

Preparation and Nonlinear Optics of Monodisperse Oligo(1,4-phenyleneethynylene)s

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Keywords: Alkynes / Conjugation / Nonlinear optics / Oligomers / Third harmonic generation

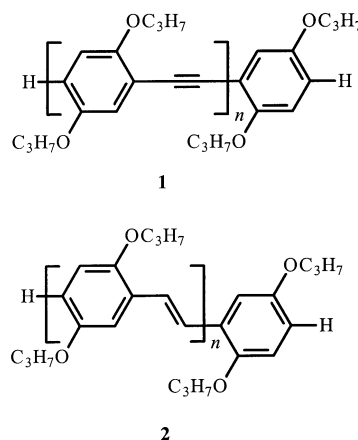
Oligo(1,4-phenyleneethynylene)s **1a–e**, with solubilizing propoxy side chains, were prepared by use of Hagihara–Sonogashira coupling reactions. The synthetic strategy was based on a building block system and on the use of trimethylsilyl and triisopropylsilyl protecting groups that could be cleaved selectively. The extension of the conjugation with an increasing number of repeat units provokes

a bathochromic shift of the long wavelength absorption and a superlinear increase of the second hyperpolarizability $\chi^{(2)}$. The corresponding third harmonic generation (THG) measurements were performed using polystyrene matrices and variable laser wavelengths. We conclude that the conjugation length is much larger than 5 repeat units.

Introduction

Because of their interesting optical, electrical, and optoelectronic properties, conjugated oligomers are target compounds for many applications in materials science; moreover, they are model compounds for conjugated polymers.^[1–9] In this context we decided to study a series of monodisperse oligo(1,4-phenyleneethynylene)s (OPEs) **1** bearing propoxy side chains. Unsubstituted higher OPEs ($n \geq 3$) are difficult to produce because of their extremely low solubilities. Alkoxy side chains enhance the solubility and reduce the HOMO–LUMO gap and the band gap in the solid state. The pattern of 2,5-disubstitution and the length of the alkoxy chains have been optimized in the 1,4-phenyleneethynylene series **2**.^[10]

Interest in OPEs and the corresponding polymers (PPEs) has increased greatly during the previous decade;^[11–36] systematic studies of structure–property relationships are thus highly desirable. Here we present the preparation of compounds **1a–e** ($n = 1–5$) and compare the third-order nonlinear optical properties in this series with those in the corresponding oligo(2,5-dipropoxy-1,4-phenylenevinylene) (OPV) series **2** (Scheme 1).^[37,38] We have used the method of third harmonic generation (THG) with variable laser wavelengths.^[37] As the optical properties of conjugated polymers are determined largely by the extent of their electron delocalization, investigation of the corresponding oligomers plays an important role in proper understanding of the scaling of linear and nonlinear optical properties with the size of the system.



Scheme 1. Oligo(2,5-dipropoxy-1,4-phenyleneethynylene)s **1** and oligo(2,5-dipropoxy-1,4-phenylenevinylene)s **2**

Results and Discussion

Synthesis

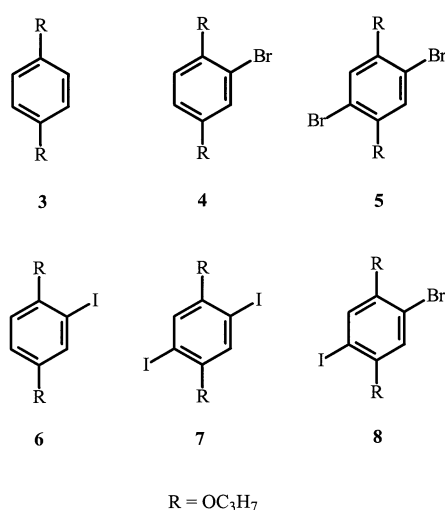
The synthetic strategy for the preparation of the monodisperse oligo(1,4-phenyleneethynylene)s **1a–e** ($n = 1–5$) is based on a building block system. The initial building blocks are represented by the mono- and dihalogenated 1,4-dipropoxybenzenes **4–8**, which were obtained through substitution reactions. Bromination of 1,4-dipropoxybenzene (**3**) with equimolar amounts of bromine gave a 76% yield of 1-bromo-2,5-dipropoxybenzene (**4**). 1,4-Dibromo-2,5-dipropoxybenzene (**5**) was obtained in 86% yield by treatment of **3** with 2 equiv. of bromine in acetic acid. Direct iodination of **3** was carried out with iodine and potassium iodate in the presence of sulfuric acid. Monoiodo compound **6** was purified by careful distillation (yield 44%), whereas the solid

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diiodo compound **7** could be purified by recrystallization (yield 82%). The mixed bromo-iodo derivative **8** was prepared in 77% yield by treatment of **4** with $I_2/KIO_3/H_2SO_4$. The opposite sequence for introduction of the halogen substituents was not successful. Bromination of **6** resulted exclusively in the dibromo compound **5**; clearly the iodine substituent had been replaced in an electrophilic *ipso* substitution.^[39]

In order to introduce ethynyl groups, Hagihara–Sonogashira reactions were applied.^[40] Trimethylsilyl- and triisopropylsilyl ethyne reacted with **4–8** (Scheme 2) in C–C coupling processes catalyzed by palladium(0)/copper(I) iodide in piperidine. In this manner, the mono- and bis(trialkylsilyl)ethynylbenzenes **9–15** (Scheme 3) were generated in high yields.

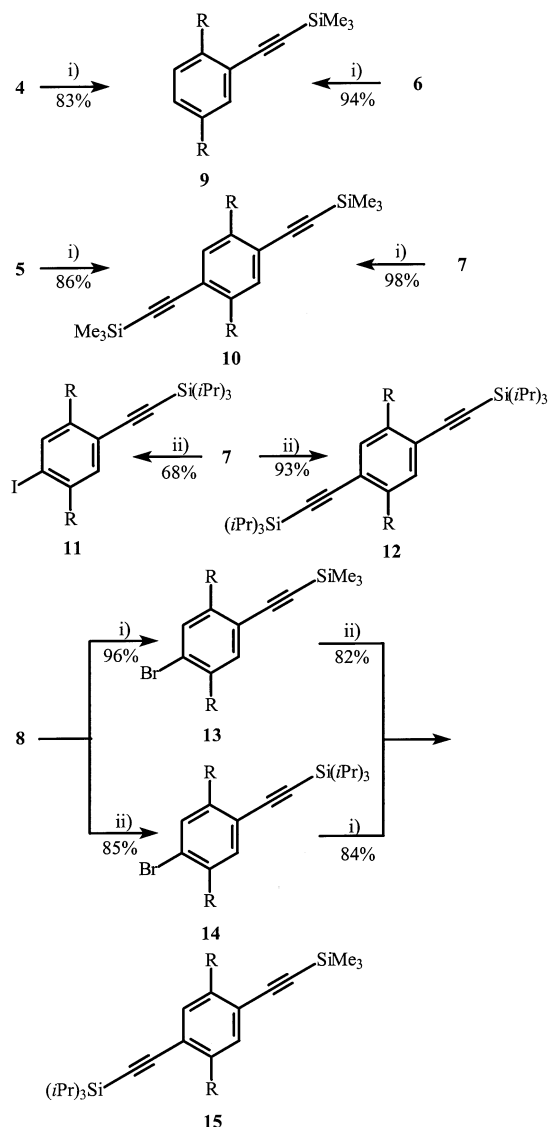


Scheme 2. Halogenation products **4–8** of 1,4-dipropoxybenzene (**3**)

The deprotection of the alkynes **9**, **10**, **12**, and **13** was achieved with sodium hydroxide in methanol or with tetrabutylammonium fluoride in THF/water (Scheme 4). Since the bonding of the triisopropylsilyl group is stronger, selective deprotection of **15** was successful by cleavage of the trimethylsilyl group with potassium carbonate in methanol/THF.

The preparation of the target compounds **1a–e** was performed by means of the Hagihara–Sonogashira reaction,^[40] in which a C–C coupling of iodo- or bromoarenes and ethynylarenes takes place. Catalytic amounts of bis(triphenylphosphane)palladium dichloride, copper(I) iodide, and triphenylphosphane were used for the process, which was normally run in piperidine. Toluene was added in some cases to improve the solubility (Scheme 5).

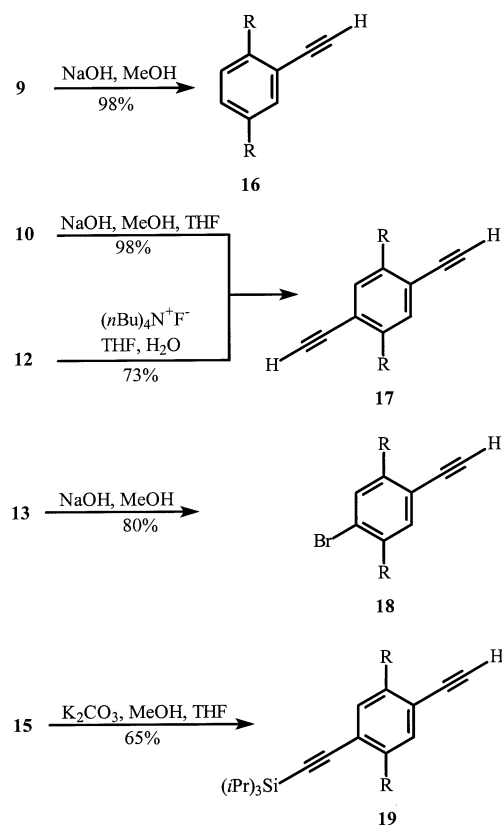
The true catalytic species is the (triphenylphosphane)Pd⁰ complex, which inserts into the carbon–halogen bond. Under the conditions applied here, the reactions would in principle also work in the absence of copper(I) iodide;^[41] however, we found that the best yields were obtained with iodoarenes and freshly precipitated CuI. Piperidine served as scavenger for the eliminated hydrogen bromide or iodide.



Scheme 3. Formation of the alkynes **9–15** by replacement of the halogen substituents in **4–8** by trialkylsilyl ethynyl groups: i) Me₃SiC≡CH, Pd⁰, CuI, piperidine; ii) (iPr)₃SiC≡CH, Pd⁰, CuI, piperidine

In some cases, in which the yield of the coupling was low, we observed increased formation of 1,3-diynes, although oxygen was carefully excluded.^[42] The tolane derivative **1a**, the first compound in the oligomer series **1**, was formed on treatment of the iodobenzene **6** with the phenylacetylene **16**, whilst the diiodo compound **7** and **16** accordingly yielded the next higher oligomer **1b**.

The original plan for the synthesis of compound **1c** was based on the C–C coupling of the bromotolane system **20** with the ethynyltolane **22**. The component **20** was obtainable from **16** and 1-bromo-4-iodobenzene (**8**) in an almost quantitative yield; the reactivity in the Hagihara–Sonogashira process was much higher on the iodo side than on the bromo side. C–C coupling of **20** with triisopropylsilyl ethyne to give **21** and deprotection of **21** to give **22** gave yields of 99 and 87%, respectively. The syn-



Scheme 4. Generation of the phenylethyne **16–19** by deprotection of **9**, **10**, **12**, **13**, and **14**

thetic strategy thus seemed very promising, but the final C–C coupling **22** + **20** $\rightarrow$ **1c** gave only poor yields. We therefore had to develop a new approach for **1c**, coupling **22** with the iodo compound **11** instead of with the bromo compound **20** to obtain **23** in a yield of 58%. Deprotection of **23** with tetrabutylammonium fluoride furnished alkyne **24**, which was coupled with the iodobenzene derivative **6**. Though the yield of the latter C–C coupling is moderate, the total yield of **1c** from **22** could be doubled by use of the alternate route.

The preparation of compound **1d** was also achieved by two different pathways. The diyne **17** was subjected to a twofold Hagihara–Sonogashira reaction (**17** + 2·**20** $\rightarrow$ **1d**) or to a twofold coupling with **8**, which reacted selectively on the iodo side (**17** + 2·**8** $\rightarrow$ **25**); oligomer **1d** could subsequently be obtained in situ by coupling of **25** with the alkyne **16** at both ends. The yield of the first variant was much better: 76% in comparison to 15%.

However, the dibromo compound **25** could be used for two consecutive couplings: namely **25** + **19** $\rightarrow$ **26** and **26** + **16** $\rightarrow$ **27**. Deprotection of **27** gave **28**, and final coupling of **28** with **6** the target oligomer **1e**.

The oligomers **1a–e** are distinct from other known OPEs or PPEs insofar as they have identical substitution patterns in each benzene ring in the chain and do not have divergent end groups that interact with the π system. Such interac-

tions can have a dramatic effect on optical properties. A striking example is represented by the push–pull-substituted OPEs obtained by HPLC separation of polydisperse products.^[17]

Optical Studies

UV/Vis absorption spectra of diluted solutions of OPEs (**1a–e**) in CHCl_3 are shown in Figure 1. The wavelengths of the absorption maxima λ_{max} show the expected strong bathochromic shift with increasing number n of repeat units, typical for short oligomers of conjugated systems. The corresponding molar extinction coefficients ϵ_{max} also increase with n (see Table 1). Our studies of nonlinear optical properties required thin films of OPEs on fused silica substrates. Films of pure OPEs lose their optical quality because OPEs tend to crystallize and exhibit strong light scattering. We therefore prepared thin films of OPEs dispersed in polystyrene (PS) as described in the Exp. Sect. The λ_{max} and absorption coefficient α_{max} data of the thin films are given in Table 1. They show spectroscopic data similar to those obtained for the CHCl_3 solutions.

