Synthesis of Monodisperse Oligo(*para*-phenyleneethynylene)s Using Orthogonal Protecting Groups with Different Polarity for Terminal Acetylene Units

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Monodisperse oligo(*para*-phenyleneethynylene)s (oligoPPEs) were synthesized by a divergent-convergent synthesis starting from 1,4-dihexyl-2-(3-hydroxyprop-1-ynyl)-5-[2-(triisopropylsilyl)ethynyl]benzene and using the Pd/Cu-catalyzed alkyne-aryl coupling. The groups hydroxymethyl (HOM) and triisopropylsilyl (TIPS) function as orthogonal protective groups for the acetylene moieties. The polar HOM group shows a strong impact on the chromatographic behaviour of the products and makes the isolation of pure compounds very easy. The synthesis was pursued up to the nonamer. The oligoPPEs were fully characterised, including absorption and emission spectral data.

Introduction

Monodisperse and shape-persistent oligomers, e.g. oligo(phenyleneethynylene)[1] and oligophenylene,[2] are attractive building blocks for molecular and supramolecular architectures. Unfortunately, the preparation of monodisperse samples is tedious, because of many steps, and demands improvement: a reduction of the number of steps and/or a simplification of the purification. Recently, two protocols[3,4] have been reported for the synthesis of monodisperse oligo(*p*-phenyleneethynylene)s (oligoPPEs) by a divergent-convergent approach.[5] This approach allows to double the number of repeating units in every third step, including two parallel steps, independent of the length of the molecule. The method of Tour et al.[4] starts with 1-diethyltriazenyl-4-(trimethylsilylethynyl)benzene substituted with an alkane chain. One part of the material is desilylated to give the alkylated 1-diethyltriazenyl-4-ethynylbenzene. The other part is transformed into the alkylated 1-iodo-4-trimethylsilylbenzene by treatment with methyl iodide. Pd/Cu-catalyzed coupling of these two products gives a dimer which carries, like the monomer, a silylated ethyne and a triazene end group. By repeating this reaction sequence the tetramer, octamer, and hexadecamer were synthesized. We described an alternative synthesis starting with 1-bromo-4-(trimethylsilylethynyl)benzene substituted with hexyl or isopentoxy chains.[3] It takes advantage of the iodine-bromine selectivity of the Pd/Cu-catalyzed alkyne-aryl coupling and uses a bromine-iodine exchange by halogen-metal exchange. We were able to synthesize octamers in gram amounts, but we were not completely satisfied with the procedure: The bromine-iodine exchange is a delicate step due to the reactivity of the intermediate aryllithium species. Furthermore, 1,4-diarylbutadiynes, resulting from the oxidative dimerization of the alkyne component, are, if at all, very difficult to separate from the target molecules because of very similar molecular weights and polarity. 1,4-Diarylbutadiynes are well-known byproducts of the alkynyl-aryl coupling.[6] Therefore, we designed an alternative approach using orthogonal acetylene protecting groups with different polarity to simplify the isolation of pure materials.

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Strategy

The idea was to start from *p*-diethynylbenzene **1a** carrying one non-polar and one polar protective group for the acetylene moieties (Scheme 1). Removing the non-polar protective group gives the polar acetylene **3a**. Reaction of **3a** with diiodobenzene **8** produces a mixture of the target iodo dimer **4b**, the disubstitution product **5a**, the acetylene dimerization product **6a**, and the starting material **8**. The products differ in the number of polar groups and therefore, the isolation of **4b** was expected to be possible. Using an excess of diiodobenzene **8** may help to increase the ratio of **4b**/**5a**. Deprotection of the polarly substituted acetylene unit of **1a**, yields acetylene **2a**. Finally, coupling of the non-polar acetylene **2a** and the polar iodo compound **4b** gives the trimer **1c**, which is substituted with one non-polar and one polar protective group at the terminal acetylene units. In contrast, the byproduct **7a** of this step, which is the dimerization product of **2a**, carries two non-polarly substituted terminal acetylene units. Therefore, a separation of the two products **1c** and **7a** might be feasible. To compensate for the loss of the acetylenic coupling partner **2a** due to formation of **7a**, an excess of **2a** should be used in order to avoid the need for separation of the two polar components, residual **4b** and product **1c**. Since trimer **1c** has the same end groups X and Y as the starting material **1a**, synthesis of longer oligoPPEs should be possible by repeating the reaction sequence.

The most popular protecting groups for acetylene are non-polar silyl groups like trimethylsilyl (TMS), triethylsilyl (TES), and triisopropylsilyl (TIPS).[1,5a,7] The conditions for deprotection are mild, e.g. K_2CO_3 in methanol for TMS and TES, nBu$_4$NF in THF for TIPS.[7] As a polar protective group, 2-hydroxyprop-2-yl is often used.[8] However, removal of this group as acetone requires heating of the compound with alkali metal hydroxide[8a,8b] or sodium hydride.[8c] Astonishingly, hydroxymethyl (HOM), another

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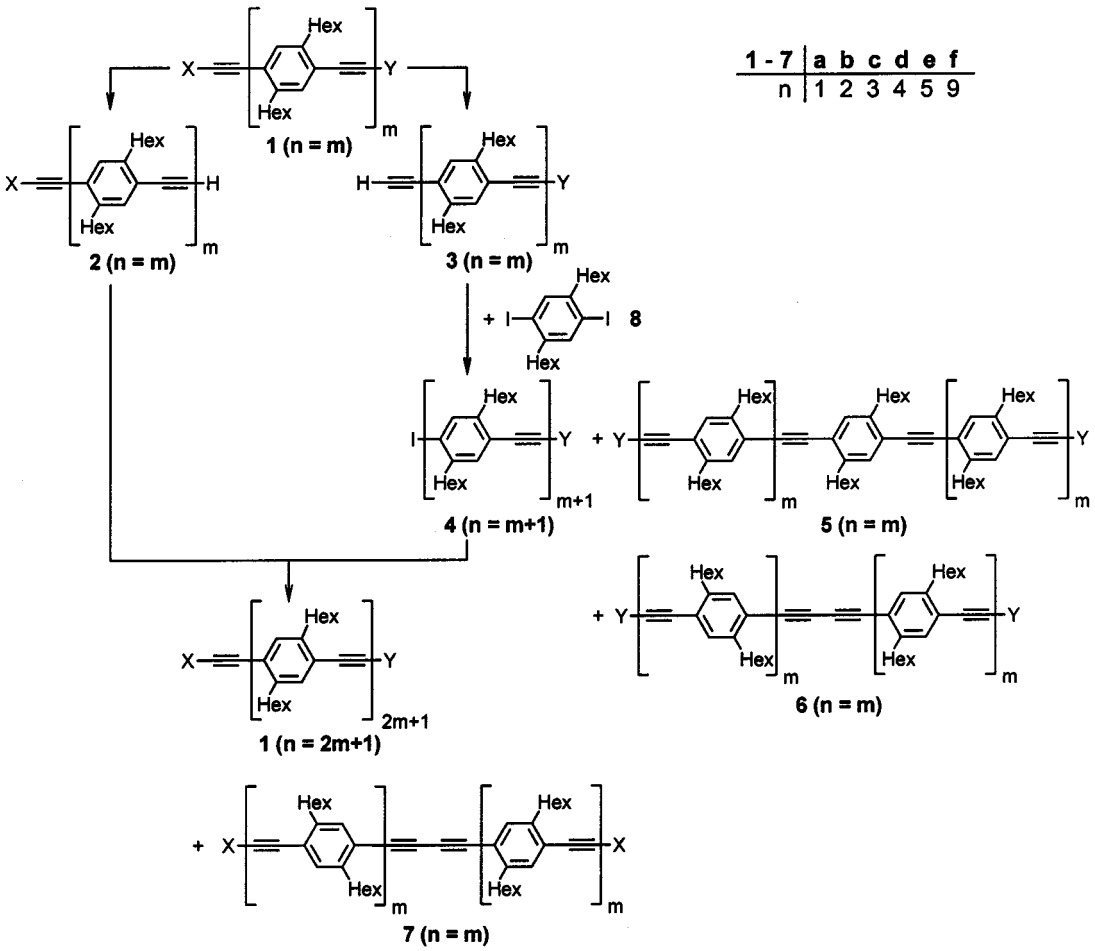


Scheme 1. Key: X = non-polar protecting group, e.g. TIPS; Y = polar protecting group, e.g. CH_2OH

polar protecting group described by Bumagin et al.,[8a,9] is rarely used although the condition for cleavage is comparatively mild, i.e. MnO_2/KOH in dichloromethane[9] or diethyl ether[10] at room temperature, and the corresponding starting material, prop-2-ynol, is inexpensive. From our recent work,[10] we knew that 1-aryl-2-(hydroxymethyl)ethyne can be deprotected to give arylethyne without affecting a TIPS-ethyne moiety. We anticipated that the reverse, the selective deprotection of 1-aryl-2-TIPS-ethyne in the presence of a HOM-ethyne moiety would be possible with *n*Bu_4NF. Therefore, the combination of the non-polar TIPS group as substitutent X and the polar HOM group as substituent Y appeared to be suitable for our synthesis of oligoPPEs.[11]

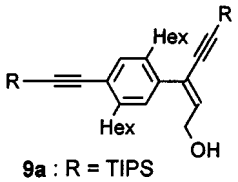
We were quite confident that the strategy would work for short oligomers, like the trimer **1c**. Whether the presence or absence of one or two hydroxy groups would sufficiently influence the chromatographic behaviour of longer rods was uncertain, but, it appeared worth to be tried.

