Synthesis and Characterization of Monodisperse Oligo(phenyleneethynylene)s

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An iterative convergent/divergent synthesis for hexyl- and isopentoxy-substituted, monodisperse oligo(phenyleneethynylene)s is reported. The strategy is based on the bromine−iodine selectivity of the Pd-catalyzed alkyne−aryl-coupling, the conversion of a bromine substituent into an iodine substituent via halogen metal exchange, and trimethylsilyl (TMS) as an acetylene protecting group. The synthesis is efficient and gave gram amounts of octamers. Further derivatization of the octamers to esters and carboxylic acids is described. The compounds are fully characterized by ^{1}H and ^{13}C NMR and UV/vis spectroscopy.

Currently an increasing interest is paid to monodisperse, well defined oligomers as models for polymers.[1] Besides this, the oligomers themselves can be used as modules for nanoscopic architectures, like e.g. rings and dendrimers.[2] For this purpose, shape persistent oligomers like oligophenylenes,[1c,d] oligo(phenyleneethynylene)s,[1a,b,2,3] and oligo(phenylenevinylene)s[1e] appear especially attractive. To use these compounds as building blocks for the construction of nanoarchitectures an efficient synthesis is vital, which yields reasonable amounts of the desired oligomers. Herein we report on the preparation and characterization of monodisperse oligo(*p*-phenyleneethynylene)s (oligoPPEs) substituted with isopentoxy and hexyl side chains and their functionalization to make them suitable modules for further constructions.

Results and Discussion

OligoPPEs with 3-ethylheptyl substituents have been prepared by Tour et al.[3] on an iterative divergent/convergent approach using the trimethylsilyl and the 3,3-diethyltriazene function as complementary protecting groups for terminal acetylene and aryl iodide, respectively. Because of unsatisfactory results of our own with the triazene−iodide conversion reaction and the desire to avoid working with large amounts of rather volatile carcinogenic methyl iodide, we developed an alternative repetitive strategy based on the bromine−iodine selectivity of the Pd-catalyzed alkyne−aryl-coupling,[4] the conversion of a bromine substituent into an iodine substituent via halogen metal exchange, and trimethylsilyl (TMS) as an acetylene protecting group (Scheme 1):[5] The synthesis starts from the dibromides **1a**,**b** which are converted into the bromoiodo-compounds **2a**,**b** by reaction with *n*-BuLi followed by treatment with 1,2-diiodoethane. The bromoiodo-compounds **2a**,**b** are cross-coupled with TMS-acetylene under Pd/Cu-catalysis yielding the "monomers" **3a**,**b**. One part of the monomers **3a**,**b** is treated with base to give the acetylenes **4a**,**b**. The other part is converted into the iodo-compounds **5a**,**b** as described above for **1a**,**b**. Then again, an iodo-bromo-selective cross-coupling follows giving the dimers **6a**,**b**. This synthetic cascade was pursued up to the octamers **12a**,**b** which were received in an amount of 1−2 g.

For the interconversion of the bromo- into the iodo-substituent, working at temperatures below −80 °C proved to be essential. If this interconversion is performed at temperatures above −60 °C, rather large quantities of byproducts, probably due to orthometalation,[6] are found. Temperature control was especially important in the case of the alkoxy-substituted compounds. However, we were not successful in suppressing the side reactions completely. Estimated from ^{1}H NMR spectra, 1−5% of byproducts were formed. NMR and MS data reveal the formation of hydrolysis product and a product with an OH group instead of the bromo-substituent, caused by traces of water and oxygen during iodination, respectively. Besides these products, traces of, to us, structurally unknown products are formed that show signals around 7 ppm. Careful chromatography gave products with correct elemental analysis.

In all cases, the cross-coupling seems to proceed very iodo-selectively as we did not find any clue to the reaction of the bromo-substituent which would produce symmetrically 1,4-disubstituted-2,5-dihexylbenzene, e.g. 1,4-bis[(trimethylsilyl)ethynyl]-2,5-dihexylbenzene in the case of the coupling of **2b** with TMS-acetylene. Even a slight

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(2) (a) Zhang, J.; Pesak, D. J.; Ludwick, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4227−39. (b) Bedard, T. C.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 10662−71. (c) Wu, Z.; Moore, J. S. *Angew. Chem.* **1996**, *108*, 320−2. (d) Kawaguchi, T.; Walker, K. L.; Wilkins, C. L.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 2159−65. (e) Höger, S.; Enkelmann, V. *Angew. Chem.* **1995**, *107*, 2917−9. (f) Grubbs, R. H.; Kratz, D. *Chem. Ber.* **1993**, *126*, 149−57. (g) Xu, Z.; Moore, J. S. *Angew. Chem.* **1993**, *105*, 1394−6. (h) Kawase, T.; Darabi, H. R.; Oda, M. *Angew. Chem.* **1996**, *108*, 2803−5.

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(4) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−30. Concerning the bromine−iodine selectivity of the coupling reaction: e.g.: Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287−91. Gray, G. W.; Hird, M.; Lacey, D.; Toyne, K. J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 2041. See also refs 2b,e.

(5) On writing this manuscript we became aware of the work of Hsung et al. They used the same approach to synthesize the unsubstituted equivalent of **8a**, i.e. **8** with R = H: Hsung, R. P.; Chidsey, C. E. D.; Sita, L. R. *Organometallics* **1995**, *14*, 4808−15.

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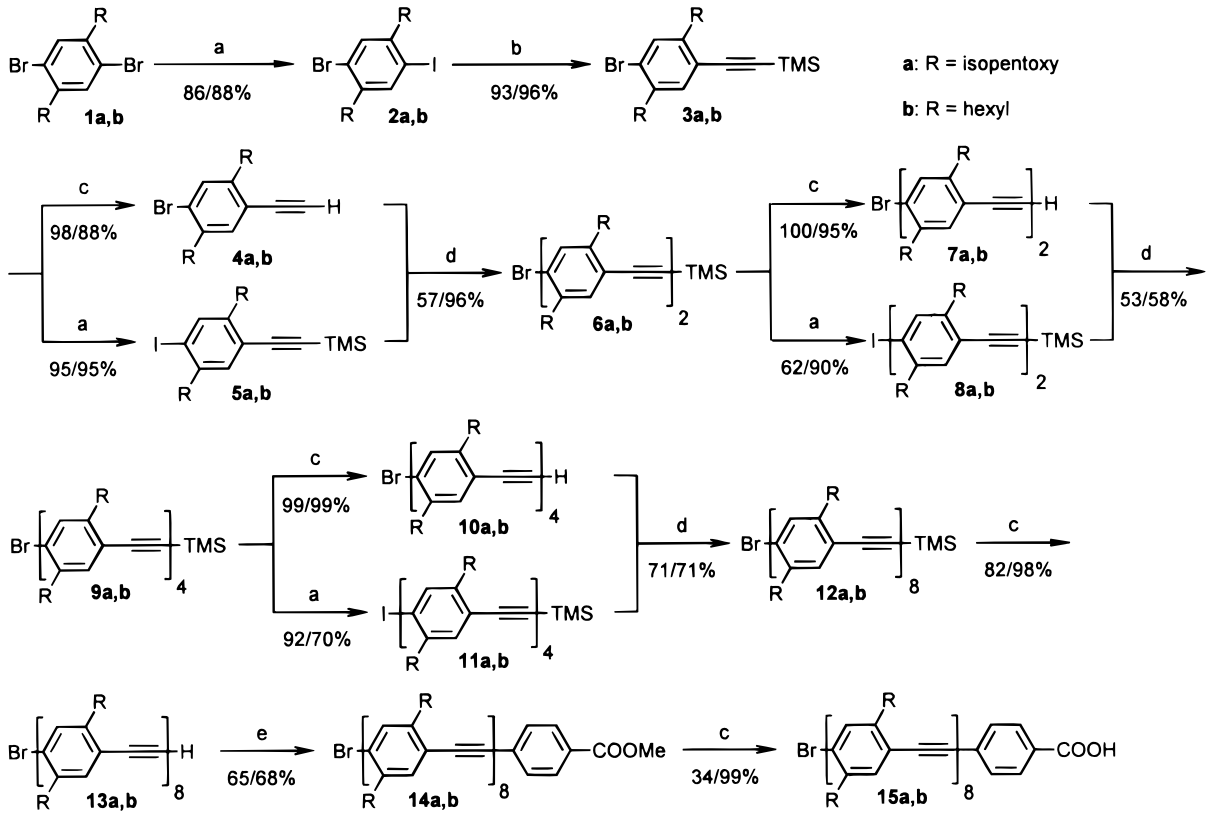
S0022-3263(97)00548-3 CCC: $14.00