Quantitative data concerning the chain length L , defined as the distance between the terminal carbon atoms of the benzene rings, were obtained by X-ray structure investigation of **1a** and **1b**. The lengths L of **1c–e** were extrapolated by using the identical lengths of the repeat unit (0.681 nm) and of the phenyl end groups (0.271 nm) found for **1a** and **1b**.^[43]

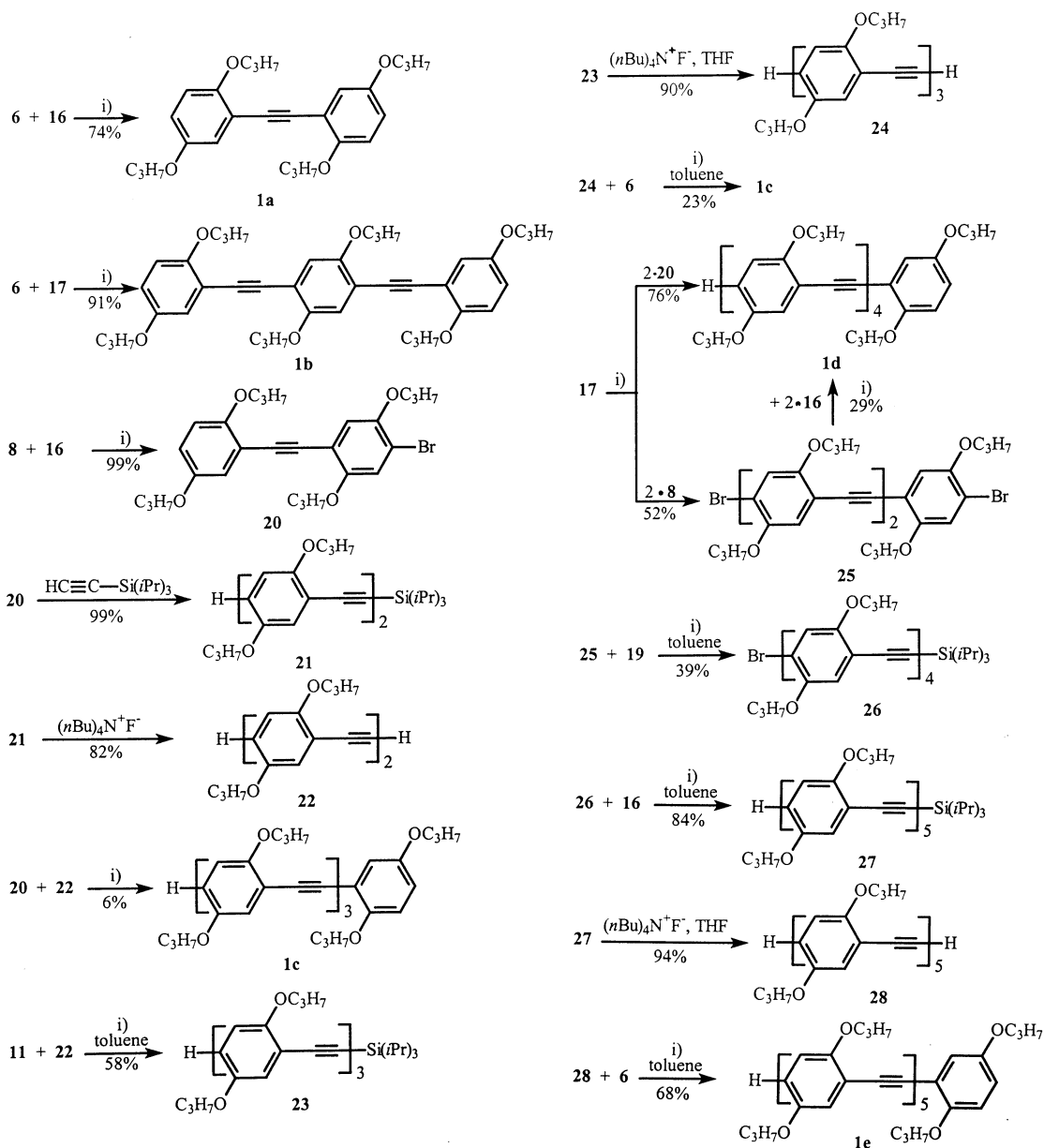
By using the method described in the Exp. Sect. for the THG (third harmonic generation) measurement, we evaluated modulus $|\chi^{(3)}|$ and phase angle ϕ of the macroscopic, complex third-order susceptibility $\chi^{(3)}(-3\omega; \omega, \omega, \omega) = |\chi^{(3)}| \exp(i\phi)$ of the films. Two points should be emphasized:

(i) the third-order susceptibility we have measured is the result of the contributions of the OPE oligomer and the PS matrix,

(ii) the $|\chi^{(3)}|$ values show strong spectral dependence on the laser frequency ω used, because of resonances with electronic states of the compounds; these occur if 3ω or 2ω match an electronic transition.^[44,45]

With this in mind, we conducted our THG experiments at the three-photon resonance condition with laser wavelengths $\lambda_L = 3\lambda_{\text{max}}$. This ensures sufficient detection sensitivity and comparable measurement conditions for the thin OPE films (**1a–e**). The results for modulus $|\chi_{\text{res}}^{(3)}|$ and phase angle ϕ are given in Table 1. Clearly the modulus of the third-order susceptibility increases with chain length L . The phase angle ϕ also increases on going from **1a** to **1c** and then stays constant – at around 90° .

We interpret these changes of ϕ in terms of different contributions of PS matrix and OPEs to the total sum of the complex $\chi^{(3)}$ value, which is the vector sum of $\chi_{\text{PS}}^{(3)}$ and $\chi_{\text{OPE}}^{(3)}$. Because our THG measurements were always performed at $\lambda_L = 3\lambda_{\text{max}}$ of the OPEs, the contribution $\chi_{\text{OPE}}^{(3)}$ is imaginary and $\phi_{\text{OPE}} = 90^\circ$, which is typically observed at the peak of the three-photon resonance.^[37,45] On the other hand, $\chi_{\text{PS}}^{(3)}$ is nonresonant and real because λ_L is much larger than $3\lambda_{\text{max}}$ of PS, which implies $\phi_{\text{PS}} = 0^\circ$. As the



Scheme 5. Preparation of the target compounds, the monodisperse oligo(2,5-dipropoxy-1,4-phenyleneethynylene)s **1a–e**: i) Pd^0 , CuI, piperidine

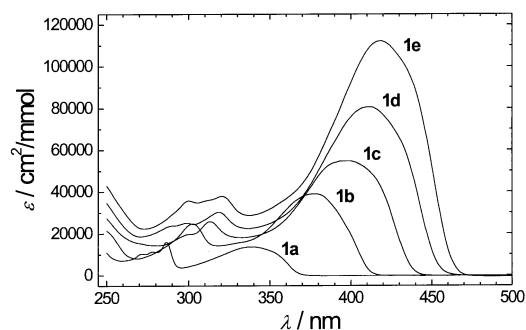


Figure 1. UV/Vis spectra of OPEs **1a–e** in CHCl_3

modulus $|\chi_{\text{OPE}}^{(3)}|$ increases strongly with chain length, the contribution of PS to the total sum of $|\chi_{\text{res}}^{(3)}|$ becomes negligible for the longer oligomers **1c–e** and the total phase angle φ approaches 90° .

In order to understand the influence of chain length on nonlinear optical properties, it is better to consider the second hyperpolarizability γ , which is a molecular parameter, instead of the macroscopic susceptibility $\chi^{(3)}$. In the cgs system of units, these quantities are related by Equation (1) where N is the number of oligomers per unit volume.^[44,45]

$$\chi^{(3)}(-3\omega; \omega, \omega, \omega) = N f(3\omega) [f(\omega)]^3 \gamma(-3\omega; \omega, \omega, \omega) \quad (1)$$

We have calculated N as in Equation (2) where N_A is the Avogadro constant, M_{OPE} and c_{OPE} are the molecular mass

Table 1. Linear and nonlinear optical properties of the oligomers **1a–e** in highly diluted solutions (CHCl_3) and in thin films of polystyrene (PS) with $(10.00 \pm 0.03)\%$ (mass) of OPE

Compound	1a	1b	1c	1d	1e
Repeat units n	1	2	3	4	5
Chain length L [nm]	0.952	1.633	2.314	2.995	3.676
Absorption in CHCl_3					
λ_{max} [nm] (± 1 nm)	338	378	399	412	419
ϵ_{max} [$\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$] ($\pm 3\%$)	15900	39000	54700	80600	112100
Absorption in PS films					
λ_{max} [nm] (± 3 nm)	335	377	394	410	417
α_{max} [10^4 cm^{-1}] ($\pm 3\%$)	0.923	1.220	1.481	1.781	2.115
THG of films					
$ \chi_{\text{res}}^{(3)} $ [10^{-13} esu]	2.05	4.82	7.96	12.1	13.4
	± 0.4	± 0.3	± 0.6	± 0.8	± 1.2
φ [$^\circ$] ($\pm 10^\circ$)	33	66	86	84	94
$ \gamma_{\text{res}} $ [10^{-32} esu]	0.134	0.81	2.04	3.93	5.47
	± 0.03	± 0.1	± 0.3	± 0.5	± 0.8

and the concentration by weight of the respective OPE compound, and ρ is the density of the film.

$$N = N_{\text{A}} \rho c_{\text{OPE}} / M_{\text{OPE}} \quad (2)$$

The dimensionless Lorentz local field factors $f(\omega)$ depend on the refractive index $n(\omega)$ and are given by^[44] Equation (3).

$$f(\omega) = [n^2(\omega) + 2]/3 \quad (3)$$

For the determination of $|\gamma_{\text{res}}|$, we used the imaginary part of the total third-order susceptibility $|\chi_{\text{res}}^{(3)}|$ of the film. The molecular hyperpolarizabilities $|\gamma_{\text{res}}|$ of the different OPEs **1a–e** are listed in the last row of Table 1 and their dependence on chain length L is plotted in Figure 2.

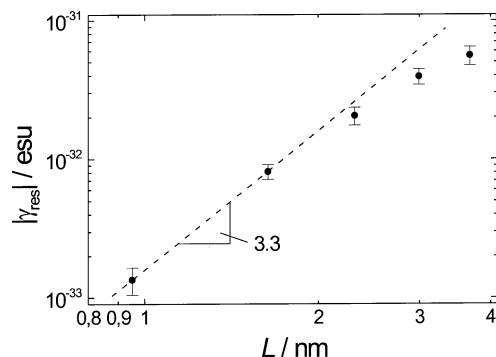


Figure 2. Double logarithmic plot of molecular hyperpolarizability $|\gamma_{\text{res}}|$ of OPEs **1a–e** versus chain length L ; the dashed line represents an increase from **1a** to **1b** according to a power law $|\gamma_{\text{res}}| \sim L^{3.3}$

The data show a superlinear increase of $|\gamma_{\text{res}}|$ with L , which has similarly been observed in the cases of other conjugated oligomers such as oligophenylenes,^[46] oligothiophenes,^[47,48] and oligo-*p*-phenylenevinyls.^[37,49] A comparison of the alkyne series **1** with the corresponding all-*trans*-alkene series **2** demonstrates that the $|\gamma_{\text{res}}|$ values in the series **1** are higher: **1d**, for example, has a $|\gamma_{\text{res}}|$ value of $3.93 \cdot 10^{-32}$ esu, whereas the corresponding conjugated oligophenylenevinylene **2** with $n = 4$ and 2,5-dipropoxy-substituted benzene rings has a $|\gamma_{\text{res}}|$ of $7.34 \cdot 10^{-33}$.^[49,50] The influ-

ence of the polystyrene matrix is negligible in both series for $n \geq 3$.

The superlinear increase of γ with L has attracted wide interest. Early theoretical investigations for very short conjugated oligomers ($L < 2$ nm) yielded a power law according to Equation (4) with an exponent μ in the order of 4 to 5, as summarized in a recent review.^[45]

$$\gamma \sim L^\mu \sim n^\mu \quad (4)$$

More refined calculations for longer chains revealed that μ is itself a function of chain length L or number of repeat units n .^[51–56] The function $\mu = \mu(n)$ describes the transition from the short chain limit ($\mu = 4–5$) to the limiting case of very long chains. In the latter case the π electrons of the entire chain are no longer correlated to each other. Individual chain segments respond independently to the external electric fields of the light wave. This situation is commonly called saturation of the polarizabilities and the critical length at which this occurs is termed the conjugation length.^[45,57]

The data for the OPEs reveal exponents $\mu_{1,2} = 3.3$ and $\mu_{4,5} = 1.6$, which refer to the changes of $|\gamma_{\text{res}}|$ from $n = 1$ to $n = 2$ and from $n = 4$ to $n = 5$, respectively. Obviously, the OPEs **1a–e** are excellent model systems with which to study conjugation effects in one-dimensional π -electron systems and, especially, to investigate the transition regime between the limiting cases of short chains and saturation.