Results and Discussion

Synthesis of OligoPPEs (Scheme 2)

1,4-Dihexyl-2,5-diiodobenzene (**8**) was used as a readily available starting material. Pd/Cu-catalyzed coupling reaction[12] of **8** with prop-2-ynol gave a mixture of diiodo compound **8**, the desired monosubstitution product **4a**, and disubstitution product 1,4-dihexyl-2,5-bis(3-hydroxyprop-1-ynyl)benzene. Experiments with a 1:1.1 ratio of **8**/prop-2-ynol gave iodo monomer **4a** in ca. 50% isolated yield. Changing the ratio to 1.5:1 resulted in an increase of **4a** and a decrease of the disubstitution product: Iodo monomer **4a** was isolated in a yield of 61−72%. Isolation of **4a** was easily achieved by column chromatography on a multigram scale.

In the next step, iodo monomer **4a** was coupled with TIPS-acetylene to give monomer **1a**. The reaction was slow and required heating to 50°C overnight. A byproduct was formed in varying amounts (2−12 mol-%; determined by ^{1}H-NMR spectroscopy of the crude products). It was chromatographically isolated. The characteristic ^{1}H-NMR signals (CD_2Cl_2), a singlet at $\delta = 6.83$, a triplet at $\delta = 6.25$, and a doublet at $\delta = 3.87$, the ^{13}C-NMR data (see Experimental Section) and the mass spectrum [MS(FD); *m*/*z*: 662.4; calcd. 661.5] suggest structure **9a** for this compound. **9a** can be understood as an addition product of TIPS-acetylene to **1a** formed by a carbometalation process.[13] Our data do not allow a decision on the configuration of the double bond. Assuming a carbometalation process, we expect **9a** to be the *syn* adduct of TIPS-acetylene to the hydroxypropyne moiety of **1a**.[13]



9a : R = TIPS
9b : R = TMS

Compound **1a** is the "monomer" of the series of oligoPPEs reported in this paper. Monomer **1a** has two terminal acetylene units substituted with the orthogonal protecting groups TIPS or HOM. Treatment of **1a** with MnO_2/KOH in diethyl ether cleanly cleaved off the polar HOM group and gave compound **2a**, a non-polar compound with one TIPS-protected and one non-protected acetylene unit. The latter was used to elongate the molecule by a coupling reaction with iodo monomer **4a**. The resulting dimer **1b** carries the same end groups as monomer **1a**. The one hydroxy group makes **1b** considerably more polar than the byproduct **7a** as is seen from the R_f values (CH_2Cl_2/petroleum ether, 1:1 v/v): R_f(**1b**) = 0.46; R_f(**7a**) = 0.82.

Repeating the two steps starting with dimer **1b**, i.e. removal of the HOM group followed by a coupling reaction of **2b** with **4a**, gives the trimer **1c**. Continuing this route should give the tetramer, pentamer, etc. However, this would be an extension of the rod length by only one repeating unit every second step. To accelerate the growth of the rods, oligoPPEs with one iodo substituent and one protected terminal acetylene unit were needed, as outlined in Scheme 1. For this purpose, the iodo dimer **4b** was synthesized by coupling the acetylene **3a** with the diiodo compound **8**. Acetylene **3a** could in principle be obtained by desilylation of **1a** with nBu$_4$NF. However, because TMS-acetylene is considerably less expensive than TIPS-acetylene, the TMS analogue of monomer **1a**, compound **1a′** was used to prepare **3a** by desilylation with NaOH in methanol/THF. Under these conditions, the HOM protective group is inert. Compound **1a′** was synthesized through the reaction of TMS-acetylene with **4a**. This reaction proceeded at room temperature and gave only traces (up to 1%) of the carbometalation product **9b**. Chromatographic separation of **9b** from **1a′** was found to be much easier than that of **9a** from **1a**. The reaction of the polar acetylene **3a** with two equivalents of diiodo compound **8** gave a mixture of starting material **8**, the monosubstitution product, iodo dimer **4b**, the disubstitution product **5a**, and the dimerization product **6a**. As in the case of the synthesis of iodo monomer **4a**, iodo dimer **4b** could be easily isolated by column chromatography in a yield of 53%. An increase of the ratio up to 1:2.3 of **3a**/**8** did not improve the yield of **4b**. As expected, the two byproducts **5a** and **6a**, both carrying two hydroxy end groups, were eluted as one fraction. Coupling of the polar iodo dimer **4b** with the non-polar acetylenic component **2b** gave tetramer **1d**. This tetramer was used to prepare the acetylenic coupling component **2d** and the iodo pentamer **4e** via compound **3d**. Coupling of **4e** with **2d** gave the nonamer **1f**. We were pleased to find that the HOM group has still significant influence on the R_f values of the products and allows a straightforward isolation of pure products. Compare for example R_f(**1f**) = 0.54 and R_f(**7d**) = 0.92 in CH_2Cl_2/petroleum ether, 1:1 v/v or R_f(**5d**/**6d**) = 0.40, R_f(**4e**) = 0.67, and R_f(**8**) = 0.88 in CH_2Cl_2/petroleum ether, 2:1 v/v.

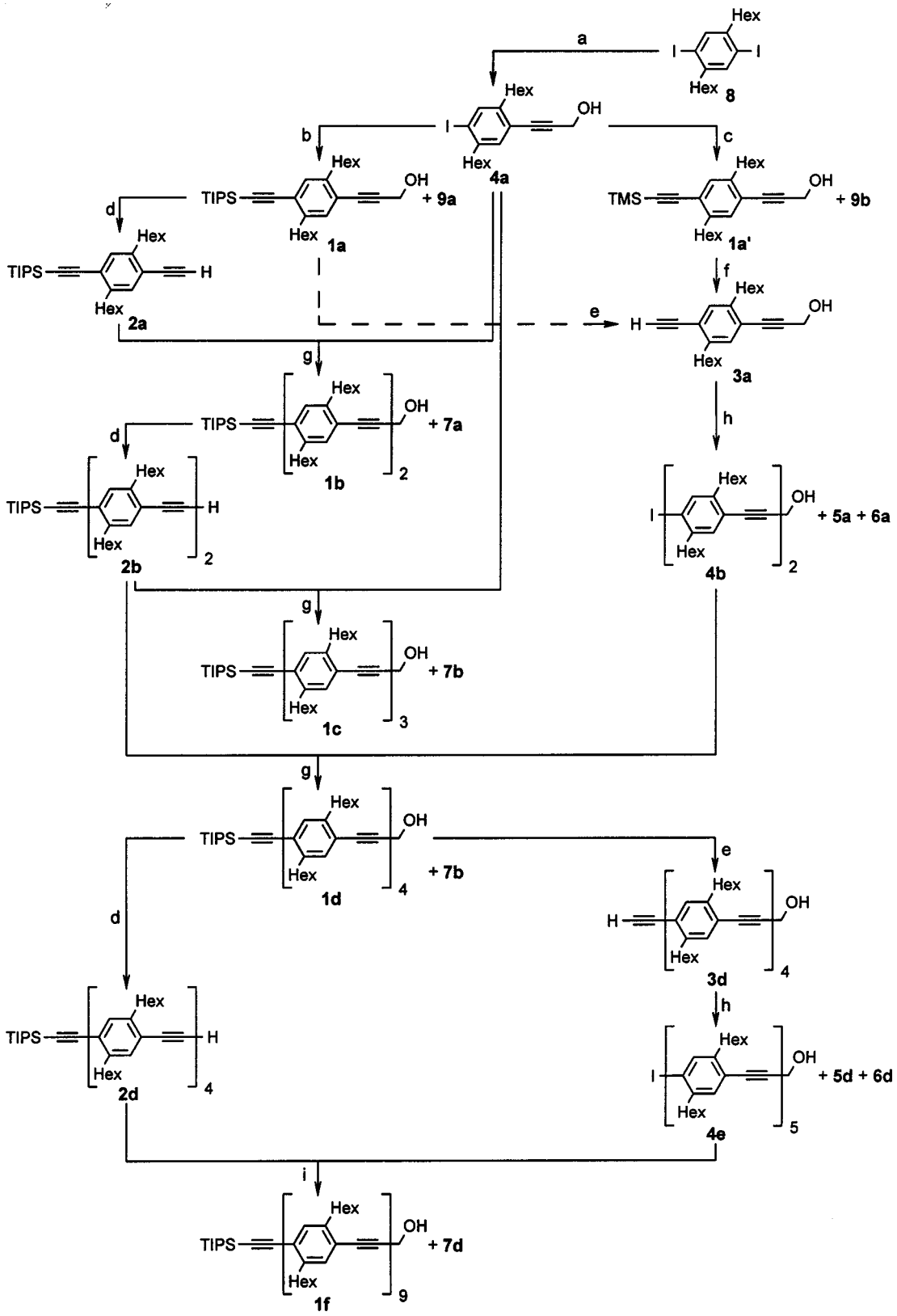
For the coupling reactions up to the tetramer **1d**, the catalyst system $Pd(PPh_3)_2Cl_2$/CuI[12] in THF and piperidine was suitable, provided that oxygen was excluded rigorously. However, for up to now unknown reasons, the coupling of **2d** with **4e** did not, and the coupling of **3d** with **8** did not reliably (two out of six experiments failed) proceed, when this catalyst system was used. Instead of the desired coupling products **1f** or **4e**, the iodo compounds **4e** or **8** and the diynes **7d** or **6d** were isolated. However, if $Pd_2(dba)_3$/PPh_3 as described by Moore and Tour,[4] was used instead of $Pd(PPh_3)_2Cl_2$, the nonamer **1f** was isolated with the very satisfying yield of 84%. Also, with this catalyst system the iodo pentamer **4e** could be prepared in 49% isolated yield. Whether this catalyst system is more reliable for the synthesis of iodo pentamer **4e** has not been examined yet.