Scheme 1[a]



[a]Key: Yields are given for isopentoxy/hexyl-substituted derivatives. (a) (1) *n*-BuLi, (2) ICH_2CH_2I; (b) TMSCCH, $Pd(PPh_3)_2Cl_2$, CuI, Et_2NH; (c) NaOH, H_2O, MeOH, THF; (d) $Pd(PPh_3)_2Cl_2$, CuI, Et_2NH; (e) methyl 4-iodobenzoate, $Pd(PPh_3)_2Cl_2$, CuI, Et_2NH.

excess of TMS-acetylene was tolerable. In contrast to this result, the cross-coupling of 1-bromo-4-iodobenzene with TMS-acetylene always gives a small amount (5%) of 1,4-bis[(trimethylsilyl)ethynyl]benzene.[7] The monomer **3b** has previously been synthesized by coupling of 1,4-diiodo-2,5-dihexylbenzene with 1 equiv of TMS-acetylene.[8] The disadvantage of this procedure is a tedious chromatographic separation of the desired 1-bromo-4-[(trimethylsilyl)ethynyl]-2,5-dihexylbenzene from the, in this case, unavoidable 1,4-bis[(trimethylsilyl)ethynyl]-2,5-dihexylbenzene.

An essential tool for characterization and structure proof of such oligomeric compounds is the NMR spectroscopy (Figure 1). A distinct ^1H NMR signal is observed for the proton H_{Hal} in the ortho position relative to the halogen substituent.[9] There is a characteristic downfield shift of around 0.2 and 0.3 ppm in the case of the isopentoxy-substituted [$\delta(H_{Br}) \sim 7.03-7.09$; $\delta(H_I) \sim 7.24-7.30$] and the hexyl-substituted compounds [$\delta(H_{Br}) \sim 7.31-7.39$; $\delta(H_I) \sim 7.61-7.70$], respectively, going from the bromo to the corresponding iodo compound, as expected from the known shift increments.[10] This is a reliable way to check whether the iodination was successful. Furthermore, there are distinct signals at $\delta < 6.99$ and $\delta < 7.34$ for the isopentoxy- and hexyl-substituted PPEs **3**, **5**, **6**, **8**, **9**, **11**, and **12**, respectively. By comparison of the ^1H NMR data going from the monomer to the tetramer, these signals are assigned to the remaining aromatic protons at the terminal rings. In some cases two of the expected three signals show the same shift. The assignment is supported by NMR data of the coupling product **12b** which was in one case received contaminated with the symmetrical diacetylene formed by homocoupling (oxidative acetylene dimerization) of the starting compound **10b**. The integration of the four distinct aromatic signals at 7.40, 7.34, 7.32, 7.31 gave a ratio of 1:1:0.3:0.3, indicating that the two aromatic signals at highest field belong to the (trimethylsilyl)ethynyl-substituted terminal ring. The homocoupling of acetylenes is a known side reaction of the coupling reaction used.[11] The extent of homocoupling can be minimized by rigorous exclusion of oxygen. However, it can most probably not totally be suppressed.[11] The separation of the homocoupling product and the cross-coupling one is difficult because of very similar length, mass, and polarity of both products. The accuracy of detection of the homocoupling product by NMR is estimated to be 5−10%. The ratio of the intensities of the discussed distinct aromatic signals and the signal intensity of the aromatic protons at the internal rings were in accordance with the length and structure of the expected PPEs. Therefore these signals might be used to determine the degree of polymerization of products

(7) A. Godt, unpublished results.

(8) Mangel, T.; Eberhardt, A.; Scherf, U.; Bunz, U. H. F.; Müllen, K. *Macromol. Rapid Commun.* **1995**, *16*, 571−80.

(9) This assignment of the signals was made on comparison of the ^1H NMR data of the oligoPPEs with those of the starting materials **1a** [$\delta(H_{Br}) = 7.09$], **1b** [$\delta(H_{Br}) = 7.35$], **2a** [$\delta(H_{Br}) = 6.97$; $\delta(Hg) = 7.26$], and **2b** [$\delta(H_{Br}) = 7.31$; $\delta(Hg) = 7.60$]. It is in accordance with the observation that after exchange of the bromine substituent by an iodo substituent the signal assigned to H_{Br} had disappeared and a new signal further downfield appeared. Furthermore, after coupling, the signal assigned to Hg had disappeared while the signal of H_{Br} was shifted only slightly.

(10) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*; Thieme: Stuttgart, 1979.

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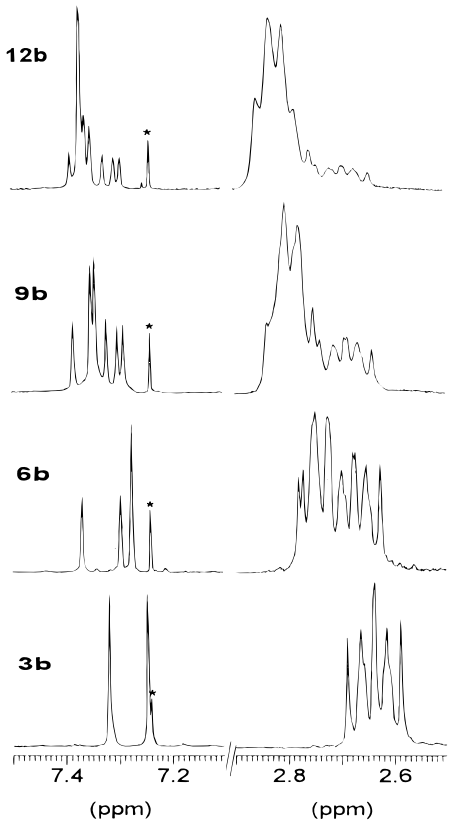

Figure 1. ^{1}H NMR spectra ($CDCl_3$; 300 MHz) of hexyl-substituted PPEs at room temperature. The signal of $CHCl_3$ is marked (*).

obtained from polymerization of desilylated **5a**,**b**. The separated signal at 2.61−2.68 ppm in the ^{1}H NMR spectra of the hexyl-substituted compounds **3b**−**15b** is assigned to one of the benzylic CH_2-groups at one of the terminal benzene rings.

