Insulated Molecular Wires: Dendritic Encapsulation of Poly(triacetylene) Oligomers, Attempted Dendritic Stabilization of Novel Poly(pentaacetylene) Oligomers, and an Organometallic Approach to Dendritic Rods

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Multinanometer-long end-capped poly(triacetylene) (PTA) and poly(pentaacetylene) (PPA) oligomers with dendritic side chains were synthesized as insulated molecular wires. PTA Oligomers with laterally appended *Fréchet*-type dendrons of first to third generation were prepared by attaching the dendrons (**8**, **13**, and **17**, respectively, *Scheme 1*) to (*E*)-enediyne **18** by a *Mitsunobu* reaction and subsequent *Glaser-Hay* oligomerization under end-capping conditions (*Scheme 2*). Whereas first-generation oligomers up to the pentamer were isolated (**1a**–**e**), for reasons of steric overcrowding, only oligomers up to the trimer (**2a**–**c**) were formed at the second-generation level, and only the end-capped monomer and dimer (**3a**,**b**) were isolated at the third-generation level. By repetitive sequences of hydrosilylation (with the *Karstedt* catalyst), followed by allylation or vinylation, a series of carbosilane dendrons were also prepared (*Schemes 3* and *4*). Attachment of the second-generation wedge **40** to (*E*)-enediyne **18**, followed by deprotection and subsequent end-capping *Hay* oligomerization, provided PTA oligomers **4a**–**d** with lateral carbosilane dendrons (*Scheme 5*). UV/VIS Studies (*Figs. 5–10*) demonstrated that the insulating dendritic layers did not alter the electronic characteristics of the PTA backbone, even at the higher-generation levels. Despite distortion from planarity due to the bulky dendritic wedges, no loss of π-electron conjugation along the PTA backbone was detected. A surprising $(E)\rightarrow(Z)$ isomerization of the diethynylethene (DEE) core in the third generation derivative **3a** was observed, possibly photosensitized by the bulky *Fréchet*-type dendritic wedge. Electrochemical investigations by steady-state voltammetry and cyclic voltammetry showed that the first reduction potential of the PTA oligomer with *Fréchet*-type dendrons is shifted to more negative values as the dendritic coverage increases. With compounds **5a**–**c**, the first oligomers with a poly(pentaacetylene) backbone were obtained by oxidative *Hay* oligomerization under end-capping conditions (*Scheme 6*). The synthesis of dendritic PPA oligomers by oxidative coupling of (*E*)-enetetrayne **60** under end-capping conditions provided oligomers **61a**–**d**, which were formed as mixtures of stereoisomers due to unexpected thermal $(E)\rightarrow(Z)$ isomerization (*Scheme 8*). In another novel approach towards dendritic encapsulation of molecular wires with a Pt-bridged tetraethynylethene (TEE) oligomeric backbone, the *trans*-dichloroplatinum(II) complex *trans*-**67** with dendritic phosphane ligands (*Fig. 14*) was coupled under *Hagihara* conditions to mono-deprotected **69** under formation of the extended monomer **65** (*Scheme 12*). Again, an unexpected thermal $(E)\rightarrow(Z)$ isomerization, possibly induced by steric strain between TEE moieties and dendritic phosphane ligands in the unstable complex, led to the isolation of **65** as an isomeric mixture only.

1. Introduction. – Among the various classes of monodisperse, rod-like oligomers with a linearly π-conjugated backbone [1][2], poly(triacetylene) (PTA) oligomers are attracting increasing interest for their electronic, nonlinear optical, and mesomorphic

properties [3–7]. On the other hand, dendrimer technology (for recent reviews, see [8]) has provided in recent years a fascinating tool for modulating optoelectronic properties through encapsulation of chromophores inside dendritic branches [9]. We now describe a merger of dendrimer chemistry with our ongoing development of monodisperse-functionalized PTA oligomers to generate insulated molecular wires, as schematically shown in *Fig. 1*.

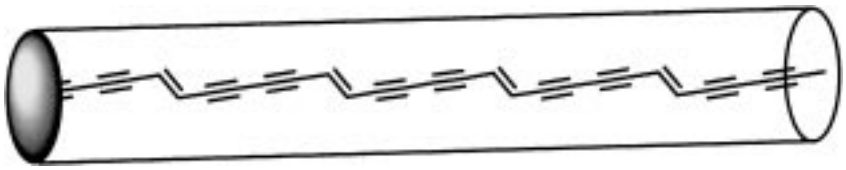
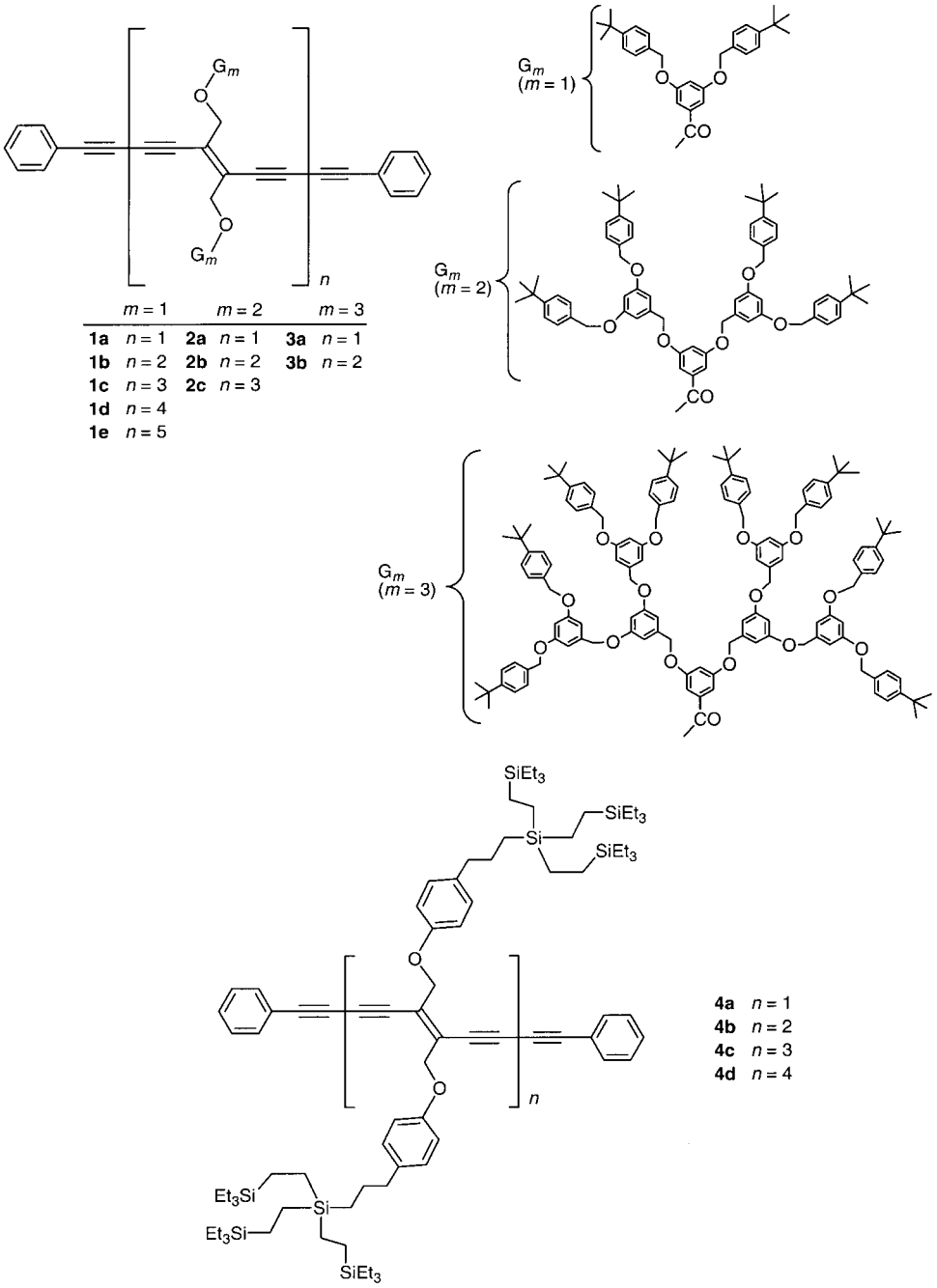


Fig. 1. *Schematic representation of PTA oligomers insulated inside a dendritic shell*

