD (Bosch GmbH, Gerlingen-Silberhöhe, Germany) adjusted to an air temperature of 100 °C was used for melting the *o*-terphenyl. The melt was crystallized in a refrigerator (4 °C) and powdered in an agate mortar. Approximately 200 mg of the powder was filled into home-

made EPR tubes with an outer diameter of 3 mm (Herasil tubing, Heraeus Quarzschmelze GmbH, Hanau, Germany) and remolten with the heat gun at 100 °C air temperature. The sample was kept at this temperature until all air bubbles had risen to the surface, then freeze-quenched in liquid nitrogen and directly inserted into the EPR probehead.

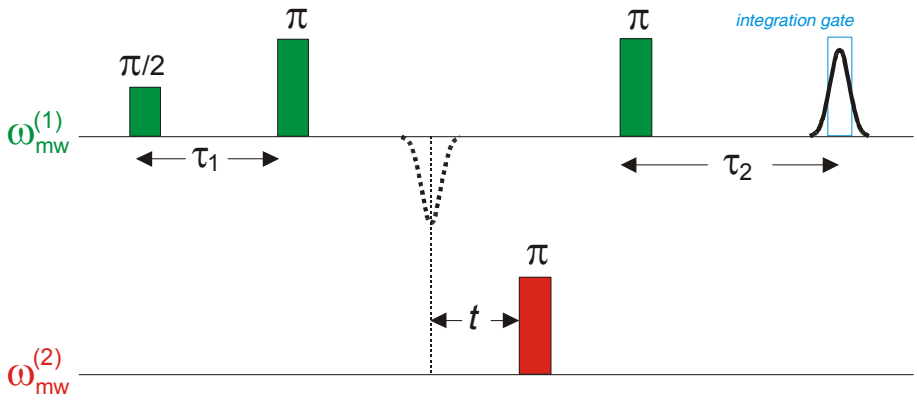


Figure S1. Label-to-label distance distributions $P(r_{LL})$ of oligoPPEs obtained by Tikhonov regularization with optimum regularization parameters α = 0.01 (**1**), 0.1 (**2**), 1 (**3**), 100 (**4**), and 100 (**5**).

Dipolar time evolution data were obtained at a temperature of 50 K at X-band frequencies (~9.3-9.4 GHz) with a Bruker Elexsys 580 spectrometer equipped with a Bruker Flexline split-ring resonator ER 4118X_MS3 using the four-pulse double electron electron resonance (DEER) experiment $\pi/2(\nu_{obs})$-τ_1-$\pi(\nu_{obs})$-t'-$\pi(\nu_{pump})$-$(\tau_1+\tau_2-t')$-$\pi(\nu_{obs})$-τ_2-*echo* (Figure S1).[10] The dipolar evolution time in this experiment is $t = t'-\tau_1$. A phase cycle $[(+x)-(-x)]$ was applied to the $\pi/2$ pulse to cancel any receiver offset. Data were analysed only for $t>0$. The resonator was overcoupled to $Q \sim 100$, the pump frequency ν_{pump} was set to the centre of the resonator dip and coincided with the maximum of the nitroxide EPR spectrum, while the observer frequency ν_{obs} was 65 MHz higher and coincided with the low-field local maximum of the spectrum at the initial external magnetic field $B_0(0)$. For orientation averaging the field was varied, adding 23 traces with a B_0 increment of 0.1 mT. For deuterium modulation averaging at each field 8 traces were added starting at $\tau_1(0)$= 400 ns and incrementing this interpulse delay by $\Delta\tau_1$= 56 ns. All experiments were performed with a pump pulse length of 12 ns, a pump pulse flip angle of π and with observer pulse lengths of 32 ns. Measurement times for each data set were approximately 12 h at repetition times of 2 ms.

3. Molecular dynamics simulation

Molecular dynamics simulations were carried out with the program package Cerius2 (v.3.8, Molecular Simulations, Inc.), using the PCFF force field. The NO groups of the nitroxide moieties were substituted by keto groups to avoid problems with force field parametrization for nitroxides.[11] The systems were first pre-equilibrated (canonical ensemble in a Berendsen temperature bath, 20 000 steps, time step 0.5×10^{-15}s, temperature of 300 K) and then sampled by a 2 ns run (Nosé-Hoover thermostat,

4×10^6 steps, time step 0.5×10^{-15}s, temperature of 300 K). Structures were written to trajectory files in time intervals of 1×10^{-13}s. Time traces of the N and O coordinates of the nitroxide groups and of the terminal C atoms of the oligo(*p*-phenyleneethynylene) backbone were extracted from the trajectory files using the gOpenMol program and converted to histograms of the distance distribution with a resolution of 0.01 nm by a home-written Matlab (The MathWorks, Inc.) program.