Surprisingly, the chemical shifts of all signals in the aromatic region were found to be remarkably dependent on the concentration.[12] With increasing concentration the signals are shifted downfield. Representatively $\delta(H_{Hal})$ of **3b**, **6b**, **9b**, and **12b** measured in $CDCl_3$ is plotted against the concentration. In all cases $\delta(H_{Hal})$ increases linearly with the concentration (Figure 2). The corresponding slopes depend on the number of repeating units n. Division of the slopes by n gives a constant a_{alkyl} = 0.024 ± 0.005 Hz L/mmol (Figure 3). The same but weaker effect (a_{alkoxy} = 0.007 ± 0.002 Hz L/mmol) was found for the alkoxy-substituted products **3a**, **6a**, **9a**, and **12a**. We interpret this finding as the result of a magnetically increasing anisotropic surrounding for a selected molecule with the increase of concentration and rod length, i.e. with the increasing number of benzene rings per volume unit. Further studies will reveal if this effect is due to aggregation as it was reported by Moore et al.[13] for cyclic oligo(*m*-phenyleneethynylene)s (oligo-MPEs). In contrast to our results on linear PPEs, the aromatic signals of the cyclic MPEs move upfield with increasing concentration. The extrapolation of the chemical shift $\delta(H_{Hal})$ of **3b**, **6b**, **9b**, and **12b** to infinite dilution exhibits an intramolecular influence of the rod length on the chemical shift (Figure 4). This influence seems to saturate between n = 4 and 8. Because this effect is much larger than the dependence on concentration, we did not extrapolate δ to infinite dilution for the NMR data given in the Experimental Section.

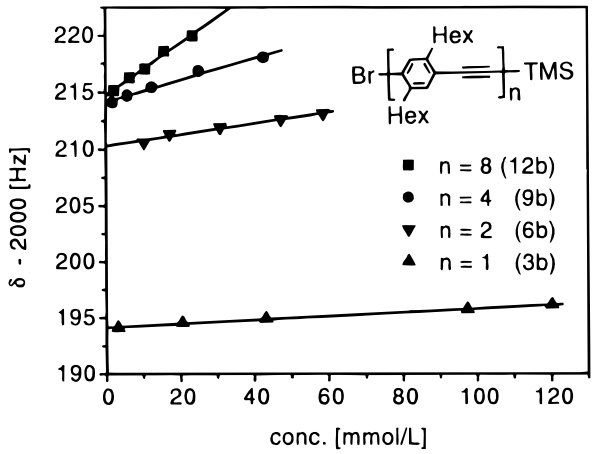

Figure 2. $\delta(H_{Hal})$ (300 MHz, room temperature) of **3b**, **6b**, **9b**, and **12b** at different concentrations in $CDCl_3$.

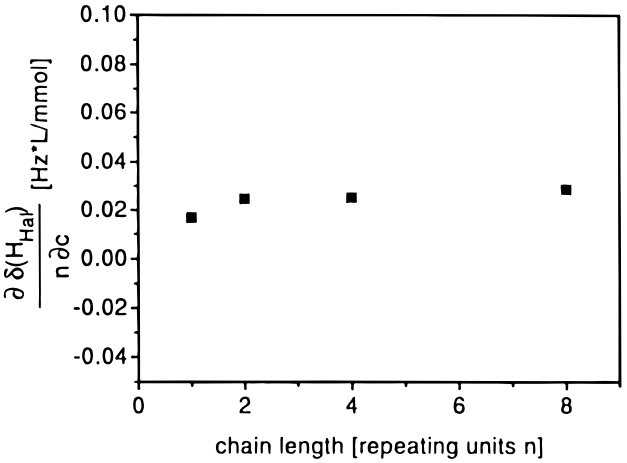

Figure 3. $\partial\,[\delta(H_{Hal})/n]/\partial c$ (300 MHz, room temperature) of compounds **3b**, **6b**, **9b**, and **12b** as a function of n.

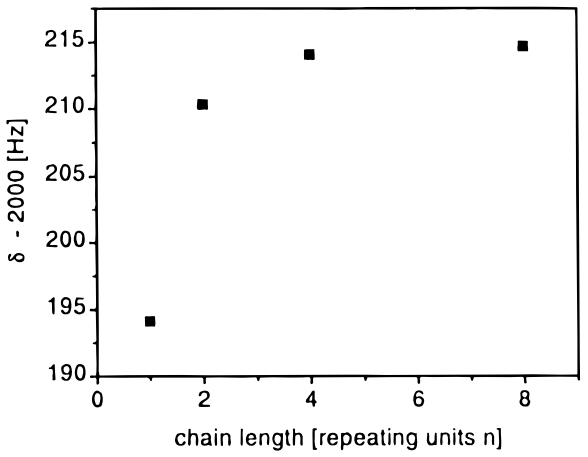

Figure 4. Dependence of $\delta(H_{Hal})$ (300 MHz, room temperature) of **3b**, **6b**, **9b**, and **12b** on the chain length at infinite dilution.

(12) A concentration dependent shift of the signals of the alkyl substituents, especially of the benzylic methylene groups or the oxo-substituted methylene groups, cannot be determined because several signals of only slightly different methylene groups overlap.

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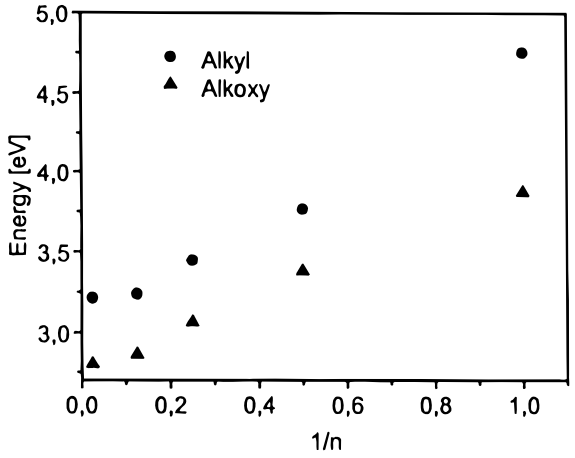

Figure 5. UV/vis-absorption energy as a function of chain length. The compounds **3**, **6**, **9**, and **12** were dissolved in CH_2Cl_2. The data taken from the literature for the methoxy- ($n = 40$)[14] and hexyl-substituted PPE ($n = 58$)[8] were obtained from solutions in $CHCl_3$ and cyclohexane, respectively. For the hexyl-substituted PPEs, the maximum of the envelope of the absorption band was used (see Supporting Information).

The UV/vis data of the oligoPPEs in CH_2Cl_2 represented by the compounds **3**, **6**, **9**, and **12** show a bathochromic shift of the maximum from 323 to 437 nm and from 267 to 382 nm in the case of the isopentoxy- and the hexyl-substituted oligomers, respectively, going from the monomer to the octamer (Figure 5). The absorption maximum of the octamers is already rather similar to those given for the corresponding oligomers with *n* around 40 and 58, i.e. 446 nm[14] and 388 nm[8] for the methoxy- (in $CHCl_3$) and hexyl-substituted (in cyclohexane) PPEs, respectively. Figure 5 reveals a rather large difference of the absorption energy of the monomers **3a**,**b** in comparison to the longer systems. Beginning with the dimers **6a**,**b** the absorption energy seems to depend roughly linearly on 1/*n* as expected for oligomers,[15] and the difference between the isopentoxy- and the hexyl-substituted oligomers with equal *n* is nearly constant. The lower absorption energy of the alkoxy-substituted oligoPPEs compared to the absorption energy of the alkyl substituted ones may be attributed to the electron donation by the oxygen-containing side chains.

For use of the synthesized rods as building blocks it is desirable to provide them with simple functional groups, such as ester or carboxyl groups. We therefore prepared derivatives of the octamers by reaction of **13a**,**b** with methyl 4-iodobenzoate. The resulting nonamers **14a**,**b** were saponified yielding the corresponding acids **15a**,**b** (Scheme 1). In the ^{1}H NMR spectra the typical AA′BB′ system of the benzoic moiety can be seen which appears at lower field than the signals of the other aromatic protons. ^{13}C NMR shows an additional four peaks in the aromatic region as expected.