Dendritic modification of π-conjugated polymers has been increasingly investigated, and these studies were recently summarized in a review by *Schlüter* and *Rabe* [10]. Three types of modification have been reported: π-conjugated oligomers and polymers with dendritic side chains [11][12] or dendritic end groups [13] and dendrimers with π-conjugated oligomers/polymers at the periphery [14]. We were interested in exploring how encapsulation of the linearly π-conjugated backbone by laterally attached, sterically shielding dendritic wedges influences the processability and stability of PTA oligomers and polymers. At the same time, we wished to explore to what extent steric hindrance between adjacent dendritic wedges of higher generation could possibly cause nonplanarity and deconjugation of the backbone. Here, we report the synthesis of monodisperse, multinanometer-long dendritic PTA rods bearing *Fréchet*-type dendrons [15] of first to third generation (**1**–**3**) (for a preliminary communication of this part of the work, see [11]) or carbosilane dendrons [8b] [16–20] of second generation (**4**) (*Fig. 2*). We show that π-electron conjugation in these tubular macromolecules is fully maintained at all generation levels. In addition, we report the first series of poly(pentaacetylene) (PPA) oligomers (**5**, *Fig. 3*) as well as attempts to stabilize these more delicate unsaturated backbones by lateral attachment of *Fréchet*-type dendrons. Poly(pentaacetylene)s $[-(C{\equiv}C-C{\equiv}C-CR{=}CR-C{\equiv}C-C{\equiv}C)_n-]$ are the fourth class of linearly conjugated polymers with a nonaromatic all-carbon backbone in the progression that starts with poly(acetylene) $[-(CR{=}CR)_n-]$, poly(diacetylene) $[-(C{\equiv}C-CR{=}CR)_n-]$, and poly(triacetylene) $[-(C{\equiv}C-CR{=}CR-C{\equiv}C)_n-]$, and ultimately leads to carbyne $[-(C{\equiv}C)_n-]$. Also, preliminary results in an organometallic approach towards dendritic rods are described.

2. Results and Discussion. – 2.1. *Synthesis of Poly(triacetylene) Oligomers Encapsulated with* Fréchet-*Type Dendrons*. The dendrons required for the synthesis of **1**–**3** (*Fig. 2*) were prepared as shown in *Scheme 1* [15]. Etherification of methyl 3,5-dihydroxybenzoate (**6**) gave **7**, and subsequent ester hydrolysis yielded the first-generation dendritic branch **8**. Etherification of 3,5-dihydroxybenzyl alcohol (**9**) provided **10**, which was transformed into benzyl bromide **11**. Etherification of **6** with **11** gave ester **12**, which was hydrolyzed to the second-generation dendron **13**. Similar sequences (**9** → **14** → **15** and **6** → **16** → **17**) provided the third-generation dendron **17**.



	m = 1		m = 2		m = 3
1a	n = 1	**2a**	n = 1	**3a**	n = 1
1b	n = 2	**2b**	n = 2	**3b**	n = 2
1c	n = 3	**2c**	n = 3		
1d	n = 4				
1e	n = 5				

4a	n = 1
4b	n = 2
4c	n = 3
4d	n = 4

Fig. 2. *Dendritically encapsulated PTA oligomers* **1**–**4**

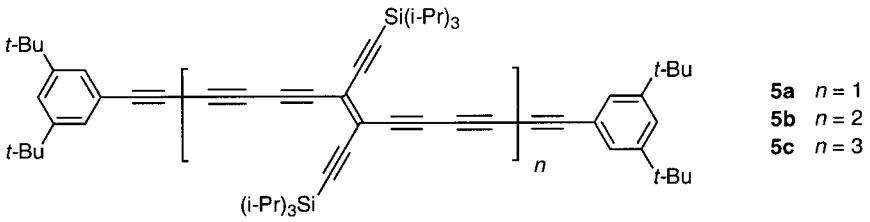


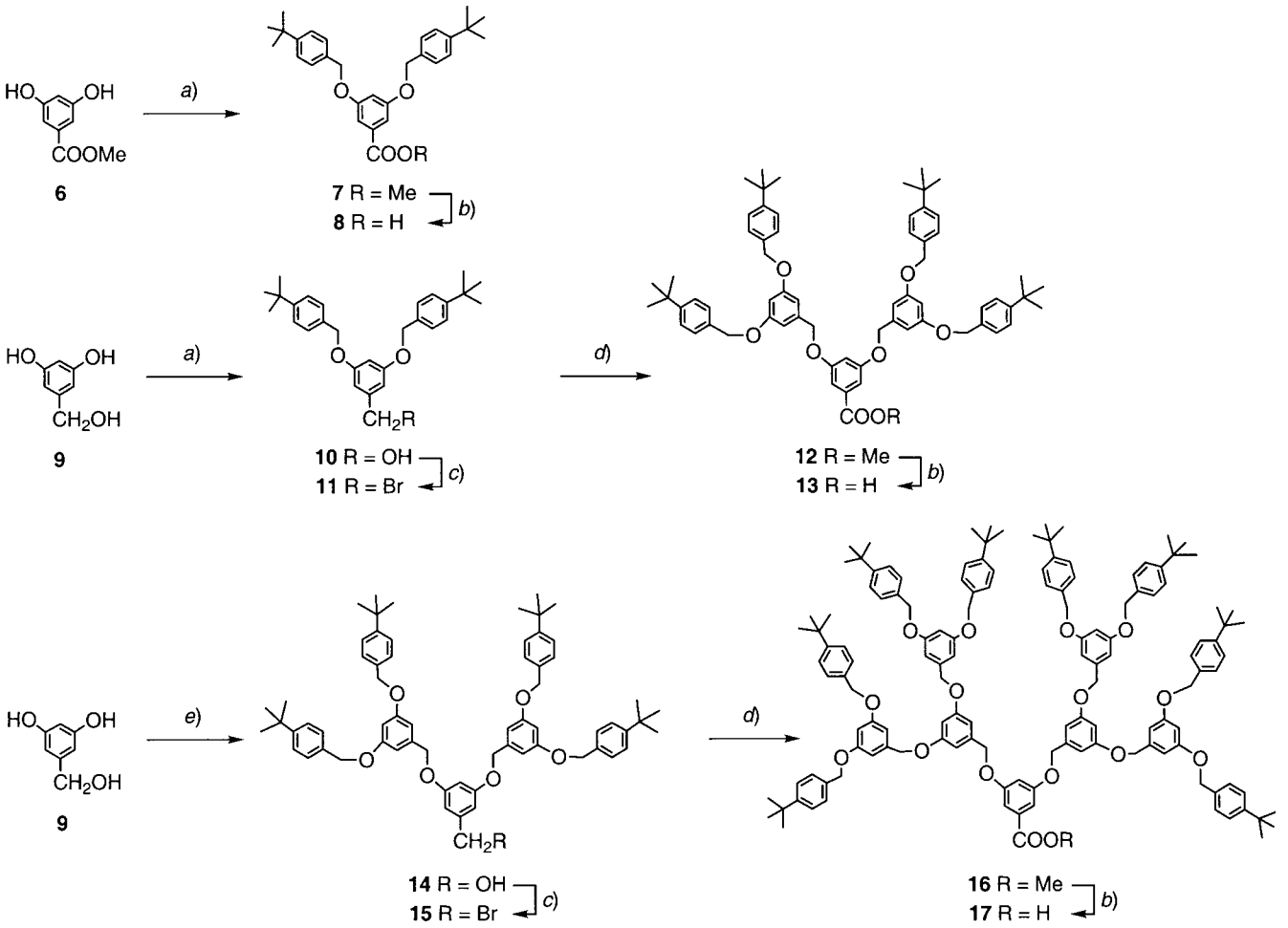
Fig. 3. *First series of poly(pentaacetylene) (PPA) oligomers* **5a**–**c**

Dendrons **8**, **13**, and **17** were subsequently attached to (*E*)-2,3-bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diol (**18**) [4][21] using the *Mitsunobu* reaction [22] to give the dendritic silyl-protected monomers **19**–**21**, respectively (*Scheme 2*). The yield of the third-generation compound **21** was very low (4%), possibly due to steric hindrance of the reacting COOH group by the bulky dendritic wedges in dendron **17**. After deprotection with Bu_4NF in wet THF, the free (*E*)-enediynes **22**–**24** were obtained. The dendritic wedges substantially stabilize the usually rather unstable free (*E*)-enediynes [23], and compounds **22**–**24** can be stored in the air at ambient temperature for months without decomposition. Oxidative *Hay* coupling [24] of **22**–**24** in the presence of PhC≡CH as an end-capping reagent [21] provided the oligomeric PTAs as solids. The first-generation compound **22** afforded separable oligomers up to the pentamer (**1a**–**e**), which extend in length from 19.4 Å (**1a**) to 49.4 Å (**1e**) [11][21]. For steric reasons, the second-generation derivative **23** yielded isolable oligomers only up to the trimer (**2a**–**c**). Finally, due to severe steric overcrowding, conversion of the third generation enediyne **24** gave only end-capped monomer and dimer (**3a,b**) in pure form and sufficient yields.