Interestingly, as in the failed experiments to synthesize iodo pentamer **4e** and nonamer **1f**, residual acetylenic component **2a**, **2b**, **2d**, **3a**, or **3d** was never found after the coupling step, although it was used in excess and the solutions had been carefully degassed. It might well be that the acetylene dimerization happens during work up as discussed by Heitz.[6a]

Compounds with monosubstituted acetylene units were used immediately after preparation. Solvent-free, but oily compounds or samples dissolved in dichloromethane, turned red and insoluble material precipitated within one to several days when kept at room temperature under air and exposed to light. This behaviour was most obvious with samples prepared by HOM cleavage: Sometimes, the compound turned red already during isolation. The instability of the product may account for the loss of material at the deprotection step. Nevertheless, the subsequent coupling reactions were successful.

All compounds were well soluble in THF and dichloromethane. Only in diethyl ether, in comparison to the other compounds, a lower solubility was noticed for the nonamer **1f** during workup.

In conclusion, a convenient, divergent-convergent synthesis for oligoPPEs has been developed. It uses orthogonal protective groups with different polarity for acetylenes and leads to a doubling of the rod length at least every fourth step. Two of the four steps are easy to be done deprotection steps, which proceed quantitatively and yield NMR-spectroscopically pure products. We followed the new strategy up to the nonamer **1f**. The favorable behaviour during chromatographic purification of **4e** or **1f** and of the accompanying byproducts of the coupling reactions suggests that even longer rods can be just as easily produced and purified. The only drop of bitterness is the loss of material on the synthesis of the iodo oligomers **4** due to formation of disubstitution products **5**. The two protected terminal acetylene groups can be successively deprotected and there-



Scheme 2. Key: (a) $HC{\equiv}CCH_2OH$, $Pd(PPh_3)_2Cl_2$, CuI, piperidine, THF, room temp.; (b) $TIPSC{\equiv}CH$, $Pd(PPh_3)_2Cl_2$, CuI, piperidine, THF, 50°C; (c) $TMSC{\equiv}CH$, $Pd(PPh_3)_2Cl_2$, CuI, piperidine, THF, room temp.; (d) MnO_2, KOH, diethyl ether, room. temp.; (e) nBu$_4$NF, THF, room temp.; (f) NaOH, methanol, THF, room temp.; (g) $Pd(PPh_3)_2Cl_2$, CuI, piperidine, THF, room temp.; (h) **8**, $Pd(PPh_3)_2Cl_2$, CuI, piperidine, THF, room temp. or **8**, $Pd_2(dba_3)$, CuI, PPh_3, piperidine, THF, room temp.; (i) $Pd_2(dba)_3$, CuI, PPh_3, piperidine, THF, room temp.; yields: see Table 1

Table 1. Yields of isolated products given in%

	a	a′	b	c	d	e	f
1	85	88	87	88	92	–	84
2	80	–	73	–	89	–	–
3	95	–	–	–	96	–	–
4	71	–	53	–	–	51	–

fore used independently from each other to finally prepare functionalized oligoPPEs.[1d]

Optical Properties

PolyPPEs attract much interest as luminescent materials.[14] As a small contribution to this field, the absorption and emission spectra were recorded for the oligomers **1a**−**1d**, and **1f** (Figure 1) and for the iodo oligomers **4a**, **4b**, and **4e** in dichloromethane (Figure 2). Increase of the rod length results in a bathochromic shift of the absorption and emission maxima. A unique feature of the dimers, including those reported in the literature, is the dinstinctive structure of the absorption and emission band. We believe that this is due to vibronically different electronic transitions.

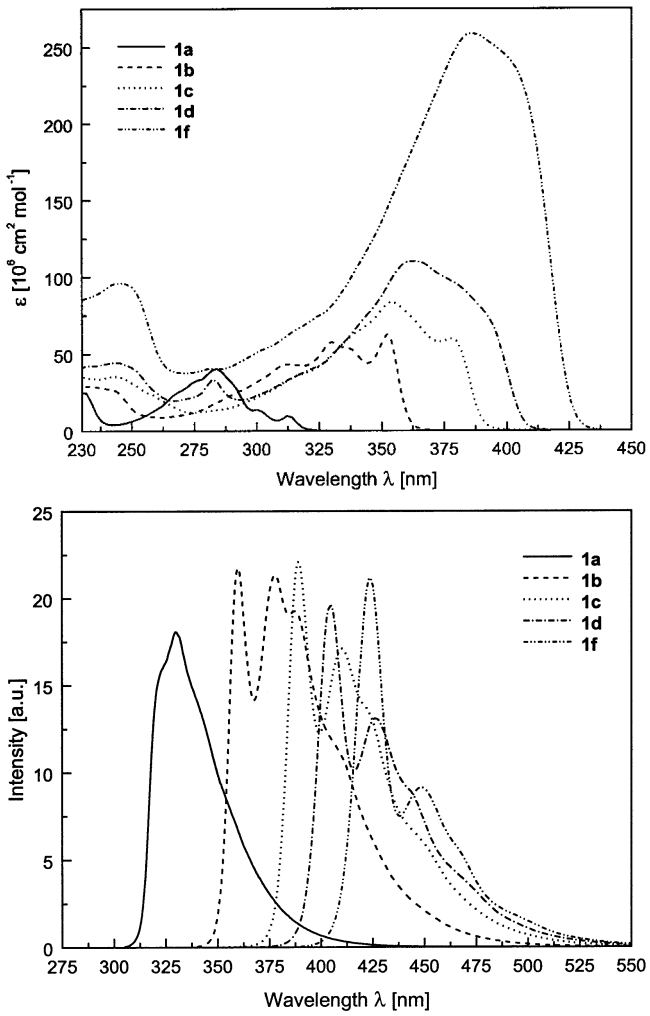


Figure 1. (a) Absorption and (b) emission spectra of oligomers **1a**, **1b**, **1d**, and **1f** in CH_2Cl_2; $\lambda_{excitation}$ = 295, 330, 340, and 360 nm for **1a**, **b**, **c**, and **d**

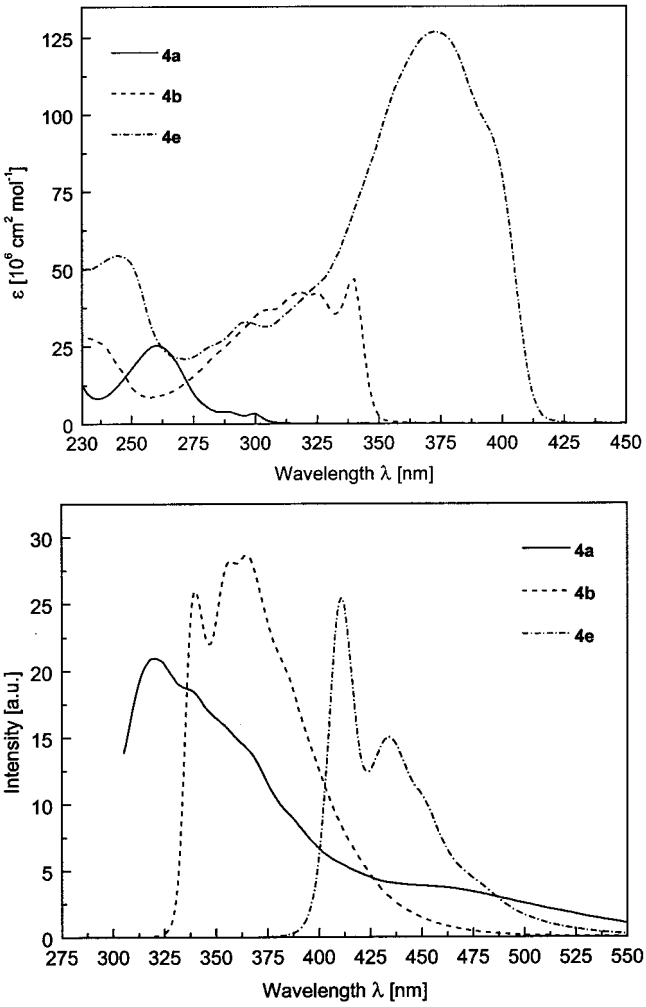


Figure 2. (a) Absorption and (b) emission spectra of iodo oligomers **4a**, **4b**, and **4e** in CH_2Cl_2; $\lambda_{excitation}$ = 290, 310, and 365 nm for **4a**, **b**, and **e**

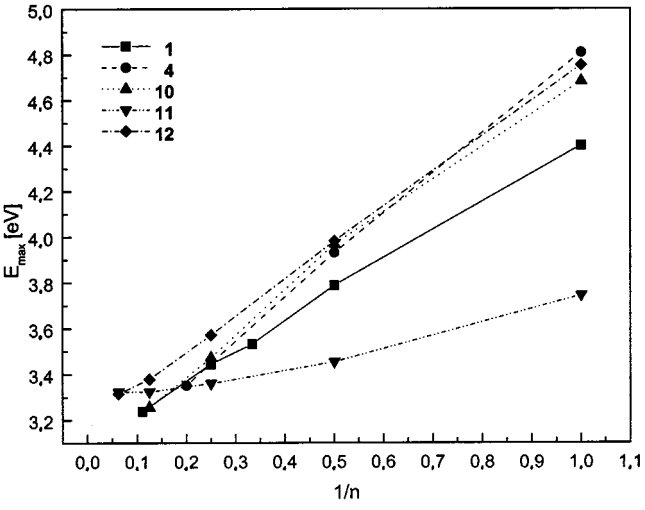
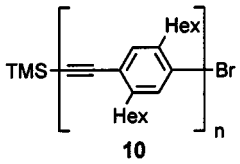


Figure 3. Absorption energy (**11** in THF; all other compounds in CH_2Cl_2) as a function of the reciprocal number of repeating units; data for **10**,[3] **11**,[4,12] and **12**[4] are taken from the literature; only for reasons of clarity, the data points of each class of compounds were connected by a line

To study the dependence of λ on the rod length for oligoPPEs with different end groups, the absorption energy E was plotted as a function of n^{-1}, with n being the number of repeating units (Figure 3).[15] For this purpose, we used λ_{max}, the wavelength of the absorption maximum, except for the dimers **1b** and **4b**. A comparison of the shape of the absorption bands of the herein studied compounds and of compounds **10**,[3] **11**, and **12**[4,16] suggested that in these cases the third maximum, when counting the maxima starting with that at the largest wavelength, is the one corresponding to λ_{max} of all the other oligmers. Figure 3 reveals that end groups like TIPS-ethynyl or triazeno, which extent the π-system, have a profound effect on the absorption as long as the rod is rather short. Already at the length of the tetramer, the absorption wavelengths of the differently substituted oligoPPEs become very similar and in the case of the octamers and nonamer, they differ only ca. 0.2 eV.