As shown in this paper we devised a new iterative divergent/convergent approach to oligoPPEs, which allowed us to synthesize substantial amounts of octamers and carboxyl-derivatives. This enables us to use such compounds as building blocks for the construction of nanoarchitectures like rod-coil-systems in ongoing investigations.

Experimental Section

All reactions with organometallic reagents and the coupling reactions were performed under argon. THF was dried over sodium/benzophenone. The petroleum ether used had a boiling range of 30−40 °C. TMS-acetylene was used as purchased from Aldrich. 1,4-Dibromo-2,5-diisopentoxybenzene (**1a**)[16] and 1,4-dibromo-2,5-dihexylbenzene (**1b**)[17] were prepared according to the literature. For flash chromatography, Merck silica gel (mesh 70−230) was used. TLC was performed on silica gel coated aluminum foils (Merck alumina foils $60F_{254}$). ^{1}H and ^{13}C NMR spectra were, if not otherwise mentioned, recorded in $CDCl_3$ as solvent and internal standard on a 300 MHz spectrometer. Mass spectra were obtained by field desorption, if not otherwise stated.

For the concentration dependent measurements of the shift of the ^{1}H NMR signals, we dissolved a definite amount of the oligoPPE in a certain volume of $CDCl_3$. To increase the concentration we added more oligomer. The error provoked by the additional volume of the oligoPPEs was neglected.

General Procedure for the Synthesis of Compounds 2a,b, 5a,b, 8a,b, 11a,b (Bromine−Iodine-Exchange). A solution of the dibromo compounds **1a**,**b** or the bromophenyleneethynylenes **3a**,**b**, **6a**,**b**, **9a**,**b** in THF was cooled to −90 °C. *n*-BuLi in hexane was added at such a rate that the internal temperature did not exceed −80 °C. This cold solution was added via a cannula to 1,2-diiodoethane in THF at −60 °C. After addition, the cooling bath was removed, and the reaction mixture was stirred for 30 min. The color changed from yellowish to brown. After discoloring by adding saturated aqueous $Na_2S_2O_3$, the water phase was extracted three times with diethyl ether. The combined organic phases were dried ($MgSO_4$). After removing the solvent, the residue was recrystallized or purified by flash chromatography.

1-Bromo-2,5-diisopentoxy-4-iodobenzene (2a). The reaction of **1a** (20.41 g, 50.0 mmol) in THF (200 mL) with 1.6 M BuLi in hexane (31.25 mL, 50.00 mmol) and 1,2-diiodoethane (15.00 g, 53.2 mmol) in THF (100 mL) gave, after recrystallization from MeOH, **2a** (19.5 g, 86%) as colorless needles: mp 103 °C; ^{1}H NMR δ 0.958 (d, 6 H, $J = 6.5$ Hz), 0.961 (d, 6 H, $J = 6.5$ Hz), 1.68 (td, 2 H, $J_1 = 7$ Hz, $J_2 = 7$ Hz), 1.70 (td, 2 H, $J_1 = 7$ Hz, $J_2 = 7$ Hz), 1.859 (sept, 1 H, $J = 6.5$ Hz), 1.864 (sept, 1 H, $J = 6.5$ Hz), 3.93 (t, 2 H, $J = 4.8$ Hz), 3.94 (t, 2 H, $J = 4.8$ Hz), 6.97 (s, 1 H), 7.26 (s, 1 H); ^{13}C NMR δ 22.6, 25.02, 25.04, 37.84, 37.87, 68.7, 84.7, 112.5, 117.0, 124.2, 150.4, 152.6. Anal. Calcd for $C_{16}H_{24}BrIO_2$: C, 42.22; H, 5.31. Found: C, 42.16; H, 5.21.

1-Bromo-2,5-dihexyl-4-iodobenzene (2b). The reaction of **1b** (20.21 g, 50.0 mmol) in THF (200 mL) with 1.6 M BuLi in hexane (31.25 mL, 50.00 mmol) and 1,2-diiodoethane (15 g, 53 mmol) in THF (100 mL) gave, after recrystallization from EtOH, **2b** (19.8 g, 88%) as colorless needles: mp 37−38 °C; ^{1}H NMR δ 0.88 (s, br, 6 H), 1.31 (s, br, 12 H), 1.54 (s, br, 4 H), 2.60 (t, 4 H, $J = 8$ Hz), 7.31 (s, 1 H), 7.60 (s, 1 H); ^{13}C NMR δ 14.1, 22.6, 28.97, 29.01, 29.8, 30.1, 31.6, 35.3, 40.1, 98.8, 124.5, 132.8, 140.3, 141.5, 144.7. Anal. Calcd for $C_{18}H_{28}BrI$: C, 47.91; H, 6.25. Found: C, 48.23; H, 6.26.

Monomer 5a. The reaction of **3a** (7.23 g, 17.00 mmol) in THF (100 mL) with 1.6 M BuLi in hexane (12.50 mL, 20.00 mmol) and 1,2-diiodoethane (5.64 g, 20.00 mmol) in THF (50 mL) gave, after chromatography (diethyl ether/petroleum ether 5/95 v/v), **5a** (7.7 g, 95%) as a yellow-brownish oil: ^{1}H NMR δ 0.23 (s, 9 H), 0.95 (d, 12 H, $J = 7$ Hz), 1.66 (td, 2 H, $J_1 = 7$ Hz, $J_2 = 7$ Hz), 1.68 (td, 2 H, $J_1 = 7$ Hz, $J_2 = 7$ Hz), 1.88 (sept, 2 H, $J = 7$ Hz), 3.94 (t, 2 H, $J = 7$ Hz), 3.95 (t, 2 H, $J = 7$ Hz), 6.82 (s, 1 H), 7.24 (s, 1 H); ^{13}C NMR δ −0.1, 22.58, 22.61, 25.0, 25.1, 37.9, 38.0, 68.2, 68.5, 97.9, 99.4, 100.8, 113.5, 116.3, 123.9,

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(16) Vahlenkamp, T.; Wegner ,G. *Macromol. Chem. Phys.* **1994**, *195*, 1933−52. Vahlenkamp, T. Dissertation, 1992, Universität Mainz.

(17) Rehahn, M.; Schlüter, A.-D.; Feast, W. J. *Synthesis* **1988**, 386−8.

151.8, 154.9. Anal. Calcd for $C_{21}H_{33}IO_2Si$: C, 53.38; H, 7.04. Found: C, 53.34; H, 6.99.

Monomer 5b. The reaction of **3b** (7.80 g, 18.50 mmol) in THF (100 mL) with 1.6 M BuLi in hexane (12.50 mL, 20.00 mmol) and 1,2-diiodoethane (5.64 g, 20.00 mmol) in THF (50 mL) gave, after chromatography (petroleum ether), **5b** (8.2 g, 95%) as a yellowish oil: ^{1}H NMR δ 0.23 (s, 9 H), 0.88 (t, 6 H, J = 6 Hz), 1.31 (m, br, 12 H), 1.55 (m, br, 4 H), 2.61 (m, 4 H), 7.22 (s, 1 H), 7.61 (s, 1 H); ^{13}C NMR δ −0.1, 14.1, 22.6, 29.0, 29.2, 30.2, 30.5, 31.6, 33.9, 40.2, 98.5, 101.1, 103.4, 122.6, 132.4, 139.4, 142.6, 144.6. Anal. Calcd for $C_{23}H_{37}ISi$: C, 58.96; H, 7.96. Found: C, 59.01; H, 7.93.