Analytical gel-permeation chromatography (GPC) proved to be extremely useful for monitoring the purification of our compounds. The separation of the oligomers was achieved by preparative GPC (*Bio-Beads S-X1*; CH_2Cl_2), and the purity of the fractions was determined by analytical GPC because, specifically for the higher oligomers, thin-layer chromatography (TLC) was useless. With other techniques such as ^{1}H- and ^{13}C-NMR spectroscopy, we could not detect impurities (lower and higher oligomers) with less than 10% abundance, while analytical GPC was sensitive for impurities with an abundance of less than 1%. The analytical GPC traces of the first-generation dendritic oligomers **1a**–**e** are shown in *Fig. 4*. Optical detection occurred at 300 nm in the absorption region of the aromatic wedges. GPC Separations of the higher-generation compounds were equally efficient.

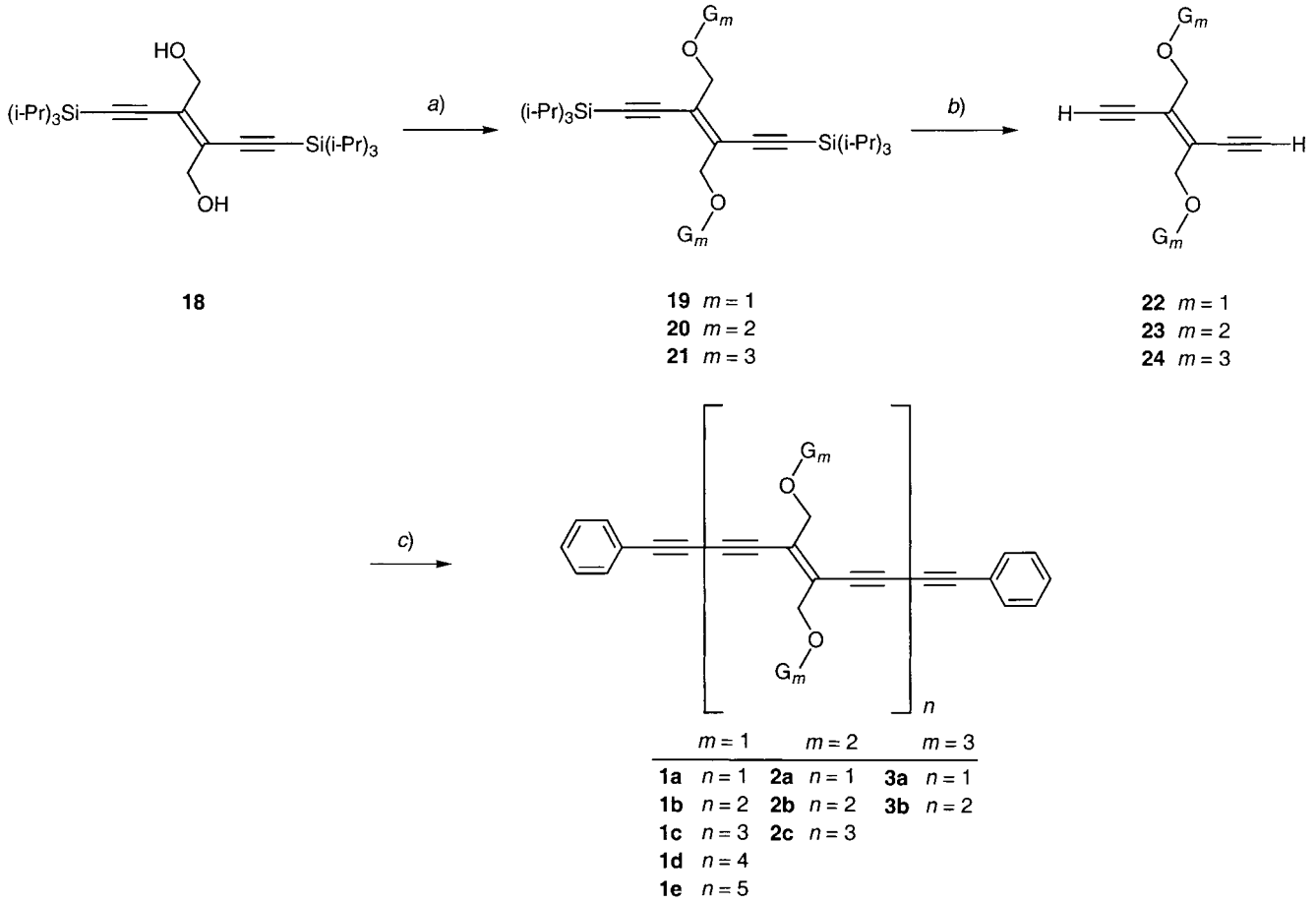
The molecular constitution of the dendritic rods was confirmed by matrix-assisted laser-desorption-ionization mass spectra (MALDI-TOF-MS; matrix: 9-nitroanthracene), which depicted either the $[M+Na]^+$ or $[M+K]^+$ ions as base peaks, and NMR spectra. In the ^{1}H-NMR spectra of the centrosymmetrical oligomers, the number of the *t*-Bu resonances increases with the number of monomeric units (*Table 1*). Similar behavior was observed for the aromatic protons positioned between the two alkoxy substituents of the central benzene rings that serve as linkers between PTA backbone and dendritic wedges.

Scheme 1. *Synthesis of Dendrons of First* (**8**), *Second* (**13**), *and Third Generation* (**17**)



a) 4-(*tert*-Butyl)benzyl bromide, [18]crown-6, K_2CO_3, acetone, Δ, 2 d; 91% (**7**), 67% (**10**). *b*) KOH, EtOH, Δ, 2 h; 99% (**8**), 97% (**13**), 99% (**17**). *c*) Br_4C, Ph_3P, THF, 20°, 30 min; 99% (**11**, **15**). *d*) **6**, [18]crown-6, K_2CO_3, acetone, Δ, 2 d; 96% (**12**), 74% (**16**). *e*) **11**, [18]crown-6, K_2CO_3, acetone, Δ, 2 d; 87%.

Scheme 2. *Synthesis of the Dendritic Rods* **1**–**3**



18

19 *m* = 1
20 *m* = 2
21 *m* = 3

22 *m* = 1
23 *m* = 2
24 *m* = 3

a) **8**, **13**, or **17**, *N*,*N*,*N*′,*N*′-tetramethylazodicarboxamide (TMAD), Bu_3P, THF, 60°, 24 h; 81% (**19**), 61% (**20**), 4% (**21**). *b*) Bu_4NF, wet THF, 20°, 1 h; 99% (**22**), 97% (**23**), 90% (**24**). *c*) CuCl, air, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), PhC≡CH, CH_2Cl_2, 20°, 2 h; 17% (**1a**), 6% (**1b**), 3% (**1c**), 1% (**1d**), 0.4% (**1e**), or 9% (**2a**), 6% (**2b**), 2% (**2c**), or 13% (**3a**), 3% (**3b**). For the structure of G_m, see *Fig. 2*.