Summary and Conclusions

Oligo(1,4-phenyleneethynylene)s **1a–e** have been prepared by a building block approach, by application of the Hagihara–Sonogashira reaction and selective deprotection of different trialkylsilyl protecting groups (Schemes 1–5).

Extension of the conjugation in the series of the oligomers **1a–e** causes a significant bathochromic shift of the long wavelength absorption; the λ_{max} values of the corresponding bands are shifted in chloroform from 338 nm for **1a** to 419 nm for **1e** and, dispersed in polystyrene, from 335 nm for **1a** to 417 nm for **1e**. These data differ significantly from other OPE series, which show convergence even at $\lambda_\infty = 387$ nm^[17] or at about 440 nm.^{[20][58]} As mentioned before, however, these series contain end groups such as nitro, dimethylamino, bromo, or trialkylsilyl, which interact with the π electrons of the conjugated chain. The absorption intensity increases with growing numbers n of repeat units; the average ϵ_{max}/n values of the solution spectra are $(19.2 \pm 3.3) \cdot 10^3 \text{ L}\cdot\text{mol}^{-1} \text{ cm}^{-1}$ for the series **1a–e**.

The THG measurements for the oligomers in polystyrene show an increase in the second hyperpolarizability $|\gamma_{\text{res}}|$ from $0.13 \cdot 10^{-32}$ esu for **1a** to $5.5 \cdot 10^{-32}$ for **1e**. The $|\gamma_{\text{res}}|$ values for the alkyne series **1** are significantly higher (by a factor of 5–7) than those for the all-*trans*-alkene series **2**.^[50] For a certain number n of repeat units, the length L of the oligomers is similar in both series; the conjugation effect $[E(n=1) - E(n \rightarrow \infty)]^{[22]}$ is somewhat greater in the alkene series. Interpretation of this result thus warrants further

study. A double logarithmic plot (Figure 2) of $|\gamma_{\text{res}}|$ versus the lengths L of the conjugated chains reveals a superlinear increase of $|\gamma_{\text{res}}|$ but its slope decreases with increasing L . However, saturation for large values of L is not yet discernible, which shows that the conjugation length of OPEs is much greater than 5 repeat units.

Experimental Section

General: Melting points were determined with a Büchi melting point apparatus and are uncorrected; IR spectra were obtained with a Beckman Acculab 4 or a Perkin–Elmer GX FT-IR spectrometer; ^1H and ^{13}C NMR spectra were recorded with a Bruker ARX 400 spectrometer in CDCl_3 (TMS as internal standard) and mass spectra with a Finnigan MAT 95 spectrometer; UV/Vis/NIR transmission spectra of solutions in CHCl_3 and reflection spectra of thin films (polystyrene matrix) were recorded with Perkin–Elmer Models 9 and 900 spectrophotometers at ambient temperature.

Preparations

1,4-Dipropoxybenzene (3): Hydroquinone (175.0 g, 1.59 mol) was dissolved in degassed ethanol (1.5 L). After addition of KOH (220.0 g, 3.92 mol), the solution was stirred under reflux for 20 min. 1-Bromopropane was added dropwise to the light brown solution over 40 min, followed by stirring under reflux for 2 h. Ethanol was then removed by distillation. The residue was dissolved in chloroform and extracted with water (3×200 mL). The combined organic phases were washed with saturated NaHCO_3 , dried with Na_2SO_4 , and concentrated. The remaining solid was recrystallized from methanol. Yield 263.6 g (85%) of colorless crystals; m.p. 49 °C. (ref.^[59]: m.p. 48 °C); ^1H NMR (CDCl_3): δ = 1.08 (t, 6 H, CH_3), 1.80 (m, 4 H, CH_2), 3.89 (t, 4 H, OCH_2), 6.68 (s, 4 H, 2-H); ^{13}C NMR (CDCl_3): δ = 10.5 (2 C, CH_3), 22.7 (2 C, CH_2), 70.1 (2 C, OCH_2), 115.4 (4 C, C-2), 153.2 (2 C_q , C-1); EI MS (70 eV): m/z (%) = 194 (17) [M^+], 152 (9) [$\text{M}^+ - \text{C}_3\text{H}_6$], 110 (100) [$\text{M}^+ - 2\text{C}_3\text{H}_6$], 81 (6), 43 (18); $\text{C}_{12}\text{H}_{18}\text{O}_2$ (194.3): calcd. C 74.18, H 9.34; found C 74.12, H 9.33.

1-Bromo-2,5-dipropoxybenzene (4): Compound 3 (65.5 g, 0.34 mol) and sodium acetate (26.7 g, 0.33 mol) were dissolved in acetic acid (200 mL). At 0 °C, bromine (53.9 g, 0.337 mol) was slowly added to the solution over 5 h. After stirring for 12 h at room temperature, the mixture was poured into water (1.5 L). After extraction with chloroform (5×150 mL), the organic phases were neutralized with saturated NaHCO_3 and dried with Na_2SO_4 . The solvent was evaporated and the remaining brown oil was distilled under vacuum. Yield 69.7 g (76%) of a colorless oil; ^1H NMR (CDCl_3): δ = 0.96/1.08 (2 t, 2×3 H, CH_3), 1.78 (m, 4 H, CH_2), 3.83/3.90 (2 t, 2×2 H, OCH_2), 6.77 (m, 2 H, 3-H, 4-H), 7.09 (d, 1 H, 6-H); ^{13}C NMR (CDCl_3): δ = 11.1/11.2 (2 C, CH_3), 23.1/23.1 (2 C, CH_2), 71.2/72.1 (2 C, OCH_2), 108.8 (1 C_q , C-1), 115.7/121.5/123.4 (3 C, C-3, C-4, C-6), 150.9/151.6 (2 C_q , C-2, C-5); EI MS (70 eV): m/z (%) = 274.1 (22) [M^+], 272.1 (23) [M^+], 232.0 (15) [$\text{M}^+ - \text{C}_3\text{H}_7$], 230.0 (15) [$\text{M}^+ - \text{C}_3\text{H}_7$], 190.1 (100) [$\text{M}^+ - 2\text{C}_3\text{H}_7$], 188.1 (95) [$\text{M}^+ - 2\text{C}_3\text{H}_7$], 43.5 (60) [C_3H_7^+]; IR (KCl): $\tilde{\nu}$ = 2980, 2930, 1590, 1565, 1485, 1455, 1380, 1260, 1205, 1060, 975, 795 cm^{-1} ; $\text{C}_{12}\text{H}_{17}\text{BrO}_2$ (273.0): calcd. C 52.76, H 6.27, Br 29.25; found C 53.01, H 6.31, Br 29.14.

1,4-Dibromo-2,5-dipropoxybenzene (5): Compound 3 (48.6 g, 0.25 mol) and sodium acetate (40.0 g, 0.49 mol) were dissolved in acetic acid (300 mL). Bromine (80.0 g, 0.50 mol) was added dropwise to

the solution over 3 h. After stirring for 12 h at room temperature, the mixture was poured into ice/water (500 mL). The water phase was extracted with chloroform (5×100 mL) and the organic phases were neutralized with saturated NaHCO_3 and dried with Na_2SO_4 . The solvent was evaporated and the residue was recrystallized from methanol. Yield: 75.4 g (86%) of colorless crystals, m.p. 73 °C; ^1H NMR (CDCl_3): δ = 1.04 (t, 6 H, CH_3), 1.79 (m, 4 H, CH_2), 3.90 (t, 4 H, OCH_2), 7.07 (s, 2 H, 3-H); ^{13}C NMR (CDCl_3): δ = 10.5 (2 C, CH_3), 22.6 (2 C, CH_2), 71.8 (2 C, OCH_2), 111.1 (2 C_q , C-1), 118.5 (2 C, C-3), 150.1 (2 C_q , C-2); EI MS (70 eV): m/z (%) = 354.3 (9) [M^+], 352.2 (20) [M^+], 350.1 (10) [M^+], 270.0 (45) [$\text{M}^+ - 2\text{C}_3\text{H}_7$], 268.0 (95) [$\text{M}^+ - 2\text{C}_3\text{H}_7$], 266.0 (47) [$\text{M}^+ - 2\text{C}_3\text{H}_7$], 43.4 (100) [C_3H_7^+]; IR (KCl): $\tilde{\nu}$ = 2970, 2930, 1495, 1455, 1360, 1270, 1215, 1070, 1020, 855, 815, 775 cm^{-1} ; $\text{C}_{12}\text{H}_{16}\text{Br}_2\text{O}_2$ (352.1): calcd. C 40.94, H 4.58, Br 45.39; found C 41.04, H 4.63, Br 45.18.

1-Iodo-2,5-dipropoxybenzene (6): Compound 3 (30.0 g, 0.15 mol) was dissolved in acetic acid (300 mL) and tetrachloromethane (20 mL). To this solution were added iodine (19.5 g, 0.08 mol), conc. sulfuric acid (6 mL), distilled water (25 mL), and finally potassium iodate (5.6 g, 0.026 mol). The mixture was stirred for 5 h at 80 °C and for 10 h at room temperature. To remove excess iodine, NaHSO_3 was added until the violet color of iodine disappeared. The mixture was poured into ice/water (1.5 L) and extracted with chloroform (5×300 mL). The organic phases were neutralized with saturated NaHCO_3 and dried with Na_2SO_4 . The solvent was evaporated and the residue was distilled under vacuum. Yield: 19.9 g (40%) of a colorless oil; ^1H NMR (CDCl_3): δ = 1.00/1.06 (2 t, 2×3 H, CH_3), 1.73 (m, 4 H, CH_2), 3.82/3.89 (2 t, 2×2 H, OCH_2), 6.70 (d, 1 H, 3-H), 6.82 (dd, 1 H, 4-H), 7.31 (d, 1 H, 6-H); ^{13}C NMR (CDCl_3): δ = 10.5/10.7 (2 C, CH_3), 22.6/22.7 (2 C, CH_2), 70.4/71.6 (2 C, OCH_2), 87.0 (1 C_q , C-1), 113.1/115.4 (2 C, C-3, C-4), 125.3 (1 C, C-6), 152.1/153.7 (2 C_q , C-2, C-5); FD MS: m/z (%) = 320 (100) [M^+]; IR (NaCl): $\tilde{\nu}$ = 2964, 2936, 2877, 1599, 1570, 1490, 1467, 1389, 1271, 1210, 1067, 1022, 981, 865, 801, 735 cm^{-1} ; $\text{C}_{12}\text{H}_{17}\text{O}_2\text{I}$ (320.2): calcd. C 45.02, H 5.35, I 39.64; found C 45.14, H 5.39, I 39.67.

1,4-Diiodo-2,5-dipropoxybenzene (7): Compound 3 (40.0 g, 0.21 mol) was dissolved in acetic acid (120 mL) and tetrachloromethane (30 mL). To this solution were added iodine (45.7 g, 0.18 mol), conc. sulfuric acid (14 mL), distilled water (7 mL), and finally potassium iodate (18.4 g, 0.086 mol). The mixture was stirred for 24 h under reflux. To remove excess iodine, NaHSO_3 was added until the violet color of iodine disappeared. The mixture was poured into ice/water (1.5 L) and extracted with chloroform (5×300 mL). The organic phases were neutralized with saturated NaHCO_3 and dried with Na_2SO_4 . After evaporation of the solvent, the residue was recrystallized from methanol. Yield: 75.0 g (82%) of colorless crystals, m.p. 85 °C; ^1H NMR (CDCl_3): δ = 1.05 (t, 6 H, CH_3), 1.57 (m, 4 H, CH_2), 3.88 (t, 4 H, OCH_2), 7.15 (s, 2 H, 3-H); ^{13}C NMR (CDCl_3): δ = 10.7 (2 C, CH_3), 22.6 (2 C, CH_2), 71.8 (2 C, OCH_2), 86.3 (2 C_q , C-1), 122.7 (2 C, C-3), 152.8 (2 C_q , C-2); FD MS: m/z (%) = 447.7 (14) [M^+], 446.7 (100) [M^+]; IR (KCl): $\tilde{\nu}$ = 2961, 2910, 2878, 1489, 1451, 1350, 1265, 1210, 1057, 1009, 852, 799, 770 cm^{-1} ; $\text{C}_{12}\text{H}_{16}\text{O}_2\text{I}_2$ (446.1): calcd. C 32.31, H 3.62, I 56.90; found C 32.34, H 3.51, I 57.29.