Dimer 8a. The reaction of **6a** (3.02 g, 4.30 mmol) in THF (100 mL) with 1.6 M BuLi in hexane (2.80 mL, 4.48 mmol) and 1,2-diiodoethane (1.27 g, 4.50 mmol) in THF (50 mL) gave, after chromatography (diethyl ether/petroleum ether 5/95 v/v), **8a** (2.0 g, 62%) as a yellow solid: mp 66 °C; ^{1}H NMR δ 0.24 (s, 9 H), 0.95 (d, 24 H, J = 7 Hz), 1.70 (m, 8 H), 1.89 (sept, 4 H, J = 7 Hz), 3.98 (m, 8 H), 6.88 (s, 1 H), 6.92 (s, 1 H), 6.94 (s, 1 H), 7.28 (s, 1 H); ^{13}C NMR δ −0.1, 22.58, 22.62, 22.69, 22.71, 25.02, 25.10, 25.17, 25.21, 37.95, 38.02, 38.05, 67.9, 68.1, 68.47, 68.50, 87.5, 90.7, 91.0, 100.1, 101.2, 113.8, 113.9, 114.5, 116.1, 117.0, 117.3, 124.0, 151.9, 153.3, 154.21, 154.25. Anal. Calcd for $C_{39}H_{57}IO_4Si$: C, 62.89; H, 7.71. Found: C, 62.73; H, 7.60.

Dimer 8b. The reaction of **6b** (5.21 g, 7.55 mmol) in THF (80 mL) with 1.6 M BuLi in hexane (5.00 mL, 8.00 mmol) and 1,2-diiodoethane (2.26 g, 8.00 mmol) in THF (40 mL) gave, after chromatography (petroleum ether), **8b** (5.0 g, 90%) as a yellow oil: ^{1}H NMR δ 0.25 (s, 9 H), 0.87 (m, br, 12 H), 1.32 (m, br, 24 H), 1.61 (m, br, 8 H), 2.64 (t, 2 H, J = 8 Hz), 2.73 (m, 6 H), 7.27 (s, 1 H), 7.28 (s, 2 H), 7.66 (s, 1 H); ^{13}C NMR δ 0.0, 14.1, 22.6, 29.0, 29.21, 29.24, 29.3, 30.2, 30.6, 31.66, 31.73, 31.75, 31.8, 33.9, 34.1, 34.2, 40.2, 92.3, 92.5, 99.0, 100.8, 104.0, 122.5, 122.8, 123.0, 132.3, 132.4, 132.5, 139.5, 141.8, 142.1, 143.7. Anal. Calcd for $C_{43}H_{65}ISi$: C, 70.08; H, 8.89. Found: C, 70.16; H, 8.87.

Tetramer 11a. The reaction of **9a** (840 mg, 0.678 mmol) in THF (50 mL) with 1.6 M BuLi in hexane (0.50 mL, 0.80 mmol) and 1,2-diiodoethane (226 mg, 0.801 mmol) in THF (10 mL) gave, after chromatography (diethyl ether/petroleum ether 8/92 v/v), **11a** (800 mg, 92%) as a yellow solid: mp 163 °C; ^{1}H NMR δ 0.26 (s, 9 H), 0.96 (d, 48 H, J = 7 Hz), 1.73 (m, 16 H), 1.91 (m, 8 H), 4.01 (m, 16 H), 6.90 (s, 1 H), 6.94 (s, 1 H), 6.96 (s, 1 H), 6.99 (s, 1 H), 7.00 (s, 3 H), 7.30 (s, 1 H); ^{13}C NMR δ −0.1, 22.6−22.7, 25.0−25.2, 38.0−38.2, 67.9−68.6, 87.5, 90.9−91.6, 100.1, 101.2, 113.8−114.6, 116.2−117.4, 124.1, 152.0, 153.4−154.3. Anal. Calcd for $C_{75}H_{105}IO_8Si$: C, 69.85; H, 8.21. Found: C, 69.87; H, 8.34.

Tetramer 11b. The reaction of **9b** (2.00 g, 1.63 mmol) in THF (80 mL) with 1.6 M BuLi in hexane (1.25 mL, 2.00 mmol) and 1,2-diiodoethane (564 mg, 2.00 mmol) in THF (20 mL) gave, after chromatography (petroleum ether), **11b** (1.46 g, 70%) as a yellow-greenish solid: mp 85 °C; ^{1}H NMR δ 0.28 (s, 9 H), 0.92 (m, br, 24 H), 1.35 (m, br, 48 H), 1.71 (m, br, 16 H), 2.68 (t, 2 H, J = 8 Hz), 2.73−2.88 (m, 14 H), 7.30 (s, 2 H), 7.31 (s, 1 H), 7.35 (s, 2 H), 7.36 (s, 2 H), 7.68 (s, 1 H); ^{13}C NMR δ 0.0, 14.1, 22.7, 29.1−29.3, 30.2−30.7, 31.7−31.8, 33.9−34.2, 92.3−93.1, 99.0, 100.8, 104.1, 122.4−123.0, 124.6, 132.4−132.5, 139.5, 141.8−141.9, 142.8, 143.8. Anal. Calcd for $C_{83}H_{121}ISi$: C, 78.26; H, 9.57. Found: C, 78.26; H, 9.53.

General Procedure for the Synthesis of Compounds 3a,b, 6a,b, 9a,b 12a,b, 14a,b (Acetylene−Aryl-Coupling). To a degassed solution of the iodo compound in Et_2NH was added the acetylenic compound. After addition of $Pd(PPh_3)_2Cl_2$ (1 mol %) and CuI (2 mol %) while cooling with an ice bath, the mixture was stirred at ambient temperature for 5−24 h. Soon a brownish oil separated. When the reaction was quantitative according to TLC (same eluent as for chromatography), the amine was removed *in vacuo*, and the residue was dissolved in water and diethyl ether or $CHCl_3$. The water phase was extracted three times with diethyl ether (**3a**,**b**, **6a**,**b**, **9a**,**b**), THF (**12a**), or $CHCl_3$ (**12b**, **14a**,**b**). The combined organic phases were washed with saturated aqueous NH_4Cl. After drying ($MgSO_4$), the solvent was removed, and the residue was flash chromatographed.

Monomer 3a. Starting from **2a** (4.55 g, 10.00 mmol) and TMS-acetylene (1.03 g, 10.5 mmol) in Et_2NH (30 mL), after chromatography (diethyl ether/petroleum ether 2/98 v/v) **3a** (4.0 g, 93%) was obtained as a yellow solid: mp 103 °C; UV/vis λ_{max} 323 nm; ^{1}H NMR δ 0.23 (s, 9 H), 0.94 (d, 6 H, J = 7 Hz), 0.95 (d, 6 H, J = 7 Hz), 1.66 (td, 2 H, J_1 = 7 Hz, J_2 = 7 Hz), 1.67 (td, 2 H, J_1 = 7 Hz, J_2 = 7 Hz), 1.86 (sept, 2 H, J = 7 Hz), 3.95 (t, 4 H, J = 7 Hz), 6.92 (s, 1 H), 7.03 (s, 1 H); ^{13}C NMR δ −0.1, 22.58, 22.61, 25.00, 25.06, 37.93, 37.97, 68.2, 68.5, 99.2, 100.6, 112.5, 113.5, 117.9, 118.0, 149.4, 154.8; MS m/z 426 (M^+). Anal. Calcd for $C_{21}H_{33}BrO_2Si$: C, 59.28; H, 7.82. Found: C, 59.91; H, 7.92.