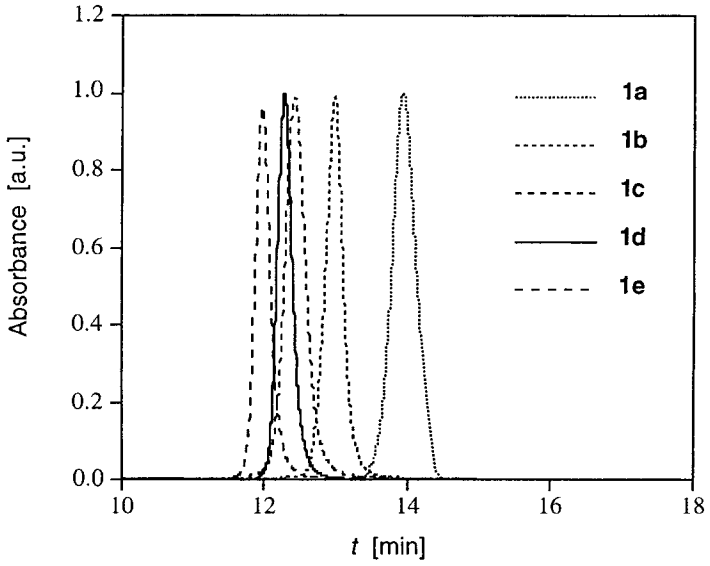


Fig. 4. *Analytical GPC traces* (*Bio-Beads S-X1*; CH_2Cl_2) *for the first-generation dendritic rods* **1a**–**e** (UV detection at 300 nm)

In the ^{13}C-NMR spectra, the number of C(sp) resonances, which appear as clearly discernable signals between 73 and 90 ppm, increases by $2+2n$, where n is the number of monomeric units in the oligomers. The spectra did not display a significant difference in chemical shift between these resonances in oligomers of same length but different dendritic generation (*Table 1*) [25]. Force-field calculations [26] showed clearly that the conformation of the PTA backbone, including the two end-capping Ph groups, is not planar in the higher-generation dendritic rods – in particular in the third-generation dimer **3b** – due to the steric hindrance of the bulky dendritic wedges. Only the first generation derivatives **1a**–**e**, similar to previous PTA oligomers [3–5], should have a planar conjugated backbone. The activation barriers for rotation of the backbone about C(sp)–C(sp) and C(sp)–C(sp^2) single bonds, however, are very small [27]; therefore, symmetrical averaged NMR spectra are observed at all generation levels.

An interesting observation was made during purification of the end-capped third-generation monomer **3a** by preparative GPC [28]. Instead of the expected single resonance, two *t*-Bu resonances were observed in the ^{1}H-NMR spectrum and TLC of the solution showed two spots. After column chromatography (SiO_2; hexane/CH_2Cl_2 1:1) in the dark, **3a** was obtained as a pure substance, and only one *t*-Bu resonance was observed. When a solution of isomerically pure **3a** was irradiated with sunlight, two *t*-Bu resonances were observed again, indicating that **3a** underwent a $(E)\rightarrow(Z)$ photoisomerization of the central C=C bond [29]. This phenomenon was not encountered with the end-capped monomers of first and second generation (**1a** and **2a**, resp.) and resembles observations made with dendrimers also containing *Fréchet*-type dendritic wedges around a photoisomerizable azobenzene core, in which IR excitation of the aromatic wedges, followed by energy transfer, induced a $(Z)\rightarrow(E)$ isomerization of the core [30].

Table 1. *Characteristic NMR* (500 MHz) *Resonances of the Dendritic PTA Oligomers in* $CHCl_3$

Oligomer	^{1}H-NMR (δ [ppm])	
	Me_3C	ArH[a])
1a	1.33	6.85
1b	1.31; 1.32	6.76; 6.81
1c	1.29; 1.30; 1.31	6.72; 6.75; 6.81
1d	1.27; 1.28; 1.29; 1.30	6.71; 6.72; 6.74; 6.80
1e	1.26; 1.27; 1.28; 1.29; 1.30	6.71 – 6.72 (*m*); 6.73; 6.80
2a	1.32	6.84
2b	1.29; 1.31	6.73; 6.79
2c	1.26; 1.27; 1.31	6.69; 6.70; 6.77
3a	1.29	6.82
3b	1.23; 1.26	[b])
Oligomer	^{13}C-NMR (δ [ppm]) $-C\equiv C-$	
1a	73.41; 76.52; 87.67; 88.75	
1b	73.41; 76.37; 82.45; 87.53; 88.23; 89.68	
1c	73.46; 76.43; 82.34; 83.06; 87.37; 88.29; 88.33; 89.81	
1d	73.47; 76.41; 82.28; 82.83; 83.11; 87.35; 88.12; 88.29; 88.45;	89.84
1e	73.42; 76.35; 82.23; 82.73; 82.82; 83.07; 87.32; 88.08; 88.20;	88.29; 88.45; 89.85
2a	73.41; 76.52; 87.79; 88.87	
2b	73.46; 76.39; 82.61; 87.71; 88.31; 89.77	
2c	73.46; 76.43; 82.46; 83.15; 87.54; 88.29; 88.35; 89.86	
3a	73.44; 76.51; 87.83; 88.94	
3b	[c])	

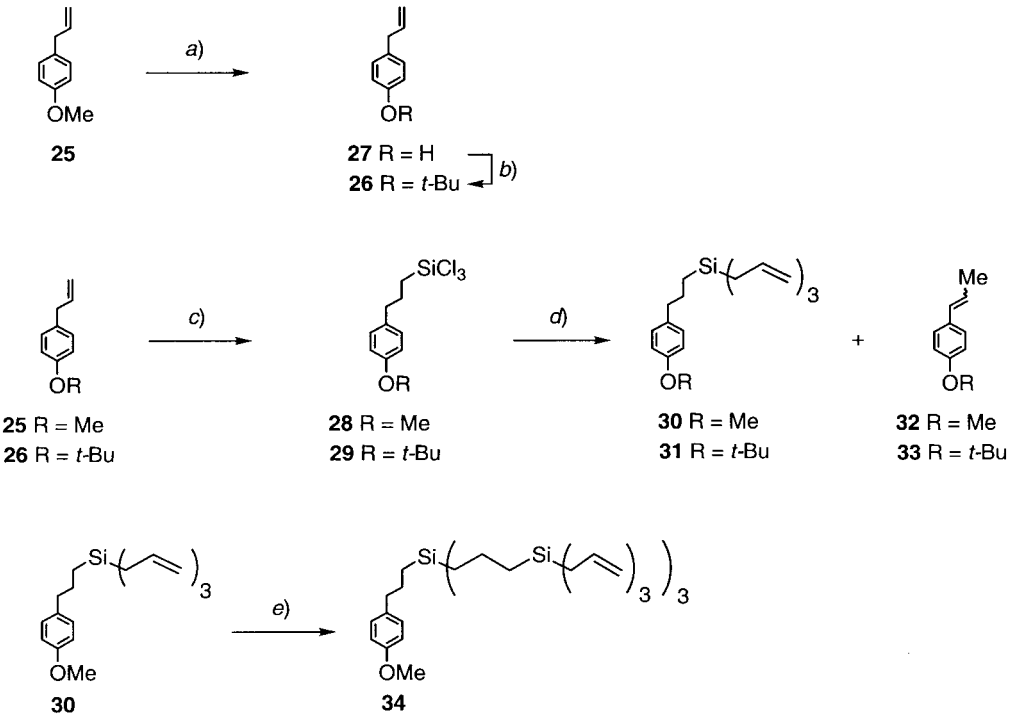
[a]) Resonance of the proton positioned between the two alkoxy substituents in the central benzene ring bridging the dendrons to the PTA backbone. [b]) Masked in a *multiplet*. [c]) Not determined.

2.2. *Synthesis of Poly(triacetylene) Oligomers Encapsulated in Carbosilane Dendrons.* Several considerations led to the preparation of the second class of PTA oligomers (**4a**–**d**, *Fig. 2*) bearing 'carbosilane' wedges. *Fréchet*-type dendrons of generations 1–3 are not spherical but rather flat. In contrast, we expected 'carbosilane' wedges to generate a more spherical encapsulation already at low generation numbers. Also, we expected enhanced stability of the 'carbosilane' dendrons and hoped to avoid the $(E) \rightarrow (Z)$ photoisomerization that apparently is promoted by the *Fréchet*-type dendrons as described in *Sect. 2.1.* We also wished to enhance the length of the spacers connecting the dendrons to the PTA monomer in order to reduce the steric hindrance in the oxidative acetylenic oligomerization.