1-Bromo-4-iodo-2,5-dipropoxybenzene (8): Compound 4 (45.0 g, 0.17 mol) was dissolved in acetic acid (110 mL) and tetrachloromethane (27 mL). To this solution were added iodine (41.4 g, 0.16 mol), conc. sulfuric acid (14 mL), distilled water (7 mL), and finally potassium iodate (14.5 g, 0.07 mol). The mixture was stirred for 5 h under reflux. To remove excess iodine, NaHSO_3 was added until

the violet color of iodine disappeared. The mixture was poured into ice/water (1.0 L) and extracted with chloroform (5×100 mL). The organic phases were neutralized with saturated NaHCO_3 and dried with Na_2SO_4 . The solvent was evaporated and the residue was recrystallized from methanol. Yield: 50.8 g (77%) of colorless crystals, m.p. 73 °C; ^1H NMR (CDCl_3): δ = 1.04/1.05 (2 t, 2×3 H, CH_3), 1.77 (m, 4 H, CH_2), 3.88/3.89 (2 t, 2×2 H, OCH_2), 6.96 (s, 1 H, 6-H), 7.26 (s, 1 H, 3-H); ^{13}C NMR (CDCl_3): δ = 10.5/10.7 (2 C, CH_3), 22.5 (2 C, CH_2), 71.8/71.8 (2 C, OCH_2), 84.8 (1 C_q , C-4), 112.5 (1 C_q , C-1), 117.1 (1 C, C-6), 124.3 (1 C, C-3), 150.4 (1 C_q , C-2), 152.5 (1 C_q , C-5); FD MS: m/z (%) = 399.9 (100) [M^+], 397.9 (91) [M^+]; IR (KBr): $\tilde{\nu}$ = 2964, 2933, 2911, 2879, 1493, 1456, 1380, 1268, 1211, 911, 852, 804, 774 cm^{-1} ; $\text{C}_{12}\text{H}_{16}\text{BrIO}_2$ (399.1): calcd. C 36.12, H 4.04, Br 20.02, I 31.80; found C 36.30, H 4.13, Br 20.51, I 31.99.

2,5-Dipropoxy-1-trimethylsilyl ethynylbenzene (9). — **Preparation from 4:** Compound **4** (19.0 g, 0.059 mol) was dissolved in dry piperidine (150 mL) and the system was flushed with nitrogen. Bis(tetraphenylphosphane)palladium dichloride (1.2 g, 1.68 mmol), copper(I) iodide (0.65 g, 3.35 mmol), and triphenylphosphane (0.88 g, 3.35 mmol) were added to the mixture. Trimethylsilylacetylene (8.2 g, 0.083 mol) was added to the clear solution. After 6 d, the solvent was evaporated, chloroform was added to the residue, and the solution was extracted with saturated NH_4Cl and water. After having been washed with saturated NaHCO_3 , the organic phases were dried with Na_2SO_4 . Filtration through a short silica gel column produced a black oil, which was purified by vacuum distillation. Yield: 14.3 g (83%) of a colorless oil. — **Preparation from 6:** Compound **6** (22.4 g, 0.07 mol) was dissolved in dry piperidine (200 mL) and the system was flushed with nitrogen. Bis(tetraphenylphosphane)palladium dichloride (1.2 g, 1.68 mmol), copper(I) iodide (0.7 g, 3.5 mmol), and triphenylphosphane (0.9 g, 3.5 mmol) were added. The reaction time was 1.5 h. Purification was according to the procedure described above. Yield: 19.1 g (94%) of a colorless oil; n_D^{20} = 1.5109; ^1H NMR (CDCl_3): δ = 0.24 (s, 9 H, Si-CH_3), 0.99/1.06 (2 t, 2×3 H, CH_3), 1.75/1.84 (2 m, 2×2 H, CH_2), 3.83/3.89 (2 t, 2×2 H, OCH_2), 6.74 (d, 1 H, 3-H), 6.80 (dd, 1 H, 4-H), 6.94 (d, 1 H, 6-H); ^{13}C NMR (CDCl_3): δ = 0.01 (3 C, Si-CH_3), 10.5/10.6 (2 C, CH_3), 22.6/22.8 (2 C, CH_2), 70.2/71.2 (2 C, OCH_2), 98.2 (1 C, Si-C), 101.4 (1 C, Ar-C), 113.5 (1 C_q , C-1), 114.2 (1 C, C-3), 117.0 (1 C, C-4), 118.7 (1 C, C-6), 152.7/154.7 (2 C_q , C-2, C-5); FD MS: m/z (%) = 289.9 (100) [M^+], 291.0 (21) [M^+], 292.0 (5) [M^+]; IR (KBr): $\tilde{\nu}$ = 2964, 2879, 2156, 1498, 1469, 1389, 1274, 1228, 1171, 1130, 1068, 857, 800 cm^{-1} ; $\text{C}_{17}\text{H}_{26}\text{O}_2\text{Si}$ (290.5): calcd. C 70.29, H 9.02; found C 70.68, H 8.90.

2,5-Dipropoxy-1,4-bis(trimethylsilyl ethynyl)benzene (10). — **Preparation from 5:** Compound **5** (20.0 g, 0.057 mol) was dissolved in dry piperidine (150 mL) and the system was flushed with nitrogen. Bis(tetraphenylphosphane)palladium dichloride (2.0 g, 2.85 mmol), copper(I) iodide (1.1 g, 5.7 mmol), and triphenylphosphane (1.5 g, 5.7 mmol) were added. Trimethylsilylacetylene (14.0 g, 0.143 mol) was added to this clear solution. The mixture was stirred for 3 h at 50 °C. The solvent was then evaporated, and chloroform was added to the residue and extracted with saturated NH_4Cl and water. After having been washed with saturated NaHCO_3 , the organic phases were dried with Na_2SO_4 . The crude product was purified by chromatography (toluene/*n*-hexane, 1:1). Yield: 19.0 g (86%) of colorless crystals, m.p. 101 °C. — **Preparation from 7:** Compound **7** (2.0 g, 4.5 mmol) was dissolved in dry piperidine (20 mL) and the system was flushed with nitrogen. Bis(tetraphenylphosphane)palladium dichloride (0.24 g, 0.55 mmol), copper(I) iodide (0.12 g, 0.63 mmol), triphenylphosphane (0.24 g, 0.91 mmol), and trime-

thylsilylacetylene (1.0 g, 9.9 mmol) were added. The mixture was stirred for 18 h and purified as described above. Yield: 1.7 g (98%) of colorless crystals, m.p. 101 °C; ^1H NMR (CDCl_3): δ = 0.23 (s, 18 H, Si-CH_3), 1.04 (t, 6 H, CH_3), 1.79 (m, 4 H, CH_2), 3.89 (t, 4 H, OCH_2), 6.88 (s, 2 H, 3-H); ^{13}C NMR (CDCl_3): δ = 0.1 (6 C, Si-CH_3), 10.5 (2 C, CH_3), 22.7 (2 C, CH_2), 71.0 (2 C, OCH_2), 100.1 (2 C, $\equiv\text{C-Si}$), 101.0 (2 C, $\text{Ar-C}\equiv$), 114.0 (2 C_q , C-1), 117.3 (2 C, C-3), 154.0 (2 C_q , C-2); FD MS: m/z (%) = 386.4 (100) [M^+], 387.4 (23) [M^+]; IR (KBr): $\tilde{\nu}$ = 2963, 2913, 2875, 2156, 1504, 1390, 1275, 1246, 1225, 1041, 1023, 899, 838, 759 cm^{-1} ; $\text{C}_{22}\text{H}_{34}\text{O}_2\text{Si}_2$ (386.7): calcd. C 68.34, H 8.86; found C 68.44, H 8.91.

1-Iodo-2,5-dipropoxy-4-triisopropylsilyl ethynylbenzene (11): Compound **7** (50.0 g, 0.112 mol) and triisopropylsilylacetylene (13.6 g, 0.075 mol) were dissolved in dry piperidine (150 mL) and the system was flushed with nitrogen. Bis(tetraphenylphosphane)palladium dichloride (2.0 g, 2.85 mmol), copper(I) iodide (0.6 g, 3.15 mmol), and triphenylphosphane (0.8 g, 3.15 mmol) were added. After 12 h stirring at room temperature, the solvent was evaporated and chloroform was added to the residue. After extraction with saturated NH_4Cl , water, and saturated NaHCO_3 , the organic phase was dried with Na_2SO_4 and the chloroform was then removed by distillation. The slightly brown crystals were recrystallized from *n*-hexane (200 mL). The product was dissolved in diethyl ether (60 mL) and mixed with ethanol (150 mL). Fractional crystallization produced a main fraction that was purified by chromatography on silica gel (*n*-hexane/ CH_2Cl_2 , 5:1). Yield: 25.4 g (68%) of colorless crystals, m.p. 63 °C; ^1H NMR (CDCl_3): δ = 1.08 (m, 27 H, CH_3 , Si-C-H , Si-C-CH_3), 1.79 (m, 4 H, CH_2), 3.88 (m, 4 H, OCH_2), 6.82 (s, 1 H, 3-H), 7.22 (s, 1 H, 6-H); ^{13}C NMR (CDCl_3): δ = 10.6/10.8 (2 C, CH_3), 11.4 (3 C, Si-CH), 18.7 (6 C, Si-C-CH_3), 22.7 (2 C, CH_2), 71.1/71.7 (2 C, OCH_2), 87.6 (1 C_q , C-1), 95.8/102.6 (2 C, $\text{Ar-C}\equiv\text{C-Si}$), 113.8 (1 C_q , C-4), 116.7 (1 C, C-3), 123.5 (1 C, C-6), 151.6 (1 C_q , C-2), 155.1 (1 C, C-5); FD MS: m/z (%) = 501.8 (18) [M^+], 500.7 (100) [M^+]; IR (KBr): $\tilde{\nu}$ = 2962, 2942, 2866, 2157, 1500, 1489, 1468, 1372, 1266, 1213, 1065, 1044, 1020, 883, 854, 831, 799, 769, 677 cm^{-1} ; $\text{C}_{23}\text{H}_{37}\text{IO}_2\text{Si}$ (500.5): calcd. C 55.19, H 7.45; found C 55.02, H 7.43.

2,5-Dipropoxy-1,4-bis(triisopropylsilyl ethynyl)benzene (12): Compound **7** (5.0 g, 11.2 mmol), bis(tetraphenylphosphane)palladium dichloride (0.4 g, 0.57 mmol), copper(I) iodide (0.21 g, 1.1 mmol), triphenylphosphane (0.3 g, 1.1 mmol), and triisopropylsilylacetylene (4.8 g, 0.026 mol) were dissolved in dry piperidine (80 mL) and the system was flushed with nitrogen. After the mixture had been stirred for 3 d, the solvent was evaporated and chloroform was added to the residue. The organic phase was extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . The crude product was added to boiling methanol and filtered. The filter residue was recrystallized from 650 mL of ethanol. Yield: 5.5 g (93%) of colorless crystals, m.p. 164 °C; ^1H NMR (CDCl_3): δ = 1.02 (t, 6 H, CH_3), 1.12 (s, 21 H, Si-C-H , Si-C-CH_3), 1.78 (m, 4 H, CH_2), 3.89 (t, 4 H, OCH_2), 6.85 (s, 2 H, 3-H); ^{13}C NMR (CDCl_3): δ = 10.6 (2 C, CH_3), 11.4 (6 C, Si-C-H), 18.7 (12 C, Si-C-CH_3), 22.7 (2 C, CH_2), 71.1 (2 C, OCH_2), 96.3/103.2 (4 C, $\text{C}\equiv\text{C}$), 114.3 (2 C_q , C-1), 117.5 (2 C, C-3), 154.2 (2 C_q , C-2); EI MS (70 eV): m/z (%) = 555.4 (48) [M^+], 554.5 (100) [M^+], 512.1 (15) [$\text{M}^+ - \text{C}_3\text{H}_7$], 511.2 (33) [$\text{M}^+ - \text{C}_3\text{H}_7$], 469.9 (8) [$\text{M}^+ - 2\text{C}_3\text{H}_7$], 468.8 (16) [$\text{M}^+ - 2\text{C}_3\text{H}_7$], 43.5 (35) [C_3H_7^+]; IR (KBr): $\tilde{\nu}$ = 2944, 2866, 2153, 1500, 1473, 1390, 1222, 1202, 1095, 887, 860, 798 cm^{-1} ; $\text{C}_{34}\text{H}_{58}\text{O}_2\text{Si}_2$ (554.4): calcd. C 73.58, H 10.53; found C 73.48, H 10.47.