Monomer 3b. Starting from **2b** (18.05 g, 40.00 mmol) and TMS-acetylene (4.13 g, 42.0 mmol) in Et_2NH (50 mL), after chromatography (diethyl ether/petroleum ether 2/98 v/v) **3b** (16.1 g, 96%) was obtained as a pale yellow oil: UV/vis λ_{max} 267 nm; ^{1}H NMR δ 0.22 (s, 9 H), 0.87 (t, br, 6 H, J = 7 Hz), 1.30 (s, br, 12 H), 1.55 (m, br, 4 H), 2.61 (t, 2 H, J = 8 Hz), 2.66 (t, 2 H, J = 8 Hz), 7.24 (s, 1 H), 7.31 (s, 1 H); ^{13}C NMR δ −0.1, 14.1, 22.57, 22.60, 29.1, 29.2, 29.8, 30.5, 31.64, 31.67, 34.1, 35.6, 98.2, 103.3, 121.7, 124.7, 132.7, 133.6, 139.3, 144.7; MS m/z 422.0 (M^+). Anal. Calcd for $C_{23}H_{37}BrSi$: C, 65.53; H, 8.85. Found: C, 64.68; H, 8.97.

Dimer 6a. The reaction of **5a** (7.09 g, 15.00 mmol) with **4a** (5.30 g, 15.00 mmol) in Et_2NH (50 mL) gave, after chromatography (diethyl ether/petroleum ether 5/95 v/v), **6a** (5.9 g, 57%) as a yellow solid: mp 62 °C; UV/vis λ_{max} 370 nm; ^{1}H NMR δ 0.24 (s, 9 H), 0.96 (d, 24 H, J = 7 Hz), 1.71 (m, 8 H), 1.88 (sept, 4 H, J = 7 Hz), 3.99 (m, 8 H), 6.92 (s, 1 H), 6.94 (s, 1 H), 6.98 (s, 1 H), 7.08 (s, 1 H); ^{13}C NMR δ −0.1, 22.6−22.7, 25.0−25.2, 37.9−38.0, 67.9, 68.1, 68.4, 68.5, 90.5, 90.8, 100.1, 101.2, 112.9, 113.3, 113.7, 114.5, 117.0, 117.3, 117.6, 118.1, 149.5, 153.3, 154.1, 154.2; MS m/z 696.1 (M^+). Anal. Calcd for $C_{39}H_{57}BrO_4Si$: C, 67.12; H, 8.23. Found: C, 66.52; H, 8.44.

Dimer 6b. The reaction of **5b** (7.26 g, 15.50 mmol) with **4b** (5.41 g, 15.50 mmol) in Et_2NH (20 mL) yielded, after chromatography (diethyl ether/petroleum ether 5/95 v/v), **6b** (10.3 g, 96%) as a yellowish oil: UV/vis λ_{max} 325 nm; ^{1}H NMR δ 0.24 (s, 9 H), 0.85 (m, br, 12 H), 1.31 (m, br, 24 H), 1.62 (m, br, 8 H), 2.63−2.78 (m, 8 H), 7.28 (s, 2 H), 7.30 (s, 1 H), 7.37 (s, 1 H); ^{13}C NMR δ 0.0, 14.1, 22.6, 29.1−29.3, 29.9, 30.6, 31.7−31.8, 34.1−34.2, 35.6, 92.2, 99.0, 122.0, 122.4, 122.9, 124.6, 132.3, 132.5, 132.8, 133.5, 139.5, 141.8, 142.8, 143.8. Anal. Calcd for $C_{43}H_{65}BrSi$: C, 74.85; H, 9.50. Found: C, 74.92; H, 9.56.

Tetramer 9a. Starting from **8a** (2.00 g, 2.69 mmol) and **7a** (1.68 g, 2.69 mmol) in Et_2NH (20 mL), after chromatography (diethyl ether/petroleum ether 1/9 v/v) **9a** (1.77 g, 53%) was obtained as a yellow solid: mp 165 °C; UV/vis λ_{max} 408 nm; ^{1}H NMR δ 0.24 (s, 9 H), 0.97 (m, 48 H), 1.73 (m, 16 H), 1.90 (m, 8 H), 4.03 (m, 16 H), 6.93 (s, 1 H), 6.95 (s, 1 H), 6.987 (s, 2 H), 6.992 (s, 2 H), 7.00 (s, 1 H), 7.09 (s, 1 H); ^{13}C NMR δ −0.1, 22.6−22.7, 25.0−25.2, 37.9−38.1, 67.9−68.5, 90.6−91.6, 100.1, 101.2, 113.3−114.6, 117.0−118.1, 149.5, 153.4−154.3. Anal. Calcd for $C_{75}H_{105}BrO_8Si$: C, 72.49; H, 8.52. Found: C, 72.44; H, 8.62.

Tetramer 9b. Starting from **8b** (4.32 g, 5.86 mmol) and **7b** (3.62 g, 5.86 mmol) in Et_2NH (25 mL), after chromatography (petroleum ether) **9b** (4.2 g, 58%) was obtained as a yellow-green solid: mp 77 °C; UV/vis λ_{max} 361 nm; ^{1}H NMR δ 0.25 (s, 9 H), 0.88 (m, br, 24 H), 1.32 (m, 48 H), 1.67 (m, br, 16 H), 2.67 (m, br, 2 H), 2.80 (m, br, 14 H), 7.29 (s, 1 H), 7.30 (s, 1 H), 7.32 (s, 1 H), 7.34 (s, 2 H), 7.35 (s, 2 H), 7.39 (s, 1 H); ^{13}C NMR δ 0.0, 14.1, 22.7, 29.1−29.3, 29.9, 30.6, 30.7, 31.7−31.8, 34.1, 34.2, 35.6, 92.3−93.1, 99.0, 104.1, 122.1−123.0, 124.6, 132.4−133.5, 139.5, 141.8−141.9, 142.8, 143.8. Anal. Calcd for $C_{83}H_{121}BrSi$: C, 81.26; H, 9.94. Found: C, 81.28; H, 9.80.

Octamer 12a. Starting from **11a** (709 mg, 0.550 mmol) and **10a** (644 mg, 0.550 mmol) in Et_2NH (30 mL) and THF (15 mL), after chromatography (gradient elution: diethyl ether → THF) **12a** (900 mg, 71%) was obtained as an orange solid: mp 260 °C; UV/vis λ_{max} 437 nm; ^{1}H NMR δ 0.24 (s, 9 H), 0.97 (m, 96 H), 1.74 (m, 32 H), 1.93 (m, 16 H), 4.02 (m, 32 H), 6.93 (s, 1 H), 6.95 (s, 1 H), 6.99 (s, 2 H), 7.00 (s, 11 H), 7.09 (s, 1 H); ^{13}C NMR δ −0.1, 22.4−22.9, 25.0−25.5, 37.8−38.1, 67.9−68.5,

90.6−91.6, 100.1, 101.2, 113.0−114.6, 117.0−118.1, 149.5, 153.4−154.2. Anal. Calcd for $C_{147}H_{201}BrO_{16}Si$: C, 75.71; H, 8.69. Found: C, 75.71; H, 8.61.

Octamer 12b. Starting from **11b** (1.40 g, 1.10 mmol) and **10b** (1.27 g, 1.10 mmol) in Et_2NH (30 mL) and THF (15 mL), after chromatography (gradient elution: petroleum ether → diethyl ether/petroleum ether 1/1 v/v) **12b** (1.80 g, 71%) was obtained as a yellow-green solid: mp 148 °C; UV/vis λ_{max} 382 nm; ^{1}H NMR δ 0.26 (s, 9 H), 0.88 (m, br, 48 H), 1.31−1.41 (m, br, 96 H), 1.71 (m, br, 32 H), 2.68 (m, br, 2 H), 2.81 (m, 30 H), 7.29 (s, 1 H), 7.31 (s, 1 H), 7.33 (s, 1 H), 7.35 (s, 2 H), 7.36 (s, 2 H), 7.37 (s, 8 H), 7.39 (s, 1 H); ^{13}C NMR δ 0.0, 14.1, 22.7, 29.1−29.9, 30.6, 30.7, 31.7−31.9, 34.2, 35.6, 92.3, 93.1, 98.9, 104.1, 122.1, 122.4, 122.7−123.0, 124.6, 132.4, 132.8, 133.5, 139.5, 141.8, 141.9, 142.8, 143.8; MS *m*/*z* 2300.4 (M^+), 1150.3 (M^{2+}). Anal. Calcd for $C_{163}H_{233}BrSi$: C, 85.10; H, 10.21. Found: C, 84.11; H, 10.24.