In analogy to the synthesis of **1**–**3**, we adopted for the preparation of **4a**–**d** a strategy in which 'carbosilane' dendrons are attached to (*E*)-enediyne **18** (*Scheme 2*) by the *Mitsunobu* reaction. Dendron synthesis was pursued *via* two routes, either repetitive hydrosilylation/allylation or repetitive hydrosilylation/vinylation. The former approach started from 4-allylanisole (**25**) or from the corresponding *tert*-butyl ether **26**, which was prepared by demethylation of **25** with Br_3B [31] to give **27**, followed by acid-catalyzed etherification with isobutene [32] (*Scheme 3*). The two aromatic ethers **25** and **26** were subsequently reacted with $HSiCl_3$ in the presence of *Karstedt* catalyst (a (divinyltetramethylsiloxane)platinum complex in xylene) [33] to yield the hydro-

silylated products **28** and **29**, respectively, with complete regioselectivity (^{1}H-NMR). Subsequent conversion with allylmagnesium bromide afforded the first-generation 'carbosilane' dendrons **30** and **31**. The hydrosilylation reaction was conducted in pure $HSiCl_3$ on the multigram scale, and the excess reagent was readily removed by vacuum distillation. The isomerized styrene derivatives **32** and **33** were formed as minor side products (yields $< 5\%$) and were readily separated by bulb-to-bulb distillation.

Scheme 3. *'Carbosilane' Dendrons by Repetitive Hydrosilylation/Allylation*



a) Br_3B, CH_2Cl_2, $-78° \rightarrow 15°$, 2 h; 70%. *b*) Isobutene, CF_3SO_3H (cat.), $-78°$, 3 h; 96%. *c*) $HSiCl_3$, *Karstedt* catalyst, 20°, 2 h. *d*) Allylmagnesium bromide, THF, 20°, 6 h; 61% (**30**), 49% (**31**), less than 5% **32** or **33** formed (yields starting from **25** and **26**, respectively). *e*) $HSiCl_3$, *Karstedt* catalyst, THF, 20°, 3 h; then allylmagnesium bromide, THF, 20°, 48 h; 26%.

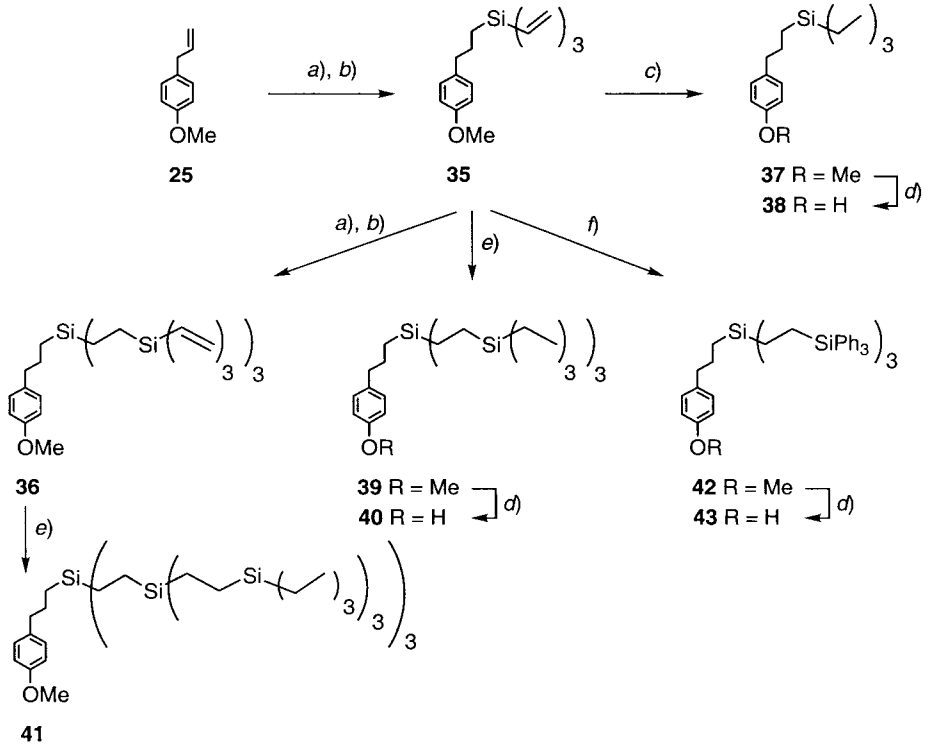
Hydrosilylation in pure $HSiCl_3$ was quite advantageous at the first-generation level, since it provided, after allylation, good yields of products that were readily purified. At the second-generation level, however, the conversion in neat reagent proceeded much too slowly, and a cosolvent (THF) was added to accelerate the reaction. In this way, anisole **30** was hydrosilylated in the presence of *Karstedt* catalyst to provide, after allylation, the second-generation dendron **34** in 26% yield. The modest yield was a result of the tedious efforts required to separate by multiple preparative GPC runs the desired product from a small impurity with similar retention time. Since the ^{1}H-NMR monitoring of the hydrosilylation step indicated a clean conversion, we presume that this side product was formed in the allylation step. The yield of the desired product was

even more disappointing in the hydrosilylation/allylation starting from *tert*-butyl ether **31**. In this case, ^{1}H-NMR monitoring showed that the *tert*-butyl ether was readily cleaved during hydrosilylation.

The purity of the dendrons of first and second generations was readily revealed by ^{29}Si-NMR spectroscopy, which showed a single ^{29}Si resonance for **30** and two for **34**.

In the second approach, **25** was hydrosilylated, and the crude product was reacted with vinylmagnesium bromide to give **35** in 66% yield (*Scheme 4*). Again, **32** was formed as a side-product in less then 5% yield but was readily removed by bulb-to-bulb distillation. In comparison to allyl derivative **30**, vinylated first-generation dendron **35** was much more reactive, and hydrosilylation was successful in neat $HSiCl_3$. After vinylation, the second-generation dendron **36** was conveniently purified by column chromatography (CC), followed by one preparative GPC run. A comparison of the yields of the second generation wedges (**34**: 26%, **36**: 67%) shows substantial advantages of the hydrosilylation/vinylation over the hydrosilylation/allylation route. 'Carbosilane' dendrons with an aliphatic periphery were prepared by catalytic hydrogenation of the terminal double bond in **35**, yielding **37**, which was demethylated

Scheme 4. *'Carbosilane' Dendrons by Repetitive Hydrosilylation/Vinylation*



a) $HSiCl_3$, *Karstedt* catalyst, 20°, 2 h. *b*) Vinylmagnesium bromide, THF, 20°, 12 h; 66% (**35** from **25**), 67% (**36** from **35**). *c*) H_2, Pd/C (10%), pentane, 20°, 2 h; 90%. *d*) Br_3B, CH_2Cl_2, $-78° \rightarrow 15°$, 2 h; 99% (**38**); 71% (**40**); 70% (**43**). *e*) Et_3SiH, *Karstedt* catalyst, THF, Δ, 48 h; 97% (**39**), 82% (**41**). *f*) Ph_3SiH, *Karstedt* catalyst, THF, Δ, 7 h; 27%.

with Br_3B to provide the phenolic wedge **38**. Alternatively, hydrosilylation of **35** with Et_3SiH gave **39**, which was demethylated to the second-generation wedge **40**. A third-generation dendron with aliphatic periphery, **41**, was obtained in very high yield (82%) by hydrosilylation of **36** with Et_3SiH. With Ph_3SiH, we also prepared derivative **42**, which was transformed by demethylation into the phenolic wedge **43** bearing nine Ph groups in its periphery.

On the way to PTA oligomers bearing 'carbosilane' dendrons, the first-generation phenolic wedge **38** was reacted with (*E*)-enediyne **18** under classical *Mitsunobu* conditions (Ph_3P, diethyl azodicarboxylate (DEAD)) [22a] to give protected monomer **44**, which was converted to **45** with Bu_4NF (*Scheme 5*). In contrast, the second-generation wedge **40** did not react with **18** under these conditions. However, application of the redox system (Bu_3P, 1,1′-(azodicarbonyl)piperidine (ADDP)) introduced by *Tsunoda et al.* [22b] provided the desired product **46** in 65% yield. For the success of this reaction, it was essential to add ADDP slowly, over a period of 24 h, to the stirred mixture. Deprotection with Bu_4NF afforded the second generation dendritic monomer **47**, which was isolated as a stable, clear oil. In contrast, the first-generation counterpart **45** was much less stable and could only be isolated as a deep-red oil, due to slow decomposition during workup. Oligomerization of **47** was achieved under *Hay* conditions in the presence of PhC≡CH as end-capping reagent and afforded the desired oligomers **4a**–**d**, which were separated by preparative GPC, first at ambient, then at high pressure. The sensitivity of the *Mitsunobu* reaction of **18** to steric hindrance was further demonstrated in the attempted conversion of the phenolic 'carbosilane' wedge **43** with nine Ph rings in the periphery. Both protocols (Ph_3P, DEAD or Bu_3P, ADDP) failed to give the desired monomer **48** (*Scheme 5*).