1-Bromo-2,5-dipropoxy-4-trimethylsilyl ethynylbenzene (13): Compound **8** (20.0 g, 0.05 mol) and a catalyst mixture of bis(tetraphen-

ylphosphane)palladium dichloride (0.9 g, 1.25 mmol), copper(I) iodide (0.5 g, 2.5 mmol), and triphenylphosphane (0.7 g, 2.5 mmol) was dissolved in dry piperidine (200 mL) and the system was flushed with nitrogen. Trimethylsilylacetylene (5.4 g, 0.055 mol) was added to the slightly brown solution in small fractions. After the solution had stirred for 2.5 h, the solvent was evaporated and chloroform was added to the oily residue. The organic phase was extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . Filtration through a short silica gel column produced a solid, which was recrystallized from 80 mL of methanol. Yield: 17.8 g (96%), m.p. 59 °C; ^1H NMR (CDCl_3): δ = 0.23 (s, 9 H, Si-CH₃), 1.04/1.05 (2 t, 2 $\times$ 3 H, CH₃), 1.80 (m, 4 H, CH₂), 3.89/3.90 (2 t, 2 $\times$ 2 H, OCH₂), 6.93 (s, 1 H, 3-H), 7.03 (s, 1 H, 6-H); ^{13}C NMR (CDCl_3): δ = 0.1 (3 C, Si-CH₃), 10.5/10.5 (2 C, CH₃), 22.6/22.6 (2 C, CH₂), 71.3/71.6 (2 C, OCH₂), 99.3 (1 C, $\equiv\text{C-Si}$), 100.6 (1 C, Ar-C $\equiv$), 112.5/113.6 (2 C_q, C-1, C-4), 118.0/118.2 (2 C, C-3, C-6), 149.3 (1 C_q, C-2), 154.7 (1 C_q, C-5); FD MS: m/z (%) = 370.4 (100) [M^+], 368.5 (99) [M^+]; IR (KBr): $\tilde{\nu}$ = 2961, 2932, 2878, 2157, 1502, 1492, 1470, 1462, 1381, 1248, 1217, 1065, 1019, 883, 859, 840, 760, 679 cm^{-1} ; $\text{C}_{17}\text{H}_{25}\text{BrO}_2\text{Si}$ (369.2): calcd. C 55.28, H 6.82, Br 21.63; found C 55.38, H 6.62, Br 21.41.

1-Bromo-2,5-dipropoxy-4-triisopropylsilylethynylbenzene (14): Compound **8** (24.7 g, 0.062 mol) and a catalyst mixture of bis(tetraphenylphosphane)palladium dichloride (1.1 g, 1.55 mmol), copper(I) iodide (0.6 g, 3.1 mmol), and triphenylphosphane (0.8 g, 3.1 mmol) were dissolved in dry piperidine (300 mL), and the system was flushed with nitrogen. Triisopropylsilylacetylene (11.6 g, 0.064 mol) was added to the clear solution in small portions. After the solution had stirred for 12 h, the solvent was evaporated and chloroform was added to the residue. The organic phase was extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . Filtration through a short silica gel column produced a solid, which was recrystallized from 70 mL of 2-propanol. Yield: 24.0 g (85%), m.p. 71 °C; ^1H NMR (CDCl_3): δ = 1.02/1.04 (2 t, 2 $\times$ 3 H, CH₃), 1.12 (s, 21 H, Si-C-H, Si-C-CH₃), 1.80 (m, 4 H, CH₂), 3.87/3.91 (2 t, 2 $\times$ 2 H, OCH₂), 6.93 (s, 1 H, 3-H), 7.02 (s, 1 H, 6-H); ^{13}C NMR (CDCl_3): δ = 10.5 (2 C, CH₃), 11.4 (3 C, Si-CH), 18.7 (6 C, Si-C-CH₃), 22.6 (2 C, CH₂), 71.1/71.8 (2 C, OCH₂), 95.6/102.5 (2 C, Ar-C $\equiv$ C-Si), 113.0/113.5 (2 C_q, C-1, C-4), 117.8/118.6 (2 C, C-3, C-6), 149.3 (1 C_q, C-2), 155.0 (1 C_q, C-5); FD MS: m/z (%) = 455.4 (27) [M^+], 454.4 (100) [M^+], 453.4 (26) [M^+], 452.4 (88) [M^+]; IR (KBr): $\tilde{\nu}$ = 2985, 2943, 2865, 2158, 1502, 1470, 1460, 1382, 1270, 1215, 1045, 1021, 883, 855, 839, 768, 679 cm^{-1} ; $\text{C}_{23}\text{H}_{37}\text{BrO}_2\text{Si}$ (453.2): calcd. C 60.91, H 8.22; found C 60.94, H 8.23.

2,5-Dipropoxy-1-triisopropylsilylethynyl-4-trimethylsilylethynylbenzene (15). – **Preparation from 13:** Compound **13** (12.0 g, 32.5 mmol), bis(tetraphenylphosphane)palladium dichloride (0.6 g, 0.83 mmol), copper(I) iodide (0.32 g, 0.17 mmol), triphenylphosphane (0.43 g, 0.17 mmol), and triisopropylsilylacetylene (6.5 g, 37.5 mmol) were dissolved in dry piperidine (230 mL), and the system was flushed with nitrogen. After the solution had stirred for 3 d, the solvent was evaporated and chloroform was added to the residue. The organic phase was extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . Filtration through a short silica gel column produced a brown solid, which was recrystallized from 100 mL of methanol. Yield: 13.0 g (82%) of yellow crystals. – **Preparation from 14:** Compound **14** (24.0 g, 53.0 mmol), bis(tetraphenylphosphane)palladium dichloride (0.95 g, 1.35 mmol), copper(I) iodide (0.5 g, 2.67 mmol), triphenylphosphane (0.7 g, 2.67 mmol), and trimethylsilylacetylene (5.9 g, 60.0 mmol) were dissolved in dry piperidine (350 mL), and the system was flushed with nitrogen.

After the solution had stirred for 12 h, the solvent was evaporated and chloroform was added to the residue. The organic phase was extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . Filtration through a short silica gel column produced a brown solid that was recrystallized from 170 mL of methanol. Yield: 21.0 g (84%) of yellow crystals, m.p. 85 °C; ^1H NMR (CDCl_3): δ = 0.23 (s, 9 H, Si-CH₃), 1.01/1.04 (2 t, 2 $\times$ 3 H, CH₃), 1.11 (s, 21 H, Si-CH, Si-CH-CH₃), 1.78 (m, 4 H, CH₂), 3.87/3.90 (2 t, 2 $\times$ 2 H, OCH₂), 6.86/6.86 (2 s, 2 $\times$ 1 H, 3-H, 6-H); ^{13}C NMR (CDCl_3): δ = -0.04 (3 C, Si-CH₃), 10.5/10.6 (2 C, CH₃), 11.4 (3 C, Si-CH), 18.7 (6 C, Si-CH-CH₃), 22.7/22.7 (2 C, CH₂), 70.9/71.2 (2 C, OCH₂), 96.5/99.8/101.2/102.9 (4 C, C $\equiv$ C), 114.0/114.4 (2 C_q, C-1, C-4), 116.9/117.9 (2 C, C-3, C-6), 154.0/154.2 (2 C_q, C-2, C-5); FD MS: m/z (%) = 472.4 (16) [M^+], 471.5 (42) [M^+], 470.5 (100) [M^+]; IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2964, 2947, 2866, 2154, 1500, 1473, 1389, 1224, 1203, 1045, 1025, 893, 858, 842; $\text{C}_{28}\text{H}_{46}\text{O}_2\text{Si}_2$ (470.9): calcd. C 71.43, H 9.85; found C 71.38, H 9.85.

1-Ethynyl-2,5-dipropoxybenzene (16): Compound **9** (15.0 g, 0.05 mol) was stirred in a mixture of methanol (300 mL) and sodium hydroxide (10.5 mL, c = 5 mol/L) at room temperature for 48 h. After evaporation of the solvent, the residue was dissolved in chloroform and extracted with water and saturated NaHCO_3 . Drying with Na_2SO_4 , filtration, and removal of the solvent provided pure product without further purification. Yield: 11.1 g (98%) of a slightly yellow oil; ^1H NMR (CDCl_3): δ = 0.99/1.02 (2 t, 2 $\times$ 3 H, CH₃), 1.80 (m, 4 H, CH₂), 3.23 (s, 1 H, $\equiv\text{C-H}$), 3.83, 3.93 (2 t, 2 $\times$ 2 H, OCH₂), 6.77 (d, 1 H, 3-H), 6.82 (dd, 1 H, 4-H), 6.97 (d, 1 H, 6-H); ^{13}C NMR (CDCl_3): δ = 10.4 (2 C, CH₃), 22.6 (2 C, CH₂), 70.2/71.1 (2 C, OCH₂), 80.1 (1 C, $\equiv\text{C-H}$), 80.8 (1 C, Ar-C $\equiv$), 112.3 (1 C, C_q-1), 113.9 (1 C, C-3), 117.0 (1 C, C-4), 119.3 (1 C, C-6), 152.6/154.6 (2 C, C-2, C-5); FD MS: m/z (%) = 217.9 (100) [M^+], 218.9 (13) [M^+]; IR (KBr): $\tilde{\nu}$ = 3290, 2965, 2938, 2878, 1605, 1577, 1497, 1470, 1390, 1274, 1227, 1164, 1067, 1023, 981, 804 cm^{-1} ; $\text{C}_{14}\text{H}_{18}\text{O}_2$ (218.3): calcd. C 77.03, H 8.31; found C 77.09, H 8.30.

1,4-Diethynyl-2,5-dipropoxybenzene (17). – **Preparation from 10:** Compound **10** (26.2 g, 0.068 mol) was dissolved in THF (100 mL), and a mixture of methanol (100 mL) and sodium hydroxide (31 mL, c = 5 mol/L) was added. After 5 min, the solvents were evaporated and the residue was washed several times with *n*-hexane. Yield: 16.4 g (98%) of beige crystals. – **Preparation from 11:** Compound **11** (6.2 g, 0.01 mol) was added to a mixture of THF (150 mL) and water (5 mL). Tetrabutylammonium fluoride (2.0 g, 0.013 mol) was added to the solution. After the mixture had been concentrated to 20% of its original volume, the residue was dissolved in chloroform and extracted with water. The organic phase was dried with Na_2SO_4 and filtered. The obtained oil was stirred in *n*-hexane until crystallization of the solid was complete. Yield: 19.98 g (73%) of beige crystals, m.p. 122 °C; ^1H NMR (CDCl_3): δ = 1.02 (t, 6 H, CH₃), 1.80 (m, 4 H, CH₂), 3.32 (s, 2 H, C-H), 3.91 (t, 4 H, OCH₂), 6.93 (s, 2 H, 3-H); ^{13}C NMR (CDCl_3): δ = 10.4 (2 C, CH₃), 22.5 (2 C, CH₂), 71.1 (2 C, OCH₂), 79.8 (2 C, Ar-C $\equiv$), 82.5 (2 C, $\equiv\text{C-H}$), 113.3 (2 C_q, C-1), 117.8 (2 C, C-3), 154.0 (2 C_q, C-2); EI MS (70 eV): m/z (%) = 243.3 (13) [M^+], 242.3 (75) [M^+], 158.2 (100) [$\text{M}^+ - 2\text{C}_3\text{H}_7$]; IR (KBr): $\tilde{\nu}$ = 3270, 2958, 2912, 2878, 1501, 1469, 1392, 1223, 1099, 1040, 1021, 863, 799 cm^{-1} ; $\text{C}_{16}\text{H}_{18}\text{O}_2$ (242.3): calcd. C 79.31, H 7.49; found C 79.20, H 7.38.

1-Bromo-4-ethynyl-2,5-dipropoxybenzene (18): Compound **13** (12.8 g, 0.035 mol) was dissolved in methanol (350 mL) and sodium hydroxide (7.2 mL, c = 5 mol/L). After the solution had stirred for 20 h, the solvent was evaporated and the residue was dissolved in chloroform. Extraction with water and saturated NaHCO_3 pro-

vided, after drying and filtration, a black solid. Recrystallization from methanol and afterwards from *n*-hexane produced the pure product. Yield: 8.2 g (80%) of yellow crystals, m.p. 86 °C; ^1H NMR (CDCl_3): δ = 1.02/1.03 (2 t, 2×3 H, CH_3), 1.80 (m, 4 H, CH_2), 3.28 (s, 1 H, $\text{C}\equiv\text{C}-\text{H}$), 3.90/3.91 (2 t, 2×2 H, OCH_2), 6.95 (s, 1 H, 3-H), 7.06 (s, 1 H, 6-H); ^{13}C NMR (CDCl_3): δ = 10.4/10.5 (2 C, CH_3), 22.5/22.6 (2 C, CH_2), 71.3/71.6 (2 C, OCH_2), 79.5 (1 C, $\text{Ar}-\text{C}\equiv$), 81.6 (1 C, $\equiv\text{C}-\text{H}$), 111.3/114.0 (2 C_q , C-1, C-4), 118.0/118.4 (2 C, C-3, C-6), 149.3 (1 C_q , C-2), 154.7 (1 C_q , C-5); FD MS: m/z (%) = 298.8 (13) [M^+], 297.8 (99) [M^+], 296.8 (15) [M^+], 295.8 (100) [M^+]; IR (KBr): $\tilde{\nu}$ = 3279, 2958, 2911, 2878, 1491, 1460, 1381, 1218, 1040, 1020, 860, 831, 771 cm^{-1} ; $\text{C}_{14}\text{H}_{17}\text{BrO}_2$ (297.2): calcd. C 56.58, H 5.77, Br 26.89; found C 56.57, H 5.83, Br 26.58.