Ester 14a. The reaction of **13a** (253 mg, 0.112 mmol) with methyl 4-iodobenzoate (80 mg, 0.305 mmol) in Et_2NH (20 mL) and THF (100 mL) yielded after chromatography (gradient elution: diethyl ether → $CHCl_3$) **14a** (170 mg, 65%) as an orange-brown solid: mp 282 °C; ^{1}H NMR δ 0.98 (m, 96 H), 1.74 (m, 32 H), 1.91 (m, 16 H), 3.91 (s, 3 H), 4.05 (m, 32 H), 6.99 (s, 1 H), 7.00 (s, 13 H), 7.01 (s, 1 H), 7.09 (s, 1 H), 7.56 and 8.01 (AA′BB′, 2 H each); ^{13}C NMR δ 22.6−22.9, 25.0−25.2, 37.9−38.1, 52.2, 68.0−68.5, 89.2, 90.6−91.6, 113.0−115.0, 116.9−118.1, 128.2, 129.4,[18] 129.5, 131.4, 131.9,[18] 133.1,[18] 149.5, 153.5−154.1, 166.5. Anal. Calcd for $C_{152}H_{199}BrO_{18}$: C, 76.26; H, 8.38. Found: C, 75.99; H, 8.32.

Ester 14b. The reaction of **13b** (366 mg, 0.164 mmol) with methyl 4-iodobenzoate (203 mg, 0.775 mmol) in Et_2NH (10 mL) and THF (70 mL) gave, after washing the residue with hot ethanol (200 mL) and filtration over a short column ($CHCl_3$), **14b** (265 mg, 68%) as a yellow-green solid: mp 159 °C; ^{1}H NMR δ 0.88 (m, br, 48 H), 1.24−1.42 (m, br, 96 H), 1.70 (m, br, 32 H), 2.67 (t, br, 2 H, J = 8 Hz), 2.83 (m, br, 30 H), 3.93 (s, 3 H), 7.33 (s, 1 H), 7.35 (s, 1 H), 7.37 (s, 12 H), 7.38 (s, 1 H), 7.39 (s, 1 H), 7.57 and 8.03 (AA′BB′, 2 H each); ^{13}C NMR δ 14.1, 22.7, 29.1, 29.3, 29.7, 29.9, 30.7, 31.7, 31.8, 34.2, 35.6, 52.2, 91.6, 92.6, 93.1, 93.2, 121.9, 122.1, 122.8, 123.4, 124.6, 128.2, 129.6, 131.3, 132.5, 132.8, 133.5, 139.5, 141.9, 142.5, 143.8, 166.6; MS *m*/*z* 2361.6 (M^+), 1180.9 (M^{2+}). Anal. Calcd for $C_{168}H_{231}BrO_2$: C, 85.41; H, 9.86. Found: C, 84.85; H, 9.71.

General Procedure for the Synthesis of Compounds 4a,b, 7a,b, 10a,b, 13a,b (Deprotection of the Acetylenes). The TMS-protected phenyleneethynylenes **3a**,**b**, **6a**,**b**, **9a**,**b**, **12a**,**b** were completely dissolved in MeOH or in a mixture of THF and MeOH and aqueous NaOH was added. After stirring the solution for 2 h at rt, water was added. The aqueous phase was extracted three times with diethyl ether (**4a**,**b**, **7a**,**b**, **10a**,**b**) or $CHCl_3$ (**13a**,**b**). After the combined organic phases were dried ($MgSO_4$), the solvent was removed, and the residue was used without further purification.

Monomer 4a. The reaction of **3a** (8.95 g, 21.04 mmol) in MeOH (200 mL) with 5 N NaOH (5 mL) gave **4a** (7.3 g, 98%) as a colorless compound which could be recrystallized from EtOH forming colorless needles: mp 76 °C; ^{1}H NMR δ 0.94 (d, 12 H, J = 7 Hz), 1.68 (td, 4 H, J_1 = 7 Hz, J_1 = 7 Hz), 1.84 (sept, 2 H, J = 7 Hz), 3.27 (s, 1 H), 3.96 (t, 2 H, J = 7 Hz), 3.98 (t, 2 H, J = 7 Hz), 6.96 (s, 1 H), 7.06 (s, 1 H); ^{13}C NMR δ 22.57, 22.59, 25.06, 25.08, 37.83, 37.89, 68.3, 68.6, 79.5, 82.4, 111.3, 113.9, 117.9, 118.3, 149.4, 154.7. Anal. Calcd for $C_{18}H_{25}BrO_2$: C, 61.19; H, 7.13. Found: C, 61.32; H, 7.20.

Monomer 4b. The reaction of **3b** (7.59 g, 18.01 mmol) in MeOH (100 mL) and THF (75 mL) with 5 N NaOH (4 mL) gave **4b** (5.6 g, 88%) as a reddish oil: ^{1}H NMR δ 0.88 (t, br, 6 H, J = 7 Hz), 1.31 (m, br, 12 H), 1.57 (m, br, 4 H), 2.63 (t, 2 H, J = 8Hz), 2.69 (t, 2 H, J = 8Hz), 3.23, (s, 1 H), 7.28 (s, 1 H), 7.34 (s, 1 H); ^{13}C NMR δ 14.1, 22.6, 29.0, 29.1, 29.8, 30.4, 31.61, 31.64, 33.8, 35.5, 80.9, 81.8, 120.7, 125.1, 132.8, 134.1, 139.4, 144.7. Anal. Calcd for $C_{20}H_{29}Br$: C, 68.76; H, 8.37. Found: C, 68.60; H, 8.45.

Dimer 7a. The reaction of **6a** (2.92 g, 4.18 mmol) in MeOH (70 mL) and THF (50 mL) with 5 N NaOH (1.5 mL) gave **7a** (2.6 g, 100%) as a yellow solid: mp 82 °C; ^{1}H NMR δ 0.95 (d, 24 H, J = 7 Hz), 1.70 (m, 8 H), 1.87 (sept, 4 H, J = 7 Hz), 3.32 (s, 1 H), 3.99 (m, 8 H), 6.955 (s, 1 H), 6.959 (s, 1 H), 6.98 (s, 1 H), 7.08 (s, 1 H); ^{13}C NMR δ 22.6−22.7, 25.1−25.2, 37.9−38.0, 68.1−68.5, 80.0, 82.3, 90.3, 90.9, 112.6−113.4, 114.9, 117.0, 117.7−118.1, 149.5, 153.3, 154.1, 154.2. Anal. Calcd for $C_{36}H_{49}BrO_4$: C, 69.11; H, 7.89. Found: C, 69.03; H, 8.01.

Dimer 7b. The reaction of **6b** (5.06 g, 7.33 mmol) in MeOH (40 mL) and THF (60 mL) with 10 N NaOH (1.5 mL) gave **7b** (4.3 g, 95%) as a pink solid: mp 39 °C; ^{1}H NMR δ 0.88 (m, br, 12 H), 1.33 (m, br, 24 H), 1.63 (m, br, 8 H), 2.67 (t, 2 H, J = 8 Hz), 2.72 (m, 6 H), 3.29 (s, 1 H), 7.32 (s, 3 H), 7.39 (s, 1 H); ^{13}C NMR δ 14.1, 22.6, 29.1−29.2, 29.9, 30.5, 30.6, 31.6−31.8, 33.9, 34.1, 35.6, 81.4, 82.5, 92.0, 92.2, 121.4, 122.0, 123.2, 124.6, 132.3, 132.8, 133.0, 133.5, 139.5, 141.8, 142.8, 143.8; MS *m*/*z* 618.1 (M^+). Anal. Calcd for $C_{40}H_{57}Br$: C, 77.77; H, 9.30. Found: C, 76.42; H, 9.37.