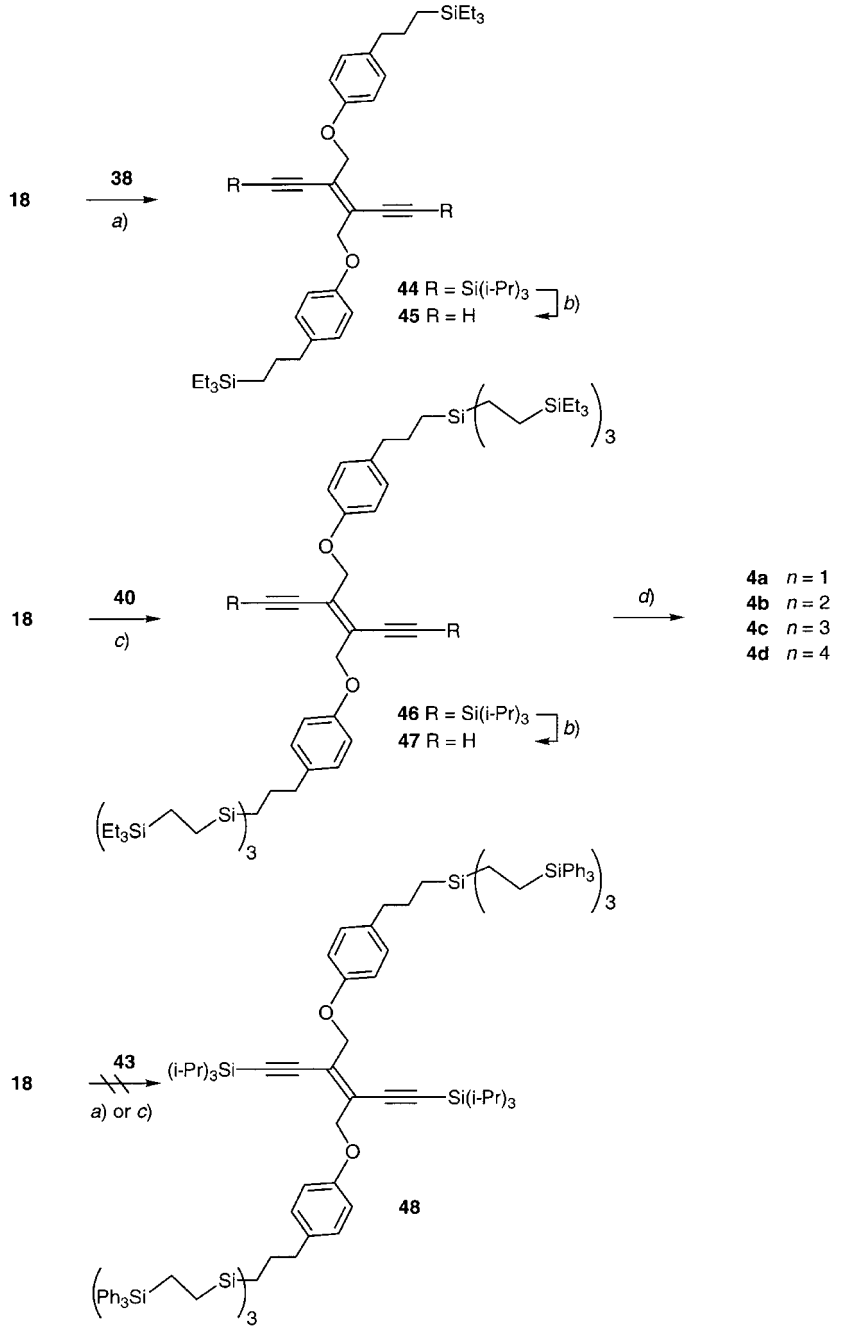
The nature and length of the oligomers **4a**–**d** was readily revealed by MALDI-TOF-MS, the number of resolved resonances in the ^{1}H- and ^{13}C-NMR spectra, and comparison of the ^{1}H-NMR integrals of the monomeric repeat units in the PTA backbone with those of the end-capping groups. In contrast to the rods with *Fréchet*-type dendrons (*Sect. 2.1*), no (*E*)→(*Z*) isomerization was observed with the 'carbosilane' derivatives.

2.3. *UV/VIS and Electrochemical Characterization of the Dendritic PTA Rods.* As mentioned in *Sect. 2.1*, force-field calculations of the higher-generation dendritic rods showed clearly that the conformation of the PTA backbone, including the two end-capping Ph groups, is not planar due to severe steric hindrance of the bulky dendritic wedges. A resulting decrease or even complete loss of the π-electron conjugation along the PTA backbone in the higher-generation compounds should be readily observable by means of electronic absorption spectroscopy.

The UV/VIS spectra of the dendritic molecular wires with *Fréchet*-type dendrons, **1**–**3**, were measured in $CHCl_3$ (*Figs. 5–7*) at 298 K. All compounds, except the monomers, are yellow solids. At all generation levels, the longest-wavelength absorption maximum (λ_{max}) is bathochromically shifted with increasing rod length, and no saturation was observed. The latter was expected from other work, which had shown that saturation of the optical properties in PTA oligomers occurs only at a length of 8–10 monomeric units [4][5].

A comparison of the spectra of dimers **1b**, **2b**, and **3b** revealed that, independent of the dendritic generation number, the longer-wavelength absorptions, which originate

Scheme 5. *Preparation of PTA Oligomers Bearing Carbosilane Dendrons*



a) Ph_3P, DEAD, 20°, 6 h; 68%. *b*) Bu_4NF, THF, 0°, 2 min; 88% (**45**), 82% (**47**). *c*) Bu_3P, ADDP, 20°, 34 h, 65%. *d*) CuCl, TMEDA, air, PhC≡CH, CH_2Cl_2, 20°, 4 h, 13% (**4a**), 7% (**4b**), 2% (**4c**), 1% (**4d**).

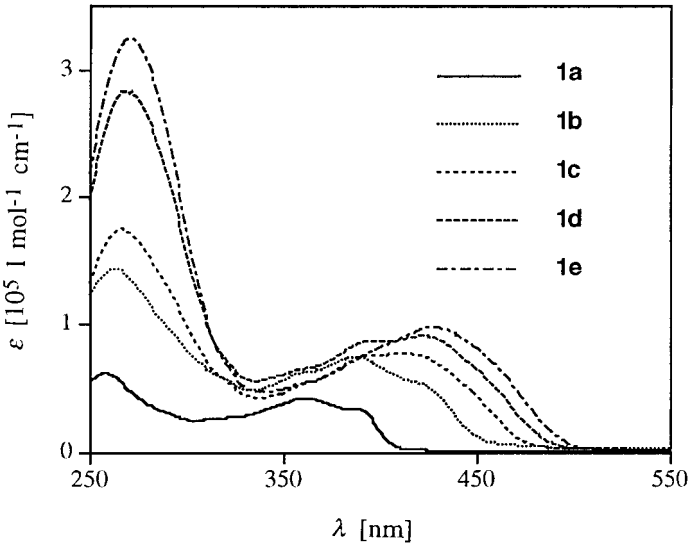


Fig. 5. *Electronic absorption spectra of* **1a**–**e** *in* $CHCl_3$ ($T = 298$ K)

from electronic transitions within the conjugated PTA backbone, appear at almost the same positions (around $\lambda = 400$ nm) with nearly identical fine structure and molar extinction coefficients (*Fig. 8*). Similarly, position, fine structure, and molar extinction coefficients of the longer-wavelength absorption bands in the spectra of trimers **1c** (first generation) and **2c** (second generation) are nearly identical (*Fig. 9*). A precise determination of λ_{max} required deconvolution of the UV/VIS spectra [34]. The values obtained for the dimers (*Fig. 8*) showed a minimal bathochromic shift in changing from