4. Coarse-grained conformational model

The *p*-phenyleneethynylene backbone was modelled as a freely rotating chain with harmonic bending potentials at the joints. The following initial segment lengths were estimated from force field minimization of the backbone of compound **5** with the MMFF94 force field as implemented in Titan (Wavefunction, Inc., Irvine, CA, USA): 0.2795 nm for a phenylene group, 0.1430 nm for a phenylene-ethynylene bond, 0.1201 nm for the triple bond of the ethynylene unit, and 0.1378 nm for the bond between two ethynylene units. In simulations all these bond lengths are scaled by the stretch factor *s*. Furthermore, a harmonic potential for bond stretching vibrations was assumed that corresponds to a normal distribution of the segment length with a standard deviation corresponding to 1.89% of the segment length. This number was obtained by analyzing the bond length variation in MD simulations. The bending potential at joints located on a sp atom of an ethynylene group is given by the fit parameter F_B, while the bending potential of a joint located at the terminal sp^2 atom of a phenylene group is assumed to be half as large. The nitroxide end labels are treated as additional segments with a length given by the external fit parameter *l* and a bending potential of the joint between the terminal phenylene unit and the label given by the external fit parameter *B*.

The conformational ensemble for this model is computed by a Monte Carlo simulation, treating the actual length r_j of each segment, the bond angle θ_j at each joint as random numbers with a normal distribution whose standard deviation is determined by the potentials and the rotation angle ϕ_j as a random number uniformly distributed between 0 and 2π. The mean value of all bond angles θ_j is 0° in the polymer physics definition given in Figure 2 of the paper, corresponding to bond angles of 180° in common chemical nomenclature. The distances between the terminal C atoms of the oligo(*p*-phenyleneethynylene) backbone and between the ends of the label segments were extracted from the Cartesian coordinates of each computed conformation and written to histograms of the distance distribution with a resolution of 0.01 nm. The whole simulation was performed by a home-written Matlab (The MathWorks, Inc.) program that is available from the authors on request.

5. Data analysis

5.1 Model-free analysis

Flexibility of the backbone causes an asymmetry of the end-to-end distance distribution $P(r_{EE})$ as shown in Figures 2 and 5 of the paper. To test whether such asymmetry is also observable in the label-

to-label distance distributions $P(r_{LL})$ we performed a model-free analysis of DEER data by Tikhonov regularization,[12] using the L curve as a criterion for determining the optimum regularization parameter.[13] Primary data from experiments without orientation averaging were background corrected by fitting an exponential decay function $B(t)$ for the intermolecular contribution, subtracting $B(t)$, and finally dividing by $B(t)$. The form factors $F(t)$ obtained in this way were then processed by Tikhonov regularization. All model-free processing was performed with the program DeerAnalysis2006.[14] Data for all five compounds in the respective relevant distance ranges are shown in Figure S2. For **1**, **2**, **3**, and **4** the expected asymmetry is clearly visible, whereas for **5** the number of observed dipolar oscillations appears to be too small to detect the true shape of the distance distribution. Nevertheless we included DEER data for **5** in model-dependent fitting, as even with the small number of oscillations they were still found to be a useful constraint for separating backbone and label contributions.