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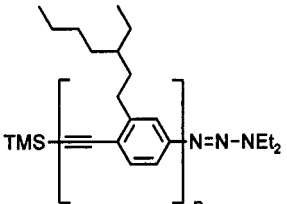

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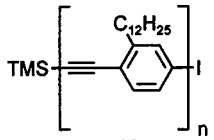

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Experimental Section

General: All reactions were performed under argon. THF and diethyl ether were distilled from sodium/benzophenone. Piperidine was dried with CaH_2. Activated MnO_2 and $Pd_2(dba)_3$ were purchased from Aldrich. $Pd(PPh_3)_2Cl_2$ was synthesized according to the literature,[16] however with 2.1 times the amount of methanol. The petroleum ether used had a boiling range of 30−40°C. For flash chromatography, Merck silica gel (mesh 70−230) was used. TLC was carried out on silica gel coated aluminum foils (Merck alumina foils $60F_{254}$). NMR spectra were, if not otherwise specified, recorded in CD_2Cl_2 as solvent and internal standard with a Bruker AMX-300 MHz at room temp. For signal assignment the carbon multiplicity [quaternary (C), tertiary (CH), secondary (CH_2), primary (CH_3)] was determined by a DEPT experiment. In the case of monosubstituted acetylenes, the signal for C≡*C*H does not appear in the DEPT spectra and is therefore reported as being due to a quaternary carbon atom. UV/Vis spectra (sh = shoulder) were recorded from solutions in CH_2Cl_2 with a Perkin Elmer Lambda 15 spectrometer. The concentrations used were in the range of 10^{-5}−10^{-6} mol/L. Emission spectra from solutions in CH_2Cl_2 were recorded with a Fluorolog 2 type F212 (SPEX USA) fluorescence spectrometer. The wavelengths of the fluorescence maxima are in *italics*. The melting points were determined in open capillaries with a Melting Point B-545 aparatus purchased from Büchi or with a melting table microscope from Reichert.

1,4-Dihexyl-2,5-diiodobenzene (8):[18] A mixture of 1,4-dihexylbenzene[19] (25.0 g, 101 mmol), iodine (28.32 g, 112 mmol), KIO_3 (10.85 g, 50 mmol) in acetic acid (300 mL), conc. H_2SO_4 (20 mL), and water (3 mL) was refluxed for 18 h. The reaction mixture was concentrated (100°C bath temp./1 atm) to about half of its volume. The residue was cooled with an ice bath and the precipitate was filtered off. The dark brown solid was purified by filtering through a short column of silica gel with petroleum ether as eluent. Twice repeated recrystallization from ethanol gave **8** (34 g, 68%) as colorless needles. − M.p. 47.8°C. − ^{1}H NMR ($CDCl_3$): δ = 7.59 (s, 2 H, 3-H, 6-H), 2.58 (m, 4 H, $ArCH_2$), 1.53 (m, 4 H, $ArCH_2CH_2$), 1.45−1.25 (m, 12 H, CH_2), 0.88 [t, ^3J(H,H) = 7 Hz, 6 H, CH_3]. − ^{13}C NMR ($CDCl_3$): δ = 144.8 (C, C-1, C-4), 139.3 (CH, C-3, C-6) 100.3 (C, C-2, C-5), 39.8 (CH_2, $ArCH_2$), 31.6, 30.2, 29.0, and 22.6 (4 CH_2), 14.1 (CH_3). − $C_{18}H_{28}I_2$ (498.23): calcd. C 43.39, H 5.66, I 50.94; found C 43.41, H 5.70, I 49.91.

Alkynyl-Aryl Coupling. − General Procedure for the Preparation of 1 and 4: To a degassed (freeze-pump-thaw cycle) solution of the two coupling components in dry THF and dry piperidine were added $Pd(PPh_3)_2Cl_2$ (1 mol-% with regard to the aryl halide) and CuI (2 mol-% with regard to the aryl halide) at room temperature. Shortly after, a voluminous precipitate formed. After stirring the reaction mixture for 12−20 h at room temp. or at 50°C for the preparation of **1a**, diethyl ether and water were added successively. The phases were separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with 2 N HCl and then with saturated aqueous NaCl and dried ($MgSO_4$). The products were isolated by flash chromatography.

1,4-Dihexyl-5-(3-hydroxyprop-1-ynyl)-2-iodobenzene (4a): Diiodo compound **8** (15.0 g, 30.1 mmol) was coupled with prop-2-ynol (1.2 mL, 20.1 mmol) in THF (150 mL) and piperidine (30 mL). Flash chromatography (petroleum ether/diethyl ether, 5:2 v/v) gave starting material **8** (5.7 g, 38%; R_f = 0.78), **4a** (6.1 g, 71%; R_f = 0.36) as a yellow-brown solid, and 1,4-dihexyl-2,5-bis(3-hydroxyprop-1-ynyl)benzene (1.0 g, 14%;R_f = 0.13) as a brown solid. An even easier separation is achieved by first eluting **8** with petroleum ether and then **4a** with petroleum ether/diethyl ether, 5:2.

4a: M.p. 38.4−38.6°C. − ^{1}H NMR ($CDCl_3$): δ = 7.63 (s, 1 H, 3-H), 7.21 (s, 1 H, 6-H), 4.50 (s, 2 H, CH_2O), 2.63 [d, ^3J(H,H) = 9 Hz, 2 H, $ArCH_2$], 2.61 [d, ^3J(H,H) = 9 Hz, 2 H, $ArCH_2$], 1.70 (br. s, 1 H, OH), 1.63−1.47 (m, 4 H, $ArCH_2CH_2$), 1.43−1.22 (m, 12 H, CH_2), 0.98−0.79 (m, 6 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 144.1 (C, C-1), 142.7 (C, C-4), 139.4 (CH, C-3), 132.5 (CH, C-6), 122.0 (C, C-5), 101.2 (C, C-2), 91.2 (C, *C*≡CCH_2O), 84.0 (C, C≡*C*CH_2O), 51.7 (CH_2, CH_2O), 40.1, 33.5, 31.63, 31.61, 30.4, 30.1, 29.05, 28.97, and 22.6 (9 CH_2), 14.1 (CH_3). − $C_{21}H_{31}IO$ (426.38): calcd. C 59.16, H 7.33; found C 59.08, H 7.34. − UV/Vis: λ (ε [10^6 cm^2 mol^{-1}]) = 260 (25.25), 289 (4.02), 300 nm (3.42). − Emission ($\lambda_{excitation}$ = 290 nm): λ = *320*, 336(sh) nm.

1,4-Dihexyl-2,5-bis(3-hydroxyprop-1-ynyl)benzene: M.p. 60.3−60.5°C. − ^{1}H NMR ($CDCl_3$): δ = 7.22 (s, 2 H, Ar-H), 4.52 (s, 4 H, CH_2O), 2.66 [t, ^3J(H,H) = 8 Hz, 4 H, $ArCH_2$], 1.75 (br. s, 2 H, OH), 1.58 (m, 4 H, $ArCH_2CH_2$), 1.40−1.23 (m, 12 H, CH_2), 0.87 (m, 6 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 142.1 (C, C-1, C-4), 132.4 (CH, C-3, C-6), 122.0 (C, C-2, C-5), 91.5 (C, *C*≡CCH_2O), 84.4 (C, C≡*C*CH_2O), 51.7 (CH_2, $ArCH_2$), 33.7, 31.6, 30.3, 29.0, and 22.5 (5 CH_2), 14.0 (CH_3). − $C_{24}H_{34}O_2$ (354.53): calcd. C 81.31, H 9.67; found C 81.26, H 9.75.

1,4-Dihexyl-2-(3-hydroxyprop-1-ynyl)-5-[2-(triisopropylsilyl)-ethynyl]benzene (1a): The reaction of iodo monomer **4a** (2.5 g, 5.9 mmol) with (triisopropylsilyl)ethyne (1.4 mL, 6.2 mmol) in THF (30 mL) and piperidine (8 mL) at 50°C overnight was incomplete.

Therefore, the crude product was once again treated with (triisopropylsilyl)ethyne (0.7 mL, 3.1 mmol). Flash chromatography (CH_2Cl_2/petroleum ether, 1:1 v/v) gave **1a** (2.4 g, 85%; R_f = 0.36) as a brown oil and the carbometalation product **9a** (54 mg impure sample, ca. 14%; R_f = 0.43) as a brown oil. Using 1.2 mol-equiv. of (triisopropylsilyl)ethyne at once, gave a quantitative conversion of **4a** at 50°C overnight.