1-Ethynyl-2,5-dipropoxy-4-triisopropylsilylphenylbenzene (19):

Compound **15** (25 g, 0.053 mol) was dissolved in a mixture of THF (100 mL) and methanol (100 mL), and potassium carbonate (7.3 g, 0.053 mol) was added. After 1 h, the solvent was evaporated and the residue was dissolved in chloroform. The organic phase was extracted with water, dried with Na_2SO_4 , and filtered, and finally the solvent was removed. The obtained oil was recrystallized from methanol. Yield: 13.7 g (65%) of yellow crystals, m.p. 92 °C; ^1H NMR (CDCl_3): δ = 1.01/1.03 (2 t, 2×3 H, CH_3), 1.12 (s, 21 H, $\text{Si}-\text{CH}_3$, $\text{Si}-\text{CH}-\text{CH}_3$), 1.80 (m, 4 H, CH_2), 3.30 (s, 1 H, $\text{C}\equiv\text{C}-\text{H}$), 3.88/3.93 (2 t, 2×2 H, OCH_2), 6.89 (s, 2 H, 3-H, 6-H); ^{13}C NMR (CDCl_3): δ = 10.5/10.6 (2 C, CH_3), 11.4 (3 C, $\text{Si}-\text{CH}$), 18.7 (6 C, $\text{Si}-\text{CH}-\text{CH}_3$), 22.6/22.6 (2 C, CH_2), 70.9/71.2 (2 C, OCH_2), 80.1 (1 C, $\text{Ar}-\text{C}\equiv$), 82.1 (1 C, $\equiv\text{C}-\text{H}$), 96.7/102.7 (2 C, $\text{Ar}-\text{C}\equiv\text{C}-\text{Si}$), 112.7/114.8 (2 C_q , C-1, C-4), 117.4/117.7 (2 C, C-3, C-6), 154.0/154.2 (2 C_q , C-2, C-5); FD MS: m/z (%) = 400.5 (5) [M^+], 399.4 (23) [M^+], 398.4 (100) [M^+]; IR (KBr): $\tilde{\nu}$ = 3290, 2959, 2943, 2866, 2150, 2063, 1500, 1473, 1390, 1219, 1045, 1022, 875, 856 cm^{-1} ; $\text{C}_{25}\text{H}_{38}\text{O}_2\text{Si}$ (398.7): calcd. C 75.32, H 9.61; found C 75.27, H 9.71.

1-Bromo-2,5-dipropoxy-4-(2,5-dipropoxyphenylethynyl)benzene (20):

Compounds **8** (22.7 g, 57.0 mmol) and **16** (12.0 g, 55.0 mmol) were dissolved in dry piperidine (300 mL) and the system was flushed with nitrogen. The catalyst mixture of bis(tetraphenylphosphane)palladium dichloride (0.97 g, 1.38 mmol), copper(I) iodide (0.52 g, 2.75 mmol), and triphenylphosphane (0.72 g, 2.75 mmol) was then added. The reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated and the residue was dissolved in chloroform. The organic phase was extracted with saturated NH_4Cl , water, and saturated NaHCO_3 , then dried with Na_2SO_4 and filtered. The solvent was evaporated. The crude product was purified by chromatography on silica gel (toluene). Yield: 26.5 g (99%) of yellow crystals, m.p. 52 °C; ^1H NMR (CDCl_3): δ = 1.05 (m, 12 H, CH_3), 1.80 (m, 8 H, CH_2), 3.90 (m, 8 H, OCH_2), 6.80 (dd, 2 H, 3'-H, 4'-H), 7.02 (d, 2 H, 6-H, 6'-H), 7.08 (s, 1 H, 3-H); ^{13}C NMR (CDCl_3): δ = 10.5/10.5/10.6 (4 C, CH_3), 22.6/22.7/22.8 (4 C, CH_2), 70.2/71.4/71.5/71.5 (4 C, OCH_2), 89.2/90.7 (2 C, $\text{C}\equiv\text{C}$), 113.0/113.3/113.9 (3 C_q), 114.4/116.6/118.0/118.4/118.7 (5 CH), 149.5 (1 C_q , C-2), 152.9/154.0/154.0 (3 C_q); FD MS: m/z (%) = 490.7 (98) [M^+], 488.7 (100) [M^+]; IR (KBr): $\tilde{\nu}$ = 2961, 2936, 2904, 2877, 1604, 1505, 1464, 1426, 1379, 1272, 1209, 1067, 1027, 981, 858, 810, 769, 738 cm^{-1} ; $\text{C}_{26}\text{H}_{33}\text{BrO}_4$ (489.5): calcd. C 63.80, H 6.80, Br 16.33; found C 63.95, H 6.78, Br 15.99.

1-(2,5-Dipropoxyphenylethynyl)-2,5-dipropoxy-4-triisopropylsilylphenylbenzene (21):

Compound **20** (9.2 g, 0.019 mol) was dissolved in toluene (20 mL) and piperidine (10 mL) and the system was flushed with nitrogen. Bis(tetraphenylphosphane)palladium dichloride (0.3 g, 0.48 mmol), copper(I) iodide (0.2 g, 0.95 mmol), triphenylphosphane (0.25 g, 0.95 mmol), and triisopropylsilyl-

tylene (6.9 g, 0.038 mol) were added to the mixture. After 20 h, CH_2Cl_2 (200 mL) was added and the solution was extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . Recrystallization from methanol gave the pure product. Yield: 10.5 g (99%) of yellow crystals, m.p. 70 °C; ^1H NMR (CDCl_3): δ = 1.02 (m, 12 H, CH_3), 1.12 (s, 21 H, $\text{Si}-\text{CH}_3$, $\text{Si}-\text{C}-\text{CH}_3$), 1.81 (m, 8 H, CH_2), 3.91 (m, 8 H, OCH_2), 6.80 (d, 2 H), 7.02 (d, 2 H), 7.01 (s, 1 H); ^{13}C NMR (CDCl_3): δ = 10.5/10.6 (4 C, CH_3), 11.4 (3 C, $\text{Si}-\text{CH}$), 18.7 (6 C, $\text{Si}-\text{C}-\text{CH}_3$), 22.8/22.8/22.9 (4 C, CH_2), 70.7/71.4/72.0 (4 C, OCH_2), 90.4/91.9/96.8/103.8 (4 C, $\text{C}\equiv\text{C}$), 114.7/114.9/115.6 (3 C_q), 115.3/117.4/117.8/119.0/119.4 (5 C), 153.9/154.2/155.0/155.3 (4 C_q); FD MS: m/z (%) = 593.3 (11) [M^+], 592.3 (36) [M^+], 591.3 (100) [M^+]; IR (KBr): $\tilde{\nu}$ = 2964, 2942, 2865, 2152, 2064, 1498, 1468, 1390, 1220, 1024, 882, 859, 792, 770 cm^{-1} ; $\text{C}_{37}\text{H}_{54}\text{O}_4\text{Si}$ (590.9): calcd. C 75.21, H 9.21; found C 75.38, H 9.13.

1-(2,5-Dipropoxyphenylethynyl)-4-ethynyl-2,5-dipropoxybenzene (22):

Compound **21** (10.0 g, 0.017 mol) was dissolved in THF (50 mL), and tetrabutylammonium fluoride (7.9 g, 0.025 mol) was added. After 10 h, the solvent was evaporated and the residue was dissolved in chloroform. Subsequent extraction with water and saturated NaHCO_3 gave a brown residue, which was purified by chromatography on silica gel (toluene). Yield: 6.0 g (82%) of yellow crystals, m.p. 56 °C; ^1H NMR (CDCl_3): δ = 1.03 (m, 12 H, CH_3), 1.79 (m, 8 H, CH_2), 3.32 (s, 1 H, $\text{C}\equiv\text{C}-\text{H}$), 3.92 (m, 8 H, OCH_2), 6.81 (m, 2 H), 6.97 (d, 2 H), 7.01 (m, 1 H); ^{13}C NMR (CDCl_3): δ = 10.4/10.5/10.6/10.6 (4 C, CH_3), 22.6/22.6/22.7/22.8 (4 C, CH_2), 70.2/71.1/71.3/71.4 (4 C, OCH_2), 80.1 (1 C, $\text{Ar}-\text{C}\equiv$), 82.1 (1 C, $\equiv\text{C}-\text{H}$), 89.5/91.6 (2 C, $\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}$), 112.4/113.9/115.4 (3 C_q), 116.7 (1 C), 117.2 (1 C, C-3), 118.2 (1 C, C-6), 118.7 (1 C), 152.9/153.3/154.0/154.1 (4 C_q); FD MS: m/z (%) = 436.0 (26) [M^+], 435.0 (100) [M^+], 217.7 (1) [M^{2+}]; IR (KBr): $\tilde{\nu}$ = 3265, 2962, 2935, 2877, 1505, 1473, 1426, 1383, 1271, 1236, 1203, 1132, 1065, 1044, 1024, 983, 859, 811, 769, 713 cm^{-1} ; $\text{C}_{28}\text{H}_{34}\text{O}_4$ (434.6): calcd. C 77.39, H 7.89; found C 77.11, H 7.73.

4-(2,5-Dipropoxyphenylethynyl)-1-[2,5-dipropoxy-4-(triisopropylsilylphenylethynyl)phenylethynyl]-2,5-dipropoxybenzene (23):

Compounds **11** (7.7 g, 15.2 mmol) and **22** (6.0 g, 13.8 mmol) were dissolved in toluene (30 mL) and piperidine (10 mL) and the system was flushed with nitrogen. A catalyst mixture of bis(tetraphenylphosphane)palladium dichloride (0.25 g, 0.35 mmol), copper(I) iodide (0.13 g, 0.70 mmol), and triphenylphosphane (0.18 g, 0.70 mmol) was added. The reaction was finished within 5 min, while the temperature increased to 34 °C. Addition of 100 mL of CH_2Cl_2 was followed by extraction with saturated NH_4Cl , water, and saturated NaHCO_3 . The crude product obtained was purified by chromatography on silica gel, firstly with toluene and secondly with toluene/cyclohexane (1:1). Yield: 6.6 g (58%) of yellow crystals, m.p. 77 °C; ^1H NMR (CDCl_3): δ = 1.06 (m, 39 H, $\text{Si}-\text{CH}_3$, $\text{Si}-\text{CH}-\text{CH}_3$, CH_3), 1.82 (m, 12 H, CH_2), 3.92 (m, 12 H, OCH_2), 6.81/6.81 (d, 2 H), 6.92/6.94 (2 s, 2×1 H, 3-H, 6-H), 7.00 (m, 3 H); ^{13}C NMR (CDCl_3): δ = 10.6 (6 C, CH_3), 11.4 (3 C, $\text{Si}-\text{CH}$), 18.7 (6 C, $\text{Si}-\text{C}-\text{CH}_3$), 22.7/22.8 (6 C, CH_2), 70.2/70.8/71.2/71.4/71.4 (6 C, OCH_2), 91.4/91.6/96.5/103.0 (6 C, $\text{C}\equiv\text{C}$), 114.0/114.4/116.8/118.0 (C_q), 116.6/117.5/118.6 (CH), 152.9/153.3/153.4/154.0/154.3 (C_qO); FD MS: m/z (%) = 808.5 (67) [M^+], 807.5 (100) [M^+], 404.0 (4) [M^{2+}]; IR (KBr): $\tilde{\nu}$ = 2964, 2941, 2866, 2149, 1501, 1417, 1389, 1274, 1209, 1045, 1025, 980, 884, 859 cm^{-1} ; $\text{C}_{51}\text{H}_{70}\text{O}_6\text{Si}$ (807.2): calcd. C 75.89, H 8.74; found C 75.43, H 8.88.

1-(2,5-Dipropoxyphenylethynyl)-4-(4-ethynyl-2,5-dipropoxyphenylethynyl)-2,5-dipropoxybenzene (24): Compound **23** (6.6 g, 8.2 mmol) was dissolved in THF (50 mL) and tetrabutylammonium fluoride (3.9 g, 12.3 mmol) was added. The solvent was evaporated

and the residue taken up in CH_2Cl_2 (100 mL). After extraction with water, the organic phase was dried with Na_2SO_4 and filtered, and the solvents were evaporated. The obtained orange crystals were purified by column chromatography on silica gel (toluene). Yield: 4.8 g (90%) of yellow crystals, m.p. 97 °C; ^1H NMR (CDCl_3): δ = 1.03 (m, 18 H, CH_3), 1.85 (m, 12 H, CH_2), 3.34 (s, 1 H, $\equiv\text{C}-\text{H}$), 3.90 (m, 12 H, OCH_2), 6.81/6.82 (d, 2×1 H), 6.96/7.00/7.01/7.02 (m, 5×1 H); ^{13}C NMR (CDCl_3): δ = 10.5/10.5/10.6/10.6 (6 C, CH_3), 22.6/22.7/22.8 (6 C, CH_2), 70.2/71.1/71.2/71.4 (6 C, OCH_2), 80.1 (1 C, $\text{Ar}-\text{C}\equiv$), 82.3 (1 C, $\equiv\text{C}-\text{H}$), 89.8/91.1/91.7 (4 C, $\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}$), 112.6/114.0/114.8/115.1 (C_q), 114.4/116.6/117.2/117.5/118.1/118.7 (CH), 152.9/153.3/153.4/153.5/154.0/154.1 (C_qO); FD MS: m/z (%) = 652.3 (40) [M^+], 651.3 (100) [M^+], 325.8 (3) [M^{2+}]; IR (KBr): $\tilde{\nu}$ = 3265, 2961, 2937, 2877, 1510, 1429, 1274, 1211, 1044, 1025, 984, 864, 810, 772 cm^{-1} ; $\text{C}_{42}\text{H}_{50}\text{O}_6$ (650.9): calcd. C 77.51, H 7.74; found C 77.61, H 7.62.