Tetramer 10a. The reaction **9a** (817 mg, 0.66 mmol) in MeOH (5 mL) and THF (20 mL) with 10 N NaOH (0.2 mL) gave **10a** (760 mg, 99%) as a yellow solid: mp 182 °C; ^{1}H NMR δ 0.97 (m, 48 H), 1.72 (m, 16 H), 1.89 (m, 8 H), 3.33 (s, 1 H), 4.03 (m, 16 H), 6.96 (s, 1 H), 6.98 (s, 1 H), 6.995 (s, 4 H), 6.999 (s, 1 H), 7.09 (s, 1 H); ^{13}C NMR δ 22.6−22.7, 25.1−25.2, 37.9−38.1, 68.1−68.5, 80.1, 82.3, 90.6−91.6, 112.6−113.3, 114.2−114.4, 115.0, 117.0−118.1, 149.5, 153.4−154.2; MS *m*/*z* 1170.6 (M^+), 585.3 (M^{2+}). Anal. Calcd for $C_{72}H_{97}BrO_8$: C, 73.88; H, 8.35. Found: C, 72.93; H, 8.35.

Tetramer 10b. The reaction of **9b** (1.99 g, 1.62 mmol) in MeOH (15 mL) and THF (25 mL) with 10 N NaOH (0.3 mL) gave **10b** (1.85 g, 99%) as a yellow-green solid: mp 78 °C; ^{1}H NMR δ 0.87 (m, br, 24 H), 1.32−1.42 (m, br, 48 H), 1.67 (m, br, 16 H), 2.67 (t, 2 H, J = 8 Hz), 2.79 (m, 14 H), 3.29 (s, 1 H), 7.32 (s, 3 H), 7.34 (s, 1 H), 7.35 (s, 3 H), 7.38 (s, 1 H); ^{13}C NMR δ 14.1, 22.7−22.8, 29.1−29.3, 29.9, 30.5−30.7, 31.7−31.8, 34.1−34.2, 35.6, 81.3, 82.5, 92.3−93.1, 121.4−123.4, 124.6, 132.4−133.5, 139.5, 141.8−143.8. Anal. Calcd for $C_{80}H_{113}Br$: C, 83.22; H, 9.86. Found: C, 82.96; H, 9.90.

Octamer 13a. The reaction of **12a** (678 mg, 0.291 mmol) in MeOH (15 mL) and THF (75 mL) with 10 N NaOH (0.1 mL) gave **13a** (540 mg, 82%) as an orange solid: mp 251 °C; ^{1}H NMR δ 0.97 (m, 96 H), 1.74 (m, 32 H), 1.90 (m, 16 H), 3.33 (s, 1 H), 4.05 (m, 32 H), 6.97 (s, 1 H), 6.98 (s, 1 H), 7.01 (s, 13 H), 7.09 (s, 1 H); ^{13}C NMR δ 22.6−22.7, 25.2, 38.0, 67.9−68.5, 80.0, 82.3, 90.6−91.6, 112.6−113.2, 114.1−114.4, 117.0−118.1, 149.5, 153.3−154.0. Anal. Calcd for $C_{144}H_{193}BrO_{16}$: C, 76.53; H, 8.61. Found: C, 76.28; H, 8.36.

Octamer 13b. The reaction of **12b** (600 mg, 0.261 mmol) in MeOH (10 mL) and THF (60 mL) with 10 N NaOH (0.1 mL) gave **13b** (570 mg, 98%) as a yellow-green solid: mp 140 °C dec; ^{1}H NMR δ 0.89 (m, br, 48 H), 1.25−1.39 (m, br, 96 H), 1.70 (m, br, 32 H), 2.68 (t, 2 H, J = 8 Hz), 2.84 (m, 30 H), 3.30, (s, 1 H), 7.34 (s, 2 H), 7.36 (s, 1 H), 7.38 (s, br, 12 H), 7.40 (s, 1 H); ^{13}C NMR δ 14.1, 22.6−22.7, 29.1−29.3, 29.9, 30.5−30.7, 31.7−31.8, 34.2, 35.6, 81.4, 82.5, 92.3, 92.8−93.1, 121.4, 122.1, 122.7−122.9, 123.3, 124.6, 132.4−133.5, 139.5, 141.8−141.9, 142.8, 143.8. Anal. Calcd for $C_{160}H_{225}Br$: C, 86.24; H, 10.18. Found: C, 86.17; H, 10.17.

Saponification of the Esters 14a,b. Acid 15a. To a solution of **14a** (140 mg, 0.058 mmol) in THF (50 mL) and MeOH (5 mL) was added 10 N NaOH (0.1 mL). The reaction mixture was heated to reflux for 15 h. After acidifying the solution with 2 N HCl, it was extracted three times with $CHCl_3$, and the combined organic phases were dried ($MgSO_4$). Chromatography (gradient elution: THF → THF/conc. HCl 10/1 v/v) yielded **15a** (51 mg, 37%) as an orange-brown solid: mp 295 °C; ^{1}H NMR δ 0.98 (m, 96 H), 1.74 (m, 32 H), 1.92 (m, 16 H), 4.04 (m, 32 H), 6.98 (s, 1 H), 7.00 (s, 12 H), 7.02 (s, 2 H), 7.08 (s, 1 H), 7.59 and 8.07 (AA′BB′, 2 H each); ^{13}C NMR δ 22.6−22.7, 25.0−25.2, 37.9−38.1, 68.0−68.5, 89.7, 90.6−92.0, 94.0, 113.0−113.3, 114.2−114.5, 115.1, 116.9−118.2, 128.4, 129.1,[18] 130.1,[18] 130.2, 131.5, 149.5, 153.5−154.1, 170.4; MS (FAB, 4-nitrobenzyl alcohol as matrix) *m*/*z* 2380 (M^+). Anal. Calcd for $C_{151}H_{197}BrO_{18}$: C, 76.20; H, 8.34. Found: C, 75.51; H, 8.32.

(18) Signals with low intensities. We are not sure about the correct assignment. The signals may be caused by, to us, unknown impurities.

Acid 15b. A solution of **14b** (250 mg, 0.106 mmol) in THF (90 mL), MeOH (10 mL), and 10 N NaOH (4 mL) was stirred at 50 °C for 3 h. Workup as described for **15a**, but without chromatography, yielded **15b** (246 mg, 99%) as a yellow-green solid: mp 203 °C; ^{1}H NMR δ 0.89 (m, br, 48 H), 1.25−1.43 (m, br, 96 H), 1.72 (m, br, 32 H), 2.68 (m, br, 2 H), 2.83 (m, br, 30 H), 7.33 (s, 1 H), 7.35 (s, 1 H), 7.37 (s, 13 H), 7.39 (s, 1 H), 7.61 and 8.10 (AA′BB′, 2 H each); ^{13}C NMR δ 14.1, 22.7, 29.1−29.9, 30.7, 31.7−31.8, 34.2, 35.6, 92.3−93.5, 121.8, 122.1, 122.7−122.8, 123.6, 124.6, 128.5, 129.2,[18] 130.2, 131.4, 132.5−133.5, 139.5, 142.0, 142.6, 143.8, 171.0. Anal. Calcd for $C_{167}H_{229}BrO_2$: C, 85.41; H, 9.83. Found: C, 85.19; H, 9.73.

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Supporting Information Available: UV spectra of **3**, **6**, **9**, and **12** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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