1a: ^{1}H NMR: δ = 7.28 (s, 1 H, Ar-H), 7.24 (s, 1 H, Ar-H), 4. 50 [d, ^3J(H,H) = 6 Hz, 2 H, CH_2O], 2.73 [d, ^3J(H,H) = 8 Hz, 2 H, $ArCH_2$], 2.69 [d, ^3J(H,H) = 8 Hz, 2 H, $ArCH_2$], 1.84 (m, 1 H, OH), 1.60 (m, 4 H, $ArCH_2CH_2$), 1.43−1.22 (12 H, CH_2),1.15 (s, 21 H, TIPS), 0.96−0.82 (m, 6 H, CH_2CH_3). − ^{13}C NMR: δ = 143.1 and 142.7 (2 C, C-1, C-4), 133.2 and 132.9 (2 CH, C-3, C-6), 123.5 and 122.5 (2 C, C-2, C-5), 106.0 and 95.7 (2 C, TIPS−*C*≡*C*), 92.4 (C, *C*≡CCH$_2$O), 84.5 (C, C≡*C*CH$_2$O), 52.0 (CH_2, CH_2O), 34.8 and 34.3 (2 CH_2, $ArCH_2$), 32.3, 32.1, 31.3, 31.1, 29.8, 29.6, 23.12, and 23.10 (10 CH_2), 19.0 [CH_3, CH(*C*H$_3$)$_2$], 14.3 (CH_3, CH_2CH_3), 11.9 (CH, SiCH). − $C_{32}H_{52}OSi$ (480.85): calcd. C 79.93, H 10.90; found C 79.90, H 10.83. − UV/Vis: λ (ε [10^6 cm^2 mol^{-1}]) = 276 (sh) (33.01), 284 (40.38), 300 (13.91), 312 nm (9.55). − Emission ($\lambda_{excitation}$ = 295 nm): λ = 324 (sh), *330* nm.

9a: ^{1}H NMR: δ = 7.22 (s, 1 H, Ar−H *ortho* to C≡C), 6.83 (s, 1 H, Ar−H *ortho* to C=C), 6.25 [t, ^3J(H,H) = 7 Hz, 1 H, C=CH], 3.87 [d, ^3J(H,H) = 7 Hz, 2 H, CH_2O], 2.67 [d, ^3J(H,H) = 8 Hz, 2 H, $ArCH_2$], 2.53 [d, ^3J(H,H) = 8 Hz, 2 H, $ArCH_2$], 1.61−1.36 (m, 4 H, $ArCH_2CH_2$), 1.36−1.12 (m, 12 H, CH_2), 1.06 (s, 21 H, TIPS), 0.97 (s, 21 H, TIPS), 0.79 (m, 6 H, CH_2CH_3). − ^{13}C NMR: δ = 143.2 (C, *C*-Hexyl), 139.6 (CH, C=*C*H), 138.6 (C), 136.7 (C), 133.9 (CH, arom. CH), 129.9 (CH, arom. CH), 125.7 (C), 122.8 (C, *C*−C≡C), 107.8, 106.2, 94.3, and 91.7 (4 C, *C*≡*C*−TIPS), 60.3 (CH_2, *C*H$_2$O), 34.8, 33.0 (2 CH_2, $ArCH_2$), 32.3, 32.1, 31.35, 31.28, 29.8, 29.7, and 23.1 (7 CH_2), 18.97 and 18.87 [2 CH_3, CH(*C*H$_3$)$_2$], 14.3 (CH_3, CH_2CH_3), 11.9 and 11.8 (2 CH, SiCH). − MS(FD); *m/z*: 662.4 [M$^+$]; calcd. for $C_{43}H_{73}OSi_2$: 661.5.

1,4-Dihexyl-2-(3-hydroxyprop-1-ynyl)-5-(2-trimethylsilylethynyl)-benzene (1a′): The reaction of iodo monomer **4a** (1.50 g, 3.52 mmol) with (trimethylsilyl)ethyne (0.6 mL, 4.22 mmol) in THF (20 mL) and piperidine (5 mL) gave, after flash chromatography (CH_2Cl_2/petroleum ether, 1:1 v/v; R_f = 0.41), **1a′** (1.2 g, 88%) as a brown oil. − ^{1}H NMR: δ = 7.25 (s, 1 H, Ar−H), 7.23 (s, 1 H, Ar−H), 4.50 [d, ^3J(H,H) = 6 Hz, 1 H, CH_2O], 2.71−2.65 (m, 4 H, $ArCH_2$), 1.82 [t, ^3J(H,H) = 6 Hz, 1 H, OH], 1.64−1.52 (m, 4 H, $ArCH_2CH_2$), 1.41−1.21 (m, 12 H, CH_2), 0.96−0.82 (m, 6 H, CH_2CH_3), 0.25 (s, 9 H, TMS). − ^{13}C NMR: δ = 143.3 and 142.7 (2 C, C-1, C-4), 132.9 and 132.8 (2 CH, C-3, C-6), 123.1 and 122.6 (2 C, C-2, C-5), 104.2 and 99.4 (2 C, TMS−*C*≡*C*), 92.5 (C, *C*≡CCH$_2$O), 84.4 (C, C≡*C*CH$_2$O), 51.9 (CH_2, CH_2O), 34.5 and 34.2, (2 CH_2, $ArCH_2$), 32.2, 32.1, 31.0, 30.9, 29.7, 29.5, 23.1, and 23.0 (8 CH_2), 14.3 (CH_3, CH_2CH_3), 0.1 (CH, −$SiCH_3$). − $C_{26}H_{40}OSi$ (396.68): calcd. C 78.72, H 10.16; found C 78.74, H 10.13.

Dimer 1b: Coupling of **2a** (2.00 g, 4.44 mmol) with iodo monomer **4a** (1.85 g, 4.35 mmol) in THF (60 mL) and piperidine (20 mL) yielded, after flash chromatography (CH_2Cl_2/petroleum ether, 1:1 v/v), dimer **1b** (99 mg, 87%; R_f = 0.46) as a dark yellow oil and dimerization product **7a** (R_f = 0.82) as a redish brown oil.

1b: ^{1}H NMR: δ = 7.33 (s, 1 H, Ar−H), 7.32 (s, 1 H, Ar−H), 7.31 (s, 1 H, Ar−H), 7.29 (s, 1 H, Ar−H), 4.51 [d, ^3J(H,H) = 4 Hz, 2 H, CH_2O], 2.85−2.66 (m, 8 H, $ArCH_2$),1.78−1.54 (m, 8 H, $ArCH_2CH_2$), 1.53 (br. s, 1 H, OH), 1.48−1.20 (m, 24 H, CH_2) 1.15 (s, 21 H, TIPS), 0.96−0.78 (m, 12 H, CH_2CH_3). − ^{13}C NMR: δ = 143.1, 142.8, and 142.4 (3 C, *C*−Hexyl), 133.3, 132.9, 132.8, and 132. 7 (4 CH, arom. CH), 123. 4, 123. 3, 123.2, and 122.4 (4 C, *C*−C≡C), 106.1 and 95.9 (2 C, TIPS−*C*≡*C*), 93.3 and 93.1 (2 C, *C*≡*C*), 92.5 (C, *C*≡CCH$_2$O), 84.5 (C, C≡*C*CH$_2$O), 52.0 (CH_2, CH_2O), 34.8, 34.6, 34.5, and 34.2 (4 CH_2, $ArCH_2$), 32.2, 32.1, 31.3, 31.2, 31.1, 31.0, 29.8, 29.7, 29.6, 29.5, 23.1, and 23.0 (12 CH_2) , 18.9 (CH_3, CH*C*H$_3$), 14.3 (CH_2CH_3), 11.8 (CH, SiCH). − UV/Vis: λ (ε [10^6 cm^2 mol^{-1}]) = 312 (42.97), 330 (57.43), 336 (54.29), 352 nm (62.34). − Emission ($\lambda_{excitation}$ = 330 nm): λ = *360*, 377, 387, 406(sh) nm. − $C_{52}H_{80}OSi$ (749.30): calcd. C 83.35, H 10.76; found C 83.32, H 10.76.

7a: ^{1}H NMR: δ = 7.34 (s, 2 H, Ar-H *ortho* to C≡C−TIPS), 7.30 (s, 2 H, Ar−H *ortho* to C≡C-C≡C), 2.80−2.71 (m, 8 H, $ArCH_2$), 1.71−1.58 (m, 8 H, $ArCH_2CH_2$), 1.45−1.24 (m, 24 H, CH_2), 1.15 (s, 42 H, TIPS), 0.95−0.82 (m, 12 H, CH_2CH_3). − ^{13}C NMR: δ = 144.2 (C, Hex−*C*−C−C≡C−C≡C), 143.2 (C, Hex−*C*−C−C≡C−TIPS), 133.6 (CH, *C*H−C−C≡C−C≡C), 133.3 (CH, *C*H−C−C≡C−TIPS), 124.3, 121.5 (2 C, *C*−C≡C), 105.6, 96.8 (2 C, TIPS−), 82.0 (C, Ar−*C*≡C−C≡*C*), 78.5 (C, C≡*C*-*C*≡C), 34.7 and 34.3 (2 CH_2, $ArCH_2$), 32.2, 32.1, 32.2, 31.1, 29.7, 29.5, 23.07, and 23.05 (8 CH_2), 18.9 [CH_3, CH(*C*H$_3$)$_2$], 14.30 and 14.26 (2 CH_3, CH_2CH_3), 11.8 (CH, SiCH).