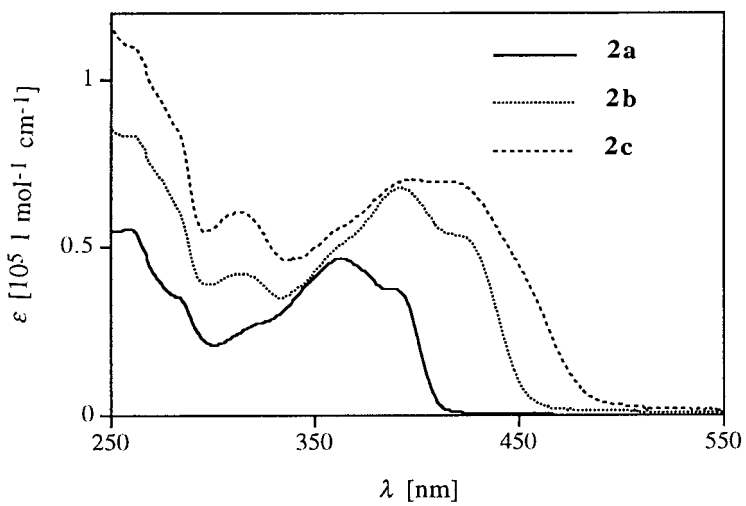


Fig. 6. *Electronic absorption spectra of* **2a**–**c** *in* $CHCl_3$ ($T = 298$ K)

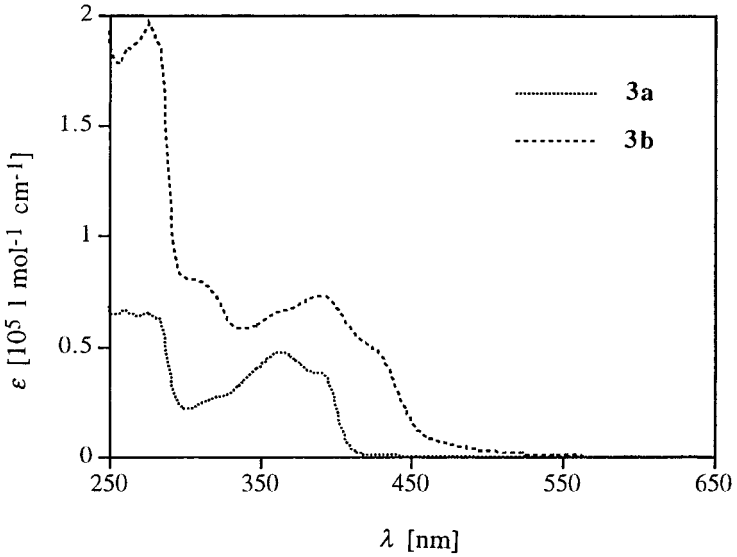


Fig. 7. *Electronic absorption spectra of* **3a**,**b** *in* $CHCl_3$ ($T = 298$ K)

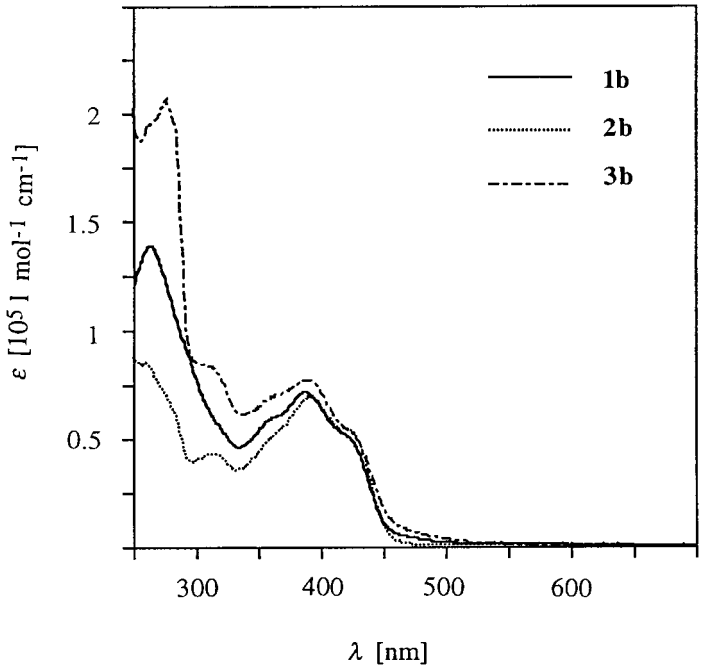


Fig. 8. *Comparison of the electronic absorption spectra of dimers* **1b**, **2b**, *and* **3b** *in* $CHCl_3$

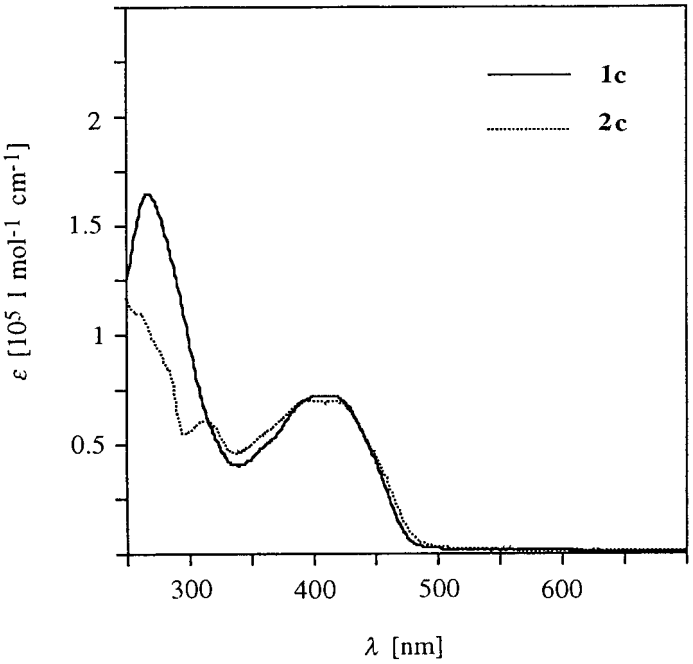


Fig. 9. *Comparison of the electronic absorption spectra of trimers* **1c** *and* **2c** *in* $CHCl_3$

generation one to three: $\lambda_{max} = 428.0 \pm 0.2$ nm (**1b**), 430.0 ± 0.3 (**2b**), and 431.1 ± 0.2 nm (**3b**). For all dendritic rods, the λ_{max} values were converted into energies (E_{max} [eV]), which were then plotted against the reciprocal number of monomeric units ($1/n$). These plots revealed for all three oligomeric series straight lines intersecting the ordinate at nearly identical $E_{max} = 2.57 \pm 0.06$ eV. This value corresponds well to the optical gap determined for other PTA oligomers lacking dendritic wedges [4][5].

All these data provide impressive support that π-electron delocalization and effective conjugation length of the PTA backbone are not affected by distortions out of planarity due to steric compression of the bulky dendritic wedges at higher generations. Apparently, π-electron conjugation involving the acetylenic fragments in the PTA backbone is best described as being cylindrical rather than resulting from orbital overlap within a distinct plane and is, therefore, fully maintained upon rotation about C(sp)–C(sp^2) and C(sp)–C(sp) single bonds.

The position, shape, and molar extinction coefficients of the longest wavelength absorptions in the dendritic rods, which result from π-electron conjugation in the PTA backbone, are nearly independent of the nature of the dendritic coverage. This is nicely shown by a comparison of the spectra of derivatives **1a**–**e** with *Fréchet*-type dendrons (*Fig. 5*) with those recorded for the carbosilane derivatives **4a**–**d** (*Fig. 10*). The only major difference between the two series is the strong increase in absorptivity below 320 nm in **1a**–**e**, due to the large increase in aromatic rings at higher dendritic generation number.