1,4-Bis(4-bromo-2,5-dipropoxyphenylethynyl)-2,5-dipropoxybenzene (25): Compounds **8** (19.0 g, 0.048 mol) and **17** (4.8 g, 0.020 mol) were dissolved in dry piperidine (240 mL) and the system was flushed with nitrogen. To this clear and slightly brown solution were added bis(tetraphenylphosphane)palladium dichloride (0.4 g, 0.50 mmol), copper(I) iodide (0.3 g, 1.58 mmol), and triphenylphosphane (0.3 g, 1.14 mmol). After 30 min, the reaction was complete and the piperidine was evaporated. The residue was taken up in chloroform (200 mL) and extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . The obtained residue was then filtered with chloroform through silica gel. The crude product was purified twice by column chromatography on silica gel (toluene/*n*-hexane 2:1). Yield: 8.0 g (52%) of ochre crystals, m.p. 95 °C; ^1H NMR (CDCl_3): δ = 1.06 (m, 18 H, CH_3), 1.82 (m, 12 H, CH_2), 3.95 (m, 12 H, OCH_2), 7.00/7.01/7.08 (3 s, 3×2 H); ^{13}C NMR (CDCl_3): δ = 10.5 (6 C, CH_3), 22.6/22.6/22.7 (6 C, CH_2), 71.3/71.5/71.6 (6 C, OCH_2), 90.6/90.9 (4 C, $\text{C}\equiv\text{C}$), 113.1/113.4/114.4 (C_q), 117.6/118.0/118.5 (CH), 149.5 (C_q), 153.5/154.1 (2 C_q); FD MS: m/z (%) = 788.4 (17) [$\text{M} + 1$] $^+$, 787.3 (100) [M^+], 786.3 (25) [M^+], 785.3 (63) [M^+], 784.3 (21) [M^+]; IR (KBr): $\tilde{\nu}$ = 2966, 2935, 2906, 2877, 1500, 1471, 1423, 1374, 1268, 1220, 1046, 1022, 986, 907, 856, 827, 778, 748 cm^{-1} ; $\text{C}_{40}\text{H}_{48}\text{Br}_2\text{O}_6$ (784.6): calcd. C 61.23, H 6.12; found C 61.27, H 6.12.

1-[4-(4-Bromo-2,5-dipropoxyphenylethynyl)-2,5-dipropoxyphenylethynyl]-4-[2,5-dipropoxy-4-(triisopropylsilyl)ethynyl]phenylethynyl-2,5-dipropoxybenzene (26): Compounds **19** (3.6 g, 9.0 mmol) and **25** (3.0 g, 3.8 mmol) were dissolved in toluene (100 mL) and piperidine (50 mL) and the system was flushed with nitrogen. To this solution were added bis(tetraphenylphosphane)palladium dichloride (0.13 g, 0.19 mmol), copper(I) iodide (0.07 g, 0.38 mmol), and triphenylphosphane (0.10 g, 0.38 mmol). The mixture was stirred for 6 h at 60 °C and the volume was reduced to 20%. The residue was taken up in CH_2Cl_2 (200 mL) and extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . Purification was achieved with column chromatography on silica gel, first with toluene/cyclohexane (1:1) and afterward with toluene as eluent. Yield: 2.1 g (39%) of yellow crystals, m.p. 124 °C; ^1H NMR (CDCl_3): δ = 1.05 (m, 45 H, $\text{Si}-\text{CH}$, $\text{Si}-\text{CH}-\text{CH}_3$, CH_3), 1.82 (m, 16 H, CH_2), 3.94 (m, 16 H, OCH_2), 6.92/6.94/7.00/7.08 (8 H); ^{13}C NMR (CDCl_3): δ = 10.4 (8 C, CH_3), 11.4 (3 C, $\text{Si}-\text{CH}$), 18.6 (6 C, $\text{Si}-\text{C}-\text{CH}_3$), 22.5/22.6/22.6/22.7 (8 C, CH_2), 70.9/71.2/71.4/71.5/71.6 (8 C, OCH_2), 90.5/90.8/91.2/91.5/96.4/103.0 (8 C, $\text{C}\equiv\text{C}$), 113.1/113.3/114.2/114.4/114.5 (C_q), 116.9/117.5/117.9/118.1/118.4 (CH), 149.5/153.3/153.5/154.0/154.3 (C_qO); FD MS: m/z (%) = 1105.8 (31) [$\text{M} + 1$] $^+$, 1104.7 (75) [M^+], 1103.8 (100) [M^+], 1102.8 (49) [M^+], 1101.8 (69) [M^+], 552.0 (16) [M^{2+}], 551.2 (17) [M^{2+}];

IR (KBr): $\tilde{\nu}$ = 2963, 2940, 2866, 2149, 1509, 1468, 1423, 1387, 1273, 1213, 1064, 1017, 986, 884, 861 cm^{-1} ; $\text{C}_{65}\text{H}_{85}\text{O}_8\text{BrSi}$ (1102.4): calcd. C 70.82, H 7.77; found C 70.84, H 7.78.

1-[4-(2,5-Dipropoxyphenylethynyl)-2,5-dipropoxyphenylethynyl]-4-[2,5-dipropoxy-4-(triisopropylsilyl)ethynyl]phenylethynyl-2,5-dipropoxybenzene (27): Compounds **16** (1.0 g, 4.58 mmol) and **26** (1.6 g, 1.48 mmol) were dissolved in toluene (5 mL) and piperidine (3 mL) and the system was flushed with nitrogen. To this solution were added bis(tetraphenylphosphane)palladium dichloride (0.052 g, 0.074 mmol), copper(I) iodide (0.007 g, 0.037 mmol), and triphenylphosphane (0.010 g, 0.037 mmol). The black solution was stirred for 16 h at 60 °C and for 2 h at 80 °C. CH_2Cl_2 (100 mL) was added to the cooled mixture, which was extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . The crude product was purified by column chromatography on silica gel (toluene/ CH_2Cl_2 , 9:1). Yield: 1.53 g (84%) of yellow crystals, m.p. 140 °C; ^1H NMR (CDCl_3): δ = 1.05 (m, 51 H, $\text{Si}-\text{CH}$, $\text{Si}-\text{CH}-\text{CH}_3$, CH_3), 1.84 (m, 20 H, CH_2), 3.93 (m, 20 H, OCH_2), 6.81 (d, 2 H), 6.93/6.94 (2 s, 2×1 H), 7.01 (d, 7 H); ^{13}C NMR (CDCl_3): δ = 10.5/10.6 (10 C, CH_3), 11.4 (3 C, $\text{Si}-\text{CH}$), 18.7 (6 C, $\text{Si}-\text{C}-\text{CH}_3$), 22.7/22.8 (10 C, CH_2), 70.2/70.8/71.2/71.4/71.4 (10 C, OCH_2), 89.8/91.4/91.6/91.6/91.7/96.6/103.0 (10 C, $\text{C}\equiv\text{C}$), 114.0/114.1/114.4/114.7 (C_q), 116.8/117.4/117.5/118.0/118.6 (CH), 152.9/153.3/153.5/154.0/154.3 (C_qO); FD MS: m/z (%) = 1243.0 (13) [$\text{M} + 1$] $^+$, 1242.0 (69) [M^+], 1241.1 (54) [M^+], 1240.0 (100) [M^+], 620.9 (23) [M^{2+}], 620.3 (39) [M^{2+}], 414.4 (1) [M^{3+}], 413.7 (3) [M^{3+}]; IR (KBr): $\tilde{\nu}$ = 2964, 2939, 2867, 2149, 1511, 1470, 1425, 1388, 1273, 1211, 1064, 1017, 987, 884, 861 cm^{-1} ; $\text{C}_{79}\text{H}_{102}\text{O}_{10}\text{Si}$ (1239.8): calcd. C 76.54, H 8.29; found C 76.41, H 8.40.

1-[4-(2,5-Dipropoxyphenylethynyl)-2,5-dipropoxyphenylethynyl]-4-[4-(2,5-dipropoxy-4-ethynylphenylethynyl)phenylethynyl]-2,5-dipropoxybenzene (28): Compound **27** was dissolved in THF (20 mL) and tetrabutylammonium fluoride (0.5 g, 1.65 mmol) was added. After 20 min, the solvent was evaporated and the residue was dissolved in CH_2Cl_2 . The organic phase was extracted with water, dried with Na_2SO_4 , and filtered. The solvent was then removed and the orange residue was purified by column chromatography on silica gel, using CH_2Cl_2 as starting eluent and changing continuously until pure toluene was reached. The resulting yellow powder was washed several times with cyclohexane. Yield: 1.15 g (94%) of yellow crystals, m.p. 152 °C; ^1H NMR (CDCl_3): δ = 1.05 (m, 30 H, CH_3), 1.84 (m, 20 H, CH_2), 3.33 (s, 1 H, $\equiv\text{C}-\text{H}$), 3.93 (m, 20 H, OCH_2), 6.81 (d, 2 H), 6.98 (m, 11 H); ^{13}C NMR (CDCl_3): δ = 10.4/10.6 (10 C, CH_3), 22.6/22.7/22.8 (10 C, CH_2), 70.2/71.1/71.2/71.4 (10 C, OCH_2), 80.1/82.3/89.8/91.2/91.4/91.5/91.6/91.7/92.5 (10 C, $\text{C}\equiv\text{C}$), 112.6/114.3/114.4/114.4/114.5/114.7/115.1 (C_q), 117.2/117.4/117.5/118.1/118.7 (CH), 152.9/153.3/153.5/154.0/154.1 (C_qO); FD MS: m/z (%) = 1085.9 (24) [$\text{M} + 1$] $^+$, 1084.9 (100) [M^+], 1083.9 (54) [M^+], 543.2 (13) [M^{2+}], 542.6 (17) [M^{2+}], 542.1 (53) [M^{2+}], 361.6 (1) [M^{3+}]; IR (KBr): $\tilde{\nu}$ = 3290, 2965, 2937, 2877, 2104, 1512, 1472, 1427, 1388, 1274, 1211, 1064, 1044, 1022, 985, 863, 770, 714 cm^{-1} ; $\text{C}_{70}\text{H}_{82}\text{O}_{10}$ (1083.4): calcd. C 77.60, H 7.63; found C 77.41, H 7.60.

1-(2,5-Dipropoxyphenylethynyl)-2,5-dipropoxybenzene (1a): Compounds **6** (0.73 g, 2.3 mmol) and **16** (0.45 g, 2.1 mmol) were dissolved in dry piperidine (15 mL) and the system was flushed with nitrogen. The catalysts bis(tetraphenylphosphane)palladium dichloride (0.05 g, 0.07 mmol), copper(I) iodide (0.03 g, 0.016 mmol), and triphenylphosphane (0.05 g, 0.019 mmol) were added one after another. After 4 d, the mixture was filtered through silica gel with ethyl acetate and the solvent was removed. The crude

product was purified by column chromatography on silica gel (toluene). Yield: 0.63 g (74%) of yellow needles, m.p. 51 °C; ^1H NMR (CDCl_3): δ = 1.01, 1.06 (2 t, 12 H, CH_3), 1.77 (m, 8 H, CH_2), 3.86, 3.97 (2 t, 8 H, OCH_2), 6.98 (d, 2 H, 6-H), 6.80 (m, 4 H, 3-H, 4-H); ^{13}C NMR (CDCl_3): δ = 10.5, 10.6 (each 2 C, CH_3), 22.7, 22.8 (each 2 C, CH_2), 70.2, 71.5 (each 2 C, OCH_2), 89.8 (2 C, $\text{C}\equiv\text{C}$), 114.3 (2C, C-1), 114.5 (2C, C-3), 116.4 (2C, C-4), 118.7 (2C, C-6), 152.9 (2C, C-2), 154.0 (2 C, C-5); EI MS (70 eV): m/z (%) = 410 (100) [M^+], 367 (7) [$\text{M}^+ - \text{C}_3\text{H}_7$], 205 (5) [M^{2+}], 43 (39) [C_3H_7^+]; IR (KBr): $\tilde{\nu}$ = 2966, 2935, 2878, 1502, 1469, 1435, 1389, 1270, 1193, 1002, 977, 875, 809 cm^{-1} ; $\text{C}_{26}\text{H}_{34}\text{O}_4$ (410.6): calcd. C 76.06, H 8.35; found C 76.04, H 8.34.