Trimer 1c: Coupling of **2b** (1.30 g, 1.81 mmol) with iodo monomer **4a** (0.73 g, 1.72 mmol) in THF (60 mL) and piperidine (20 mL) gave, after flash chromatography (CH_2Cl_2/petroleum ether, 1:1 v/v), trimer **1c** (1.5 g, 88%) as a colorless solid. − M.p. 46.8−47.2°C. − ^{1}H NMR: δ = 7.38 (s, 2 H), 7.35 (s, 1 H), 7.34 (s, 1 H), 7.32 (s, 1 H), 7.30 (s, 1 H), 4.52 (br. s, 2 H, CH_2O), 2.88−2.68 (m, 12 H, $ArCH_2$), 1.78−1.57 (m, 12 H, $ArCH_2CH_2$), 1.53 (br. s, 1 H, OH), 1.48−1.23 (m, 36 H, CH_2), 1.16 (s, 21 H, TIPS), 0.96−0.82 (m, 18 H, CH_2CH_3). − ^{13}C NMR: δ = 143.2, 142.8, 142.5, 142.41, and 142.39 (5 C, *C*−Hexyl), 133.3, 132.9, 132.84, 132.79, and 132.77 (5 CH, arom. CH), 123.4, 123.3, 123.24, 123.20, and 122.4 (5 C, *C*−C≡C), 106.1 and 95.9 (2 C, TIPS−*C*≡*C*), 93.45 93.36, 93.34, and 93.29 (4 C, *C*≡*C*), 92.5 (C, *C*≡CCH$_2$O), 84.5 (C, C≡*C*CH$_2$O), 52.0 (CH_2, CH_2O), 34.8, 34.6, 34.5, 34.3, 32.3, 32.1, 31.4, 31.3, 31.2, 31.1, 31.0, 29.8, 29.74, 29.70, 29.67, 29.5, 23.1, and 23.0 (18 CH_2), 18.9 (CH_3, CH*C*H$_3$), 14.3 (CH_3, CH_2CH_3), 11.9 (CH, SiCH). − $C_{72}H_{108}OSi$ (1017.74): calcd. C 84.97, H 10.70; found C 84.96, H 10.72. − UV/Vis: λ (ε [10^6 cm^2 mol^{-1}]) = 242 (35.74), 354 (83.89), 378 (59.61) nm. − Emission ($\lambda_{excitation}$ = 340 nm): λ = *389*, 410, 421(sh), 447(sh) nm.

Tetramer 1d: Coupling of **2b** (0.89 g, 1.24 mmol) with iodo dimer **4b** (0.78 g, 1.13 mmol) in THF (30 mL) and piperidine (9 mL) gave, after flash chromatography (CH_2Cl_2/petroleum ether, 1:1 v/v), tetramer **1d** (1.3 g, 92%; R_f = 0.54) as a slowly solidifying, yellow-brown oil and the dimerization product **7b** (R_f = 0.88).

1d: M.p. 92°C. − ^{1}H NMR: δ = 7.40 and 7.39 (2 s, 2 H each, Ar−H), 7.36 and 7.35 (2 s, 1 H each, Ar−H), 7.33 and 7.31 (2 s, 1 H each, TIPS−C≡C−Ar−*H*), 4.52 [d, ^3J(H,H) = 6 Hz, 2 H, CH_2O], 2.88−2.71 (m, 16 H, $ArCH_2$), 1.79−1.54 (m, 16 H, $ArCH_2CH_2$), 1.52−1.35 (m, 48 H, CH_2), 1.16 (s, 21 H, TIPS), 1.0−0.8 (m, 24 H, CH_2CH_3). − ^{13}C NMR: δ = 143.2, 142.8, 142.5 and 142.4 (4 C, *C*−Hexyl), 133.3, 132.9, 132.84, and 132.78 (4 CH, arom. CH), 123.4, 123.3, 123.2 and 122.4 (4 C, *C*−C≡C), 106.1 and 95.9 (2 C, TIPS−*C*≡*C*−), 93.50, 93.46, 93.34, 93.31, and 92.5 (5 C, *C*≡C), 84.5 (C, C≡*C*-CH$_2$O), 52.0 (CH_2, CH_2O), 34.8, 34.6, 34.5, and 34.2 (4 CH_2, Ar*C*H$_2$), 32.3, 32.1, 31.34, 31.25, 31.2, 31.1, 31.0, 29.8, 29.7, 29.65, 29.5, 23.1, and 23.0 (13 CH_2) 18.9 (CH_3, CH(*C*H$_3$)$_2$), 14.3 (CH_3, CH_2CH_3), 11.9 (CH, SiCH). − UV/Vis: λ (ε [10^6 cm^2 mol^{-1}]) = 244 (44.88), 282 (33.42), 322 (sh) (40.79), 363 (110.36), 376 (sh) (99.44), 381 (sh) nm (93.81). − Emission

($\lambda_{excitation}$ = 360 nm): λ = *405*, 426, 442(sh) nm. − $C_{92}H_{136}OSi$ (1286.18): calcd. C 85.91, H 10.57; found C 85.78, H 10.50.

7b: ^{1}H NMR: δ = 7.40 (s, 2 H, Ar−H), 7.37 (s, 2 H, Ar−H), 7.34 (s, 2 H, Ar−H *ortho* to C≡C−TIPS), 7.33 (s, 2 H, Ar−H *ortho* to C≡C−C≡C), 2.87−2.74 (m, 16 H, $ArCH_2$), 1.75−1.62 (m, 16 H, $ArCH_2CH_2$), 148−1.27 (m, 48 H, CH_2), 1.15 (s, 42 H, TIPS), 0.98−0.82 (m, 24 H, CH_2CH_3). − ^{13}C NMR: δ = 144.2 (C, Hex−*C*−C−C≡C−C≡C), 143.2 (C, Hex−*C*−C−C≡C−TIPS), 142.5 and 142.4 (2 C, *C*−Hexyl), 133.7 (CH, *C*H−C−C≡C−C≡C), 133.3 (CH, *C*H−C−C≡C−TIPS), 132.9 and 132.8 (2 CH, arom. CH), 124.3 and 121.5 (2 C, *C*−C≡C−TIPS, *C*−C≡C−C≡C), 123.4 and 123.0 (2 C, *C*−C≡CAr), 106.1 and 96.0 (2 C, TIPS−*C*≡*C*), 94.1 and 93.1 (2 C, Ar*C*≡*C*Ar), 82.2 (C, *C*≡C−C≡*C*), 78.7 (C, C≡*C*−*C*≡C), 34.8, 34.54, 34.46, and 34.4 (4 CH_2, $ArCH_2$), 32.2, 32.2, 32.1, 31.3, 31.2, 31.1, 31.0, 29.8, 29.7, 29.6, 29.5, 23.1, and 23.0 (13 CH_2), 18.9 [CH_3, $CH(CH_3)_2$], 14.29, 14.26 (CH_3, CH_2CH_3), 11.9 (CH, SiCH). − MS (FD); *m/z*: 1437.5 [M^+]; calcd. for $C_{102}H_{154}Si_2$: 1435.2.

Nonamer 1f: Iodo pentamer **4e** (65 mg, 0.043 mmol) was coupled with **2d** (70 mg, 0.056 mmol) in the presence of $Pd_2(dba)_3$ (2.5 mg, 0.003 mmol), CuI (1.0 mg, 0.005 mmol), and PPh_3 (3.0 mg, 0.01 mmol) in THF (15 mL) and piperidine (5 mL). The general procedure given above was followed for running the reaction and for workup. The $MgSO_4$ used for drying, was washed with CH_2Cl_2. Flash chromatography (CH_2Cl_2/petroleum ether, 1:1 v/v) gave **1f** (96 mg, 84%; R_f = 0.54) and **7d** (R_f = 0.92), both as yellow-green solids.

1f: M.p. 187°C. − ^{1}H NMR: δ = 7.44−7.37 (m, 14 H, Ar−H), 7.36 and 7.35 (2 s, 1 H each, Ar−H), 7.33 (s, 1 H, Ar−H), 7.30 (s, 1 H, Ar−H), 4.52 [d, ^3J(H,H) = 6 Hz, 2 H, CH_2O], 2.89−2.70 (m, 36 H, $ArCH_2$), 1.78−1.62 (m, 36 H, $ArCH_2CH_2$), 1.51−1.25 (m, 108 H, CH_2), 1.16 (s, 21 H, TIPS), 0.98−0.82 (m, 54 H, CH_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 142.6, 142.3, 141.9, and 141.8 (4 C, *C*−Hexyl), 132.9, 132.6, 132.44, and 132.37 (4 CH, *C*H−C−Hexyl), 123.1, 122.8, and 121.8 (3 C, *C*−C≡C), 105.7 and 95.3 (2 C, TIPS−*C*≡*C*), 93.1, 92.9, and 91.6 (3 C, *C*≡C), 84.7 (C, C≡*C*CH_2O), 51.8 (CH_2, CH_2O), 34.2, 34.1, and 34.0 (3 CH_2, $ArCH_2$), 31.8, 31.7, 30.8, 30.7, 30.6, 30.5, 29.4, 29.3, 29.2, 29.1, 22.7, and 22.6 (12 CH_2), 18.7 [CH_3, $CH(CH_3)_2$], 14.1, (CH_3, CH_2CH_3), 11.4 (CH, SiCH). − UV/Vis: λ (ε [10^6 cm^2 mol^{-1}]) = 245 (96.17), 386 (259.04), 395 (sh) nm (250.17). − Emission ($\lambda_{excitation}$ = 380 nm): λ = *424*, 448, 465 (sh) nm. − MS (FD); *m/z*: 2626.8 [M^+]. − $C_{192}H_{276}OSi$ (2628.38): calcd. C 87.74, H 10.50; found C 87.76, H 10.58.