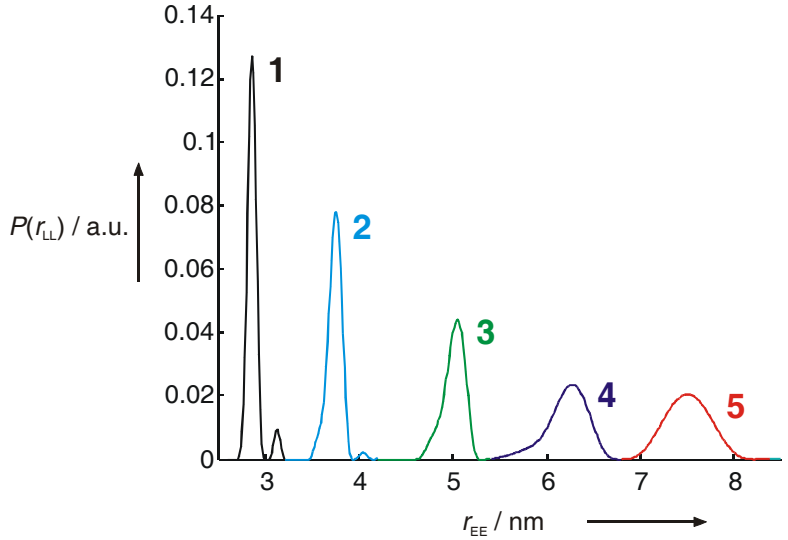


Figure S2. Label-to-label distance distributions $P(r_{LL})$ of oligoPPEs obtained by Tikhonov regularization with optimum regularization parameters α = 0.01 (**1**), 0.1 (**2**), 1 (**3**), 100 (**4**), and 100 (**5**).

5.2 Fitting of the coarse-grained conformational model

For global fitting of MD data, the label-to-label distance distributions $P(r_{LL})$ extracted from MD simulations of **2**, **3**, and **4** were normalized by their integrals. The root mean square (r.m.s.) deviation for a given parameter set (s, F_B, l, B) was computed by simulating the model for all three compounds, extracting the $P(r_{LL})$ of the model, calculating the three r.m.s. deviations, and adding them. Preliminary minimization of the r.m.s. deviation was performed by a four-dimensional grid search within the following ranges: $0.99 \le s \le 1.01$ with increment $\Delta s = 0.002$, $10 \le F_B \le 50$ with increment $\Delta F_B = 4$, $0.64 \le l \le 0.68$ with increment $\Delta l = 0.004$, and $1 \le B \le 10$ with increment $\Delta B = 1$. During this grid search the number of Monte Carlo trials was 2000. It was checked that within the whole grid no pronounced local minima existed and that the r.m.s. deviation at the edges of the grid exceeded the r.m.s. deviation at the global minimum by more than one order of magnitude. Starting at the global

minimum of the grid search, a final minimization was performed using the Nelder-Mead simplex algorithm as implemented in Matlab and simulations with 20000 Monte Carlo trials. For the best parameter set obtained in this way the end-to-end distance distribution of the backbone $P(r_{EE})$ was computed with 500000 Monte Carlo trials.

The background function in orientation-averaged DEER data is not an exponential decay, since the decay constants at different pump/observer position pairs differ from each other and the sum of exponential decays with different time constant is not exponential. We found that these decay functions could be well fitted by a stretched exponential $\exp(-kt^{D/3})$ with $D = 3.35$ for all five compounds. This background function $B(t)$ was subtracted from the primary data and the result was divided by $B(t)$. The form factors $F(t)$ thus obtained were normalized at $t = 0$ and used as the experimental data sets for fitting.

Global fitting of DEER data was performed in a similar fashion as for the MD data, however the label-to-label distance distributions $P(r_{LL})$ were converted to the corresponding DEER form factors using the function `pcf2deer` of the program package DeerAnalysis2006.[14] The ranges for the initial grid search were $0.97 \le s \le 1.00$ with increment $\Delta s = 0.005$, $15 \le F_B \le 30$ with increment $\Delta F_B = 5$, $0.63 \le l \le 0.67$ with increment $\Delta l = 0.005$, and $1 \le B \le 4$ with increment $\Delta B = 0.5$. Refinement by simplex minimization and computation of the final $P(r_{EE})$ were performed as for the MD data.

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[4] A mixture of Et_2O and THF is most probably sufficient.

[5] When recording the spectra on the 250 MHz instrument the decoupling power was insufficient which resulted in signal splitting in the case of aromatic CH groups. Under better conditions it may be possible to resolve more signals than are reported here.

[6] The signal of the protons in ortho position relative to OR is missing. ^{1}H NMR spectra of the shorter analogues of **4** (ref. 1) show the corresponding signal at around 7.2 ppm as an extremely broad one. In case of **4**, this signal is most probably covered by the intense and broad signal of the aromatic protons of the PPE units.

[7] The carbon signal for C_{Ar}-O is expected at 149.0 ppm (ref. 1). The signal to noise ratio of the ^{13}C NMR spectrum of **4** is insufficient to detect this signal.

[8] The signal of the protons in ortho position relative to OR is expected at 7.2 ppm as a very broad signal (ref. 1). This is most probably covered by the signal of $CHCl_3$.

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