1,4-Bis(2,5-dipropoxyphenylethynyl)-2,5-dipropoxybenzene (1b): Compounds **6** (0.51 g, 1.14 mmol) and **17** (0.5 g, 2.3 mmol) were dissolved in dry piperidine and the system was flushed with nitrogen. To this yellow solution were added bis(tetraphenylphosphane)palladium dichloride (0.06 g, 0.085 mmol), copper(I) iodide (0.05 g, 0.26 mmol), and triphenylphosphane (0.06 g, 0.23 mmol). The reaction was complete within 5 d and the mixture was filtered through silica gel with CH_2Cl_2 . The obtained brown oil was purified by column chromatography on silica gel (toluene). Yield: 0.65 g (91%) of yellow crystals, m.p. 98 °C; ^1H NMR (CDCl_3): δ = 1.01, 1.07 (2 t, 12 H, CH_3), 1.81 (m, 12 H, CH_2), 3.86 (t, 4 H, OCH_2), 3.96, 3.98 (2 t, 8 H, OCH_2), 6.81, 6.82 (2 s, 4 H), 7.03 (s, 2 H), 7.01 (s, 2 H); ^{13}C NMR (CDCl_3): δ = 10.40, 10.46, 10.5 (each 2 C, CH_3), 22.59, 22.65, 22.7 (each 2 C, CH_2), 70.2 (2 C, OCH_2), 71.2, 71.4 (each 2 C, OCH_2), 89.9 (2 C, Ar-CC), 91.3 (2 C, Ar-CC), 114.1 (2 C), 114.5 (4 C), 116.5 (2 C), 117.7 (2 C), 118.7 (2 C), 152.9, 153.5, 154.0 (C_qO); FD MS: m/z (%) = 627 (100) [M^+]; IR (KBr): $\tilde{\nu}$ = 2966, 2933, 2873, 1497, 1473, 1390, 1275, 1221, 1047, 1024, 874, 858, 796 cm^{-1} ; $\text{C}_{40}\text{H}_{50}\text{O}_6$ (626.8): calcd. C 76.65, H 8.04; found C 76.70, H 7.95.

1-(2,5-Dipropoxyphenylethynyl)-4-[4-(2,5-dipropoxyphenylethynyl)-2,5-dipropoxyphenylethynyl]-2,5-dipropoxybenzene (1c). – Preparation from 20 and 22: Compounds **20** (1.35 g, 2.76 mmol) and **22** (1.2 g, 2.76 mmol) were dissolved in dry piperidine (150 mL) and the system was flushed with nitrogen. To this clear solution were added bis(tetraphenylphosphane)palladium dichloride (0.01 g, 0.053 mmol), copper(I) iodide (0.01 g, 0.038 mmol), and triphenylphosphane (0.01 g, 0.038 mmol). When the reaction was complete, the solvent was evaporated and the residue was taken up in chloroform. The organic phase was extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . The crude product was purified by column chromatography on silica gel (toluene). Yield: 0.13 g (6%) of yellow crystals. – **Preparation from 6 and 24:** Compounds **6** (0.98 g, 3.07 mmol) and **24** (1.0 g, 1.54 mmol) were dissolved in toluene (10 mL) and piperidine (2 mL) and the system was flushed with nitrogen. Bis(tetraphenylphosphane)palladium dichloride (0.027 g, 0.038 mmol), copper(I) iodide (0.015 g, 0.077 mmol) and triphenylphosphane (0.02 g, 0.077 mmol) were added to the solution. The reaction was complete after 10 min and CH_2Cl_2 (100 mL) was added, followed by extraction of the organic phase with saturated NH_4Cl , water, and saturated NaHCO_3 . The crude product was purified by column chromatography on silica gel (toluene) and subsequently washed with cyclohexane. Yield: 0.3 g (23%) of yellow crystals with m.p. 117 °C – ^1H NMR (CDCl_3): δ = 1.01 (t, 6 H)/1.07 (m, 18 H) (CH_3), 1.82 (m, 16 H, CH_2), 3.86 (t, 4 H)/3.97 (m, 4 H) (OCH_2), 6.81 (d, 4 H), 7.01 (s, 4 H), 7.02 (d, 2 H); ^{13}C NMR (CDCl_3): δ = 10.5/10.6/10.6 (8 C, CH_3), 22.6/22.7/22.8 (8 C, CH_2), 70.2/71.2/71.2/71.4 (8 C, OCH_2), 89.6/92.2 (6 C, $\text{C}\equiv\text{C}$), 114.2/114.3/114.8 (6 C_q), 114.6/116.6 (4 C), 117.4/117.5 (4 C), 118.5 (2 C), 152.9/153.5/153.6/154.1 (C_qO); FD MS: m/z (%) = 845.5 (13)

[$\text{M} + 1$] $^+$, 844.5 (75) [M^+], 843.4 (100) [M^+], 422.1 (4) [M^{2+}]; IR (KBr): $\tilde{\nu}$ = 2965, 2932, 2875, 1512, 1466, 1430, 1386, 1271, 1209, 1065, 1042, 1022, 980, 864, 815, 769, 730 cm^{-1} ; $\text{C}_{54}\text{H}_{66}\text{O}_8$ (843.1): calcd. C 76.93, H 7.89; found C 77.02, H 7.91.

1,4-Bis[4-(2,5-dipropoxyphenylethynyl)-2,5-dipropoxyphenylethynyl]-2,5-dipropoxybenzene (1d). – Preparation from 17 and 20: Compounds **17** (0.5 g, 2.06 mmol) and **20** (2.3 g, 2.54 mmol) were dissolved in piperidine (100 mL) and the system was flushed with nitrogen. Bis(tetraphenylphosphane)palladium dichloride (0.07 g, 0.10 mmol), copper(I) iodide (0.04 g, 0.21 mmol), and triphenylphosphane (0.05 g, 0.21 mmol) were added to the solution. The reaction mixture was stirred for 5 d at 40 °C. The piperidine was evaporated and the residue was taken up in 100 mL of CH_2Cl_2 . The organic phase was extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . The crude product was purified by column chromatography on silica gel (toluene). Yield: 1.6 g (76%) of yellow crystals. – **Preparation from 8, 17, and 16:** In this two-step reaction, compounds **8** (3.01 g, 7.55 mmol) and **17** (0.91 g, 3.78 mmol) were dissolved in dry piperidine (100 mL) and the system was flushed with nitrogen. Bis(tetraphenylphosphane)palladium dichloride (0.2 g, 0.29 mmol), copper(I) iodide (0.1 g, 0.53 mmol), and triphenylphosphane (0.01 g, 0.38 mmol) were added to the solution. Completion of the reaction was detected by TLC after 3 h and the ethynyl component **16** (1.8 g, 8.25 mmol) was added. After an additional 12 h, the solvent was removed and the residue was dissolved in a small amount of CH_2Cl_2 . Methanol was added until precipitation was finished. The obtained product was purified twice by column chromatography on silica gel, the first time with toluene/chloroform (9:1) as eluent, and the second time toluene. Yield: 0.61 g (15%) of yellow crystals, m.p. 147 °C; ^1H NMR (CDCl_3): δ = 1.05 (m, 30 H, CH_3), 1.83 (m, 20 H, CH_2), 3.86, t, 4 H/3.98, m, 16 H, (OCH_2), 6.81 (d, 4 H, 3-H, 4-H), 7.02 (m, 8 H); ^{13}C NMR (CDCl_3): δ = 10.5/10.6/10.6 (10 C, CH_3), 22.6/22.7/22.8 (10 C, CH_2), 70.2/71.2/71.2/71.4 (10 C, OCH_2), 89.8 (2 C), 91.4/91.5/91.6 (6 C), 113.9/114.0/114.3/114.6 (8 C_q), 114.2 (2 C), 116.6 (2 C), 117.3 (2 C), 117.4 (4 C), 118.5 (2 C, C-6), 152.8/153.3/153.4/153.9 (C_qO); FD MS: m/z (%) = 1061.9 (6) [M^+], 1059.9 (20) [M^+], 1059.0 (100) [M^+], 530.4 (29) [M^{2+}], 529.4 (60) [M^{2+}], 352.9 (8) [M^{3+}]; IR (KBr): $\tilde{\nu}$ = 2964, 2936, 2876, 1513, 1472, 1429, 1388, 1272, 1211, 1065, 1042, 1023, 987, 863, 814, 770, 725 cm^{-1} ; $\text{C}_{68}\text{H}_{82}\text{O}_{10}$ (1059.4): calcd. C 77.10, H 7.80; found C 77.10, H 7.84.

1-[4-(2,5-Dipropoxyphenylethynyl)-2,5-dipropoxyphenylethynyl]-4-[4-[4-(2,5-dipropoxyphenylethynyl)-2,5-dipropoxyphenylethynyl]-2,5-dipropoxyphenylethynyl]-2,5-dipropoxybenzene (1e): Compounds **6** (0.6 g, 1.85 mmol) and **28** (1.0 g, 0.92 mmol) were dissolved in toluene (12 mL) and piperidine (5 mL), and the system was flushed with nitrogen. To enhance the solubility, the temperature was raised to 60 °C. After the catalyst mixture of bis(tetraphenylphosphane)palladium dichloride (0.016 g, 0.023 mmol), copper(I) iodide (0.009 g, 0.046 mmol), and triphenylphosphane (0.012 g, 0.046 mmol) had been added, the reaction was stirred for 1 h. After removal of the solvent, the residue was taken up in CH_2Cl_2 (50 mL) and extracted with saturated NH_4Cl , water, and saturated NaHCO_3 . The crude product was purified by column chromatography on silica gel (toluene). Yield: 0.8 g (68%) of yellow crystals, m.p. 181 °C; ^1H NMR (CDCl_3): δ = 1.05 (m, 36 H, CH_3), 1.84 (m, 24 H, CH_2), 3.87 (t, 4 H)/3.99 (m, 20 H) (OCH_2), 6.81 (d, 4 H), 7.01 (m, 10 H); ^{13}C NMR (CDCl_3): δ = 10.4/10.5 (12 C, CH_3), 22.6/22.7/22.8 (12 C, CH_2), 70.3/71.3/71.5 (12 C, OCH_2), 89.8 (2 C), 91.4/91.6 (8 C, $\text{C}\equiv\text{C}$), 114.2/114.3/114.5/114.9 (C_q), 114.6 (2 C), 116.7 (2 C), 117.7 (4 C), 117.8 (4 C), 118.8 (2 C), 153.0/153.6/154.1 (C_qO); FD MS: m/z (%) = 1278.9 (20) [$\text{M} + 1$] $^+$, 1277.9 (37)

[M⁺], 1276.8 (100) [M⁺], 1275.9 (95) [M⁺], 639.7 (10) [M²⁺], 638.8 (78) [M²⁺], 638.1 (63) [M²⁺], 426.2 (4) [M³⁺], 425.2 (12) [M³⁺]; IR (KBr): $\tilde{\nu}$ = 2964, 2936, 2876, 1512, 1471, 1427, 1388, 1273, 1211, 1065, 1020, 985, 863, 805, 768, 722 cm⁻¹; C₈₂H₉₈O₁₂ (1275.7): calcd. C 77.21, H 7.74; found C 77.09, H 7.74.

THG Measurements: Thin films for the nonlinear optical studies were prepared in the following way: Compounds **1a–e** were mixed with polystyrene (M_w = 100.000) at (10.00 ± 0.03)% of concentration by weight, dissolved in toluene using a concentration by weight of the mixture of 2.7%, and spincoated on fused silica substrates at spinning speeds of 500 rpm and 9000 rpm. This resulted in final film thicknesses d of the order of 212 nm and 50 nm, respectively, as measured with a Tencor model P10 step profiler. Absorption coefficients α were evaluated from transmission spectra of ultrathin films (d = 50 nm) after correction for reflection losses at film/air and film/substrate interfaces as in earlier work.^[37] The dispersion of the refractive index $n(\lambda)$ of the films (d = 50 nm) was determined from reflection spectra measured at nearly perpendicular incidence.^[37] The experimental setup for third-harmonic generation has been described previously.^[37] We used an Nd:YAG laser (EKSPLA model PL 2143B), the second harmonic output of which pumped a parametric generator (EKSPLA model PG 501), which gave laser pulses with a duration of 20 ps, repetition rate 10 Hz, and a wavelength tuning range between 680 nm and 2000 nm. The laser beam was focused on the sample, which was mounted on a rotation stage and positioned in an evacuated chamber. We measured the Maker fringes of the samples (films on substrate and substrate alone after wiping off the film) and evaluated them using thickness, refractive indices and absorption coefficients at the fundamental and harmonic wavelengths, as described earlier.^[37,60] The only fitting parameters were the modulus $|\chi^{(3)}|$ and the phase angle ϕ of the complex third-order susceptibility $\chi^{(3)} = |\chi^{(3)}| \exp(i\phi)$. The $\chi^{(3)}$ data were related to the reference value for fused silica ($|\chi^{(3)}| = 3.11 \cdot 10^{-14}$ esu). Compounds **1a–e** are photostable under the irradiation conditions used for the THG measurements.

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the DAAD for financial support. Technical support for thin film measurements was supplied by G. Herrmann and W. Scholdei and for the preparations by S. Weißmann and S. Prehl.

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Received June 29, 2001
[O01317]