7d: ^{1}H NMR: δ = 7.414, 7.407, 7.395 (3 s, 12 H altogether; Ar−H), 7.35 (s, 2 H, Ar−H *ortho* to C≡C−TIPS), 7.33 (s, 2 H, Ar−H *ortho* to C≡C−C≡C), 2.91−2.75 (m, 32 H, $ArCH_2$), 1.79−1.62 (m, 32 H, $ArCH_2CH_2$), 1.50−1.27 (m, 96 H, CH_2), 1.16 (s, 42 H, TIPS), 0.98−0.83 (m, 48 H, CH_2CH_3). − ^{13}C NMR: δ = 144.3 (C, Hex−*C*−C−C≡C−C≡C), 143.2 (C, Hex−*C*−C−C≡C−TIPS), 142.6, 142.5, 142.4 (3 C, *C*−Hexyl), 133.7 (CH, *C*H−C−C≡C−C≡C), 133.3 (CH, *C*H−C−C≡C−TIPS), 132.90, 132.85, 132.79 (CH, *C*H−C−Hexyl), 124.3 and 121.5 (2 C, *C*−C≡C−TIPS, *C*−C≡C-C≡C), 123.4, 123.3, 123.2, and 123.1 (4 C, *C*−C≡CAr), 106.1 and 95.9 (2 C, TIPS−*C*≡*C*), 94.2, 93.6, 93.5, 93.35, and 93.27 (5 C, Ar*C*≡*C*Ar), 82.2 (C, *C*≡C−C≡*C*), 78.7 (C, C≡*C*−*C*≡C), 34.8, 34.6, 34.5, and 34.4 (4 CH_2, $ArCH_2$), 32.3, 32.1, 31.4, 31.3, 31.2, 31.1, 31.0, 29.8, 29.71, 29.65, 29.5, 23.11, and 23.07 (13 CH_2), 18.9 [CH_3, $CH(CH_3)_2$], 14.32, 14.28 (2 CH_3, CH_2CH_3), 11.9 (CH, SiCH). − UV/Vis: λ (ε [10^6 cm^2 mol^{-1}]) = 244 (78.98), 291 (42.27), 386 (206.22), 398 (sh) nm (195.02). − Emission ($\lambda_{excitation}$ = 385 nm): λ = *426*, 453 nm. − MS (FD); *m/z*: 2509.2 [M^+]; calcd. for $C_{182}H_{266}Si_2$: 2508.0.

Iodo Dimer 4b: The reaction of **3a** (1.08 g, 3.33 mmol) with **8** (3.35 g, 6.66 mmol) in THF (30 mL) and piperidine (8 mL) gave, after flash chromatography (diethyl ether/petroleum ether, 2:5 v/v), starting material **8** (2.3 g, 69%; R_f = 0.90), iodo dimer **4b** (1.2 g, 53%; R_f = 0.55) as a pinkish solid, and a third fraction consisting mainly of disubstitution product **5a** (0.46 g, 15%; R_f = 0.18) as a beige-colored solid.

4b: M.p. 62°C. − ^{1}H NMR: δ = 7.71 (s, 1 H, H *ortho* to I), 7.34 and 7.32 (2 s, 1 H each, H *ortho* to −C≡CAr), 7.29 (s, 1 H, H *ortho* to −C≡CCH_2O), 4.52 [d, ^3J(H,H) = 6 Hz, 2 H, CH_2O], 2.85−2.63 (m, 8 H, $ArCH_2$), 1.84 [t, ^3J(H,H) = 6 Hz, 1 H, OH], 1.75−1.53 (m, 8 H, $ArCH_2CH_2$), 1.51−1.21 (m, 24 H, CH_2), 1.01−0.82 (m, 12 H, CH_2CH_3). − ^{13}C NMR: δ = 144.3 (C, I−C−*C*−Hexyl), 143.4, 142.8, and 142.4, (3 C, *C*−Hexyl), 139.9 (CH, *C*H−C−I), 132.9, 132.8, and 132.7 (3 CH, *C*H−C−C≡C), 123.4, 123.3, 122.5 (C, *C*−C≡C), 101.2 (C, *C*−I), 92.7, 92.6, and 92.5, (3 C, *C*≡C), 84.5 (C, C≡*C*CH_2O), 52.0 (CH_2, CH_2O), 40.6 (CH_2, I−C−C−*C*H_2), 34.5, 34.3, 34.2, (CH_2, $ArCH_2$), 32.3, 32.2, 32.11, 32.09, 31.10, 31.06, 30.9, 30.7, 29.6, 29.5, 29.4, 23.1, 23.0 (CH_2), 14.3 (CH_3, CH_2CH_3). − UV/Vis: λ (ε [10^6 cm^2 mol^{-1}]) = 304 (36.83), 318 (42.56), 325 (41.99), 340 nm (46.61). − Emission ($\lambda_{excitation}$ = 310 nm): λ = 340, 357, *365* nm. − $C_{41}H_{59}IO$ (694.82): calcd. C 70.88, H 8.49, I 18.26; found C 70.66, H 8.47, I 19.22.

5a: ^{1}H NMR: δ = 7.38 (s, 2 H, Ar−H), 7.35 (s, 2 H, Ar−H), 7.29 (s, 2 H, Ar−H), 4.52 [d, ^3J(H,H) = 6 Hz, 4 H, CH_2O], 2.86−2.78 (two overlapping t, 8 H, $ArCH_2$), 2.73 [t, ^3J(H,H) = 8 Hz, 4 H, $ArCH_2$], 1.80 [t, ^3J(H,H) = 6 Hz, 2 H, OH], 1.75−1.58 (m, 12 H, $ArCH_2CH_2$), 1.50−1.25 (m, 36 H, CH_2), 1.01−0.80 (m, 18 H, CH_3). − ^{13}C NMR: δ = 142.8, 142.5, and 142.4 (3 C, *C*−Hexyl), 132.9, 132.8, and 132.7 (3 CH, *C*H−C−C≡C), 123.4, 123.2, and 122.4 (3 C, *C*−C≡C), 93.30, 93.27, and 92.5 (3 C, *C*≡*C*), 84.5 (C, C≡*C*−CH_2O), 52.0 (CH_2, CH_2O), 34.54, 34.48, and 34.2 (3 CH_2, $ArCH_2$), 32.2, 32.1, 31.13, 31.07, 30.92, 29.7, 29.6, 29.5, 23.1, and 23.0 (10 CH_2), 14.3 (CH_3, CH_2CH_3). − MS (FD); *m/z*: 890.7 [100%; M^+ of **5a**]; 646.3 [26%; M^+ of **6a**]. − $C_{64}H_{90}O_2$ (891.39) (**5a**): calcd. C 86.24, H 10.18; found C 86.23, H 10.17.

Iodo Pentamer 4e: a) The coupling of **3d** (0.31 g, 0.28 mmol) with diiodo compound **8** (0.55 g, 1.10 mmol) in THF (20 mL) and piperidine (8 mL) with $Pd(PPh_3)_2Cl_2$/CuI as catalyst gave, after flash chromatography (CH_2Cl_2/petroleum ether, 2:1 v/v), starting material **8** (0.42 g; 76%, R_f = 0.88) and iodo pentamer **4e** (0.2 g, 51%; R_f = 0.67) a a yellow solid. The third fraction (R_f = 0.40), which contained the dimerization product **6d** and possible disubstitution product **5d** was not eluted. − b) The coupling of **3d** (261 mg, 0.231 mmol) with diiodo compound **8** (0.46 g, 0.93 mmol) in THF (15 mL) and piperidine (6 mL) in the presence of $Pd_2(dba)_3$ (10 mg, 0.01 mmol), CuI (4 mg, 0.02mmol), and PPh_3 (12 mg, 0.05 mmol) gave, after flash chromatography (CH_2Cl_2/petroleum ether, 2:1 v/v), iodo pentamer **4e** (168 mg, 49%).

M.p.: 121°C. − ^{1}H NMR: δ = 7.72 (s, 1 H, H *ortho* to I), 7.40 (br. s, 6 H, Ar−H), 7.36 (s, 1 H, Ar−H) 7.34 (s, 1 H, Ar−H), 7.31 (s, 1 H, Ar−H), 4.52 [d, ^3J(H,H) = 6 Hz, 2 H, CH_2O], 2.88−2.65 (m, 20 H, $ArCH_2$), 1.83−1.58 (m, 20 H, $ArCH_2CH_2$), 1.50−1.25 (m, 60 H, CH_2), 1.0−0.8 (m, 30 H, CH_3). − ^{13}C NMR: δ = 144.3 (C, I−C−*C*−Hexyl), 143.4, 142.8, 142.5, 142.4 (4 C, *C*-Hexyl), 140.0 (CH, I−C−*C*H), 132.9, 132.84, 132.76 (3 CH, *C*H−C−C≡C), 123.4, 123.29, 123.26, 123.22, 123.15, 122.4 (6 C, *C*−C≡C), 101.2 (C, *C*−I), 93.5, 93.34, 93.31, 92.9, 92.8, and 92.5 (6 C, *C*≡C), 84.5 (C, C≡*C*CH_2O), 52.0 (CH_2, CH_2O), 40.6 (CH_2, I−C−C−*C*H_2), 34.6, 34.5, and 34.3 (3 CH_2, $ArCH_2$), 32.3, 32.2, 32.12, 32.10, 31.2,

31.1, 30.9, 30.7, 30.1, 29.7, 29.6, 29.5, 29.4, 23.1, and 23.0 (15 CH_2), 14.3 (CH_3, CH_2CH_3). – UV/Vis: λ (ε [10^6 cm^2 mol^{-1}]) = 245 (54.24), 296 (32.88), 373 (126.90), 392 (sh) nm (99.04). – Emission ($\lambda_{excitation}$ = 365 nm): λ = *411*, 434 nm. – $C_{101}H_{143}IO$ (1500.15): calcd. C 80.87, H 9.53; found C 80.80, H 9.64.