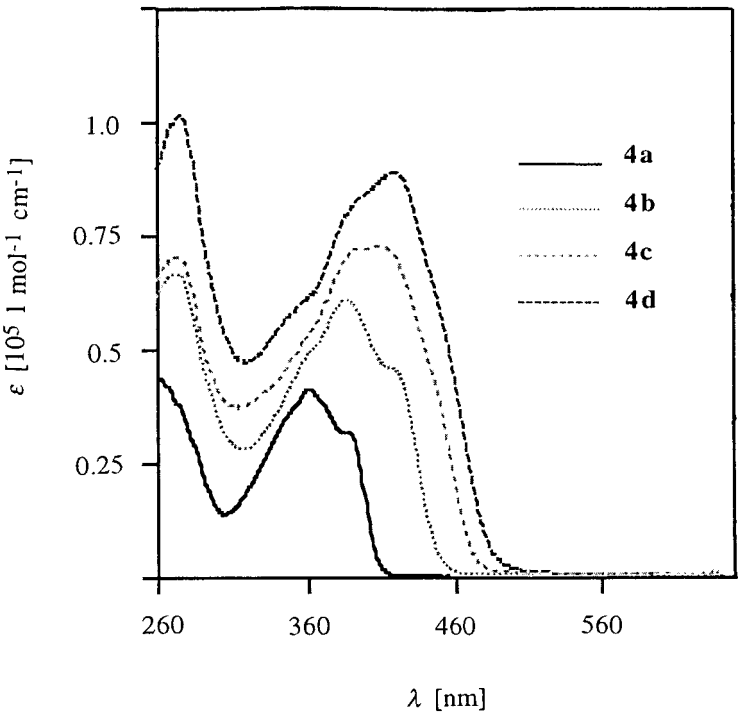


Fig. 10. *Electronic absorption spectra of* **4a**–**d** *in* $CHCl_3$ ($T = 298$ K)

The electrochemical properties of the dendritic rods **1a**–**c** and **2a**–**c** were studied by steady-state voltammetry and cyclic voltammetry in CH_2Cl_2 (+0.1M Bu_4NPF_6) on a glassy carbon electrode. All oligomers could not be oxidized in the accessible potential range but were reduced in several irreversible steps, the electrons being transferred to the conjugated PTA backbone [4][5] (*Table 2*). The irreversibility increases with the dendritic generation, due probably to steric hindrance [35]. Interestingly, the first reduction potential is shifted to more negative values as the dendritic coverage increases (*e.g.*, −1.79 V (**1a**) and −1.84 V (**2a**); *vs.* Fc/Fc^+). We tentatively explain

Table 2. *Electrochemical Data for the Dendritic Rods* **1a**–**c** *and* **2a**–**c** *Measured by Steady-State Voltammetry on a Glassy Carbon Electrode*

Oligomer	$E^1_{1/2}$ [V][a])	$E^2_{1/2}$ [V]	$E^3_{1/2}$ [V]
1a	−1.79 (98)[b])	−2.30 (120)	–
1b	−1.60 (90)	−1.76 (90)	–
1c	−1.54 (140)	−1.76 (110)	−2.21 (100)
2a	−1.84 (135)	−2.35 (114)	–
2b	−1.62 (105)	−1.82 (110)	−2.30 (75)
2c	−1.56 (145)	−1.78 (100)	−2.22 (105)

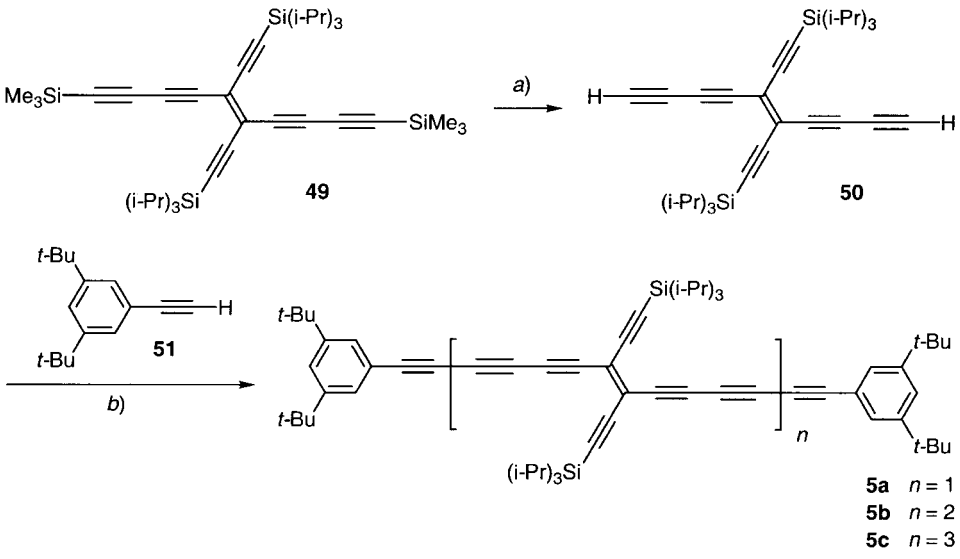
[a]) Half-wave potentials in CH_2Cl_2 + 0.1M Bu_4NPF_6 *vs.* Fc/Fc^+ (ferrocene/ferricinium couple). [b]) The slopes of the waves (given in parentheses in mV/log unit) were obtained by plotting the potential E *vs.* $\log[i(i_d - i)]$ (i is the current and i_d is the limiting current).

these data by pointing out that the encapsulating *Fréchet*-type dendrons provide an electron-rich environment in which it becomes more difficult – with increasing coverage – to inject an electron into the PTA backbone. As the oligomeric length increased, the first reduction step occurred at increasingly less-negative potential; plots of $E_{1/2}$ *vs.* $1/n$ (n = number of monomeric units in the oligomer) gave a straight line in both series.

2.4. *Poly(pentaacetylene) Oligomers and Attempted Dendritic Encapsulation.* In our efforts to further extend the progression leading from polyacetylene to carbyne (see *Introduction*), we prepared the first series of oligomeric poly(pentaacetylene)s (PPAs) **5a**–**c** (*Scheme 6*). PPAs were hitherto unknown, and we were interested to explore *i*) whether oxidative acetylenic coupling could be employed for oligomerization, as in the case of PTA materials (see above), and *ii*) whether the conjugated PPA backbone, with its high acetylenic content, would still display sufficient environmental stability for isolation and characterization of the new materials and study of their physical properties.

The first series of PPA oligomers **5a**–**c** was prepared starting from (*E*)-enetetrayne **49** [36], which was selectively bis-deprotected, with a catalytic amount of Bu_4NF adsorbed on SiO_2, to give **50** as an unstable yellow oil (*Scheme 6*). All attempts to remove the Me_3Si groups of **49** under basic conditions (K_2CO_3/MeOH or 45% KOH) failed due to the instability of product or starting material. Possible degrading reactions of **50** with base may involve deprotonation in the initial step, in view of the enhanced acidity of the terminal H-atoms [37], or nucleophilic attack at the extended unsaturated chromophore [38]. Oligomerization of **50** under *Hay* conditions in the presence of 3,5-di(*tert*-butyl)phenylacetylene **51** [39] as end-capping reagent led to a

Scheme 6. *Synthesis of the PPA Oligomers* **5a**–**c**



a) Bu_4NF/SiO_2, THF/H_2O, 20°, 5 min; 90%. *b*) CuCl, TMEDA, air, CH_2Cl_2, 20°, 2 h; 10% (**5a**), 6% (**5b**), 3% (**5c**).

mixture of the oligo(pentaacetylene)s **5a–c** in a total yield of 19%, which was separated by preparative GPC (PhMe). Analysis of the crude oligomerization mixture by MALDI-TOF-MS (matrix: α-cyano-4-hydroxycinnamic acid) revealed that oligomers up to the heptamer had been formed. The material quantities of the higher oligomers beyond trimeric **5c** were, however, too small to allow isolation and characterization; furthermore, workup was severely hampered by insolubility of the compounds.

A comparison of the UV/VIS spectra of PPA oligomers **5a–c** (*Fig. 11*) with those of the corresponding PTA oligomers **52a–c** (neglecting the influence of the *t*-Bu groups in the former series) [40] shows that the extension of the π-conjugated backbone – expectedly – leads to a substantial bathochromic shift of both the longest wavelength absorption maximum λ_{max} and the optical end-absorption, while the overall spectral shape is similar in both series. Thus, λ_{max} in $CHCl_3$ increases from 422 (**52a**) to 458 (**5a**) nm, from 478 (**52b**) to 508 (**5b**) nm, and from 506 (**52c**) to 519 nm (**5c**). The pronounced vibrational fine structure in the spectra of **5a–c** is indicative of a rigid backbone, as was previously found for the PTA oligomers [40].

To prepare more soluble oligomers with the PPA backbone, (*E*)-hex-3-ene-1,5-diyne **53** with appended $Me_2(t\text{-Bu})SiOCH_2$ groups [41] was subjected to [Pd/Cu]-catalyzed C(sp)–C(sp) heterocoupling [24b] with 1-bromo-2-(trimethylsilyl)acetylene (**54**) [42] to give the Me_3Si-protected monomer **55a**, which was isolated in 21% yield, in addition to dimeric **55b** (18%) and trimeric **55c** (3%) (*Scheme 7