1-Ethynyl-2,5-dihexyl-4-(3-hydroxyprop-1-ynyl)benzene (3a): To a solution of **1a′** (1.4 g, 3.5 mmol) in methanol (20 mL) and THF (15 mL) was added 5 N NaOH (4 mL). After stirring the reaction mixture for 2 h at room temp., diethyl ether (30 mL) and water (30 mL) were added. The aqueous phase was extracted with diethyl ether. The combined organic phases were washed with saturated aqueous NaCl and dried ($MgSO_4$). Removal of the solvent gave **3a** (1.1 g, 95%) as a light brown oil. – ^{1}H NMR ($CDCl_3$): δ = 7.27 (s, 1 H, Ar–H), 7.23 (s, 1 H, Ar–H), 4.51 [d, ^3J(H,H) = 6 Hz, 2 H, CH_2O], 3.26 (s, 1 H, C≡C–H), 2.72–2.63 (m, 4 H, $ArCH_2$), 1.65–1.51 (m, 4 H, $ArCH_2CH_2$), 1.38–1.20 (m, 12 H, CH_2), 0.91–0.82 (m, 6 H, CH_3).

Polar Acetylene 3d: To a solution of **1d** (0.40 g, 0.31 mmol) in THF (20 mL) 1 M tetrabutylammonium fluoride in THF (0.63 ml, 0.63 mmol) was added. The reaction mixture was stirred for 2h at room temp. After the addition of diethyl ether (30 mL) and water (30 mL), the phases were separated, the aqueous phase was extracted with diethyl ether and the combined organic phases were washed with saturated aqueous NaCl and finally dried ($MgSO_4$). Removal of the solvent gave an olive-colored solid, which was suspended in methanol (10 mL) for 0.5 h at room temp. The suspension was cooled with an ice bath. The solid was isolated and washed with ice-cold methanol to give **3d** [0.3 g, 96%; R_f (CH_2Cl_2/petroleum ether, 1:1 v/v) = 0.46] as a light green solid. – M.p. 91°C (decomposition). – ^{1}H NMR: δ = 7.40, 7.39 (2 s, 4 H, Ar–H), 7.363 (s, 1 H, Ar–H), 7.357 (s, 1 H, Ar–H), 7.349 (s, 1 H, Ar–H), 7.30 (s, 1 H, Ar–H), 4.52 [d, ^3J(H,H) = 6 Hz, 2 H, CH_2O], 3.37 (s, 1 H, C≡C–H), 2.87–2.71 (m, 16 H, $ArCH_2$), 1.76–1.59 (m, 16 H, $ArCH_2CH_2$), 1.40–1.25 (m, 48 H, CH_2), 0.97–0.82 (m, 24 H, CH_3). – ^{13}C NMR: δ = 143.3, 142.8, 142.5 and 142.4 (4 C, *C*–Hexyl), 133.4, 132.84, and 132.76 (3 CH, arom. CH), 123.7, 123.4, 123.2, 122.4, and 121.9 (5 C, *C*–C≡C), 93.5, 93.3, 93.2, 92.5, 84.5, 82.7, and 81.9 (7 C, *C*≡*C*), 51.9 (CH_2, CH_2O), 34.6, 34.5, and 34.2 (3 CH_2, $ArCH_2$), 32.2, 32.1, 31.14, 31.08, 30.9, 29.7, 29.5, and 23.1 (8 CH_2), 14.3 (CH_3). – $C_{83}H_{116}O$ (1129.83):calcd. C 88.24, H 10.27; found C 88.17, H 10.12.

Removal of the Hydroxymethyl (HOM) Group. – General Procedure for the Preparation of 2a, 2b, and 2d: To a solution of oligoPPEs **1** in dry diethyl ether were added activated MnO_2 and powdered KOH in four portions, one every hour. The suspension was stirred with protection from light at room temp. The reaction can be monitored by TLC (CH_2Cl_2/petroleum ether, 1:1 v/v). Sometimes, especially with increasing amounts of starting materials, the reaction needed more MnO_2/KOH. Therefore, more reagents were added, until the reactions were quantitative. Filtration of the reaction mixture through a short column with silica gel gave the compounds **2a**, **2b**, and **2d**, which were used as obtained.

1-Ethynyl-2,5-dihexyl-4-[2-(triisopropylsilyl)ethynyl]benzene (2a): Starting with **1a** (3.50 g, 7.28 mmol), MnO_2 (10.12 g, 116 mmol), and KOH (3.28 g, 58 mmol) in diethyl ether (80 mL), **2a** (2.6 g, 80%) was isolated as a slightly red oil. – ^{1}H NMR: δ = 7.31 (s, 2 H), 3.35 (s, 1 H, C≡C–H), 2.75 (m, 4 H, $ArCH_2$), 1.61 (m, 4 H, $ArCH_2CH_2$), 1.45–1.25 (m, 12 H, CH_2), 1.17 (s, 21 H, TIPS), 0.95–0.85 (m, 6 H, CH_2CH_3). – ^{13}C NMR: δ = 143.3 and 143.2 (*C*–Hexyl), 133.4 and 133.3 (arom. CH), 123.9 and 122.0 (*C*–C≡C), 106.0 and 96.0 (TIPS–*C*≡*C*), 82.8 and 81.9 (*C*≡*C*H), 34.8, 34.4, 32.4, 32.2, 31.4, 31.2, 29.9, 29.7, 23.21, and 23.17 (10 CH_2), 19.0 [$CH(CH_3)_2$], 14.4 (CH_2CH_3), 12.0 (SiCH). – $C_{31}H_{50}Si$ (450.83): calcd. C 82.59, H 11.18; found C 82.51, H 11.12.

Non-Polar Acetylene 2b: Starting with **1b** (2.50 g, 3.34 mmol), MnO_2 (4.6 g, 53 mmol), and KOH (1.5 g, 26 mmol) in diethyl ether (60 mL), **2b** (1.8 g, 73%) was isolated as a slightly red oil. – ^{1}H NMR: δ = 7.34, 7.335, 7.32, and 7.32 (4 s, 1 H each, arom. CH), 3.37 (s, 1 H, C≡C–H), 2.86–2.68 (m, 8 H, $ArCH_2$), 1.73–1.56 (m, 8 H, $ArCH_2CH_2$), 1.48–1.22 (m, 24 H, CH_2), 1.15 (s, 21 H, TIPS), 0.96–0.82 (m, 12 H, CH_2CH_3). – ^{13}C NMR: δ = 143.3, 143.2, and 142.4 (4 C, *C*–Hexyl), 133.4, 133.3, 132.82, and 132.78 (4 CH, arom. CH), 123.8, 123.4, 123.2, and 121.9 (C, *C*–C≡C), 106.1 and 95.9 (2 C, TIPS–*C*≡*C*), 93.4 and 93.1 (2 C, Ar*C*≡*C*Ar), 82.7 and 81.9 (2 C, *C*≡*C*H), 34.8, 34.6, 34.5, 34.3, 32.3, 32.2, 32.1, 31.4, 31.3, 31.1, 31.0, 29.8, 29.73, 29.66, 29.56, 23.1, and 23.0 (17 CH_2), 18.9 [CH_3, $CH(CH_3)_2$], 14.3 (CH_3, CH_2CH_3), 11.9 (CH, SiCH). – $C_{51}H_{78}Si$ (719.27): calcd. C 85.16, H 10.93; found C 85.08, H 10.88.

Non-Polar Acetylene 2d: Starting from **1d** (0.10 g, 0.08 mmol), MnO_2 (160 mg, 1.84 mmol), and KOH (40 mg, 71 mmol) in diethyl ether (15 mL), **2d** (87 mg, 89%) was isolated as a light green, waxy solid. M.p. 79°C. – ^{1}H NMR: δ = 7.40 (br. s, 4 H, Ar–H), 7.36 (s, 1 H, Ar–H), 7.35 (s, 2 H, Ar–H), 7.33 (s, 1 H, Ar–H), 3.37 (s, 1 H, C≡C–*H*), 2.87–2.73 (m, 16 H, $ArCH_2$), 1.76–1.60 (m, 16 H, $ArCH_2CH_2$), 1.50–1.26 (m, 48 H, CH_2), 1.16 (s, 21 H, TIPS), 0.95–0.89 (m, 24 H, CH_2CH_3). – ^{13}C NMR: δ = 143.3, 143.2, 142.52, 142.49, 142.41, and 142.38 (6 C, *C*–Hexyl), 133.4, 133.3, 132.84, and 132.78 (4 CH, arom. CH), 123.8, 123.31, 123.27, 123.22, 123.16, and 121.9, (6 C, *C*–C≡C), 106.1, and 95.9 (2 C, TIPS–*C*≡*C*), 93.51, 93.45, 93.3, and 93.2 (4 C, Ar*C*≡*C*Ar), 82.7 and 81.9 (2 C, *C*≡*C*H), 34.8, 34.6, 34.5, and 34.2 (4 CH_2, $ArCH_2$), 32.3, 32.1, 31.3, 31.24, 31.16, 31.1, 31.0, 30.1, 29.8, 29.69, 29.65, 29.5, 23.1, and 23.0 (14 CH_2), 18.9 [CH_3, $CH(CH_3)_2$], 14.3 (CH_3, CH_2CH_3), 11.9 (CH, SiCH). – $C_{91}H_{134}Si$ (1256.14): calcd. C 87.01, H 10.75; found C 83.16, H 11.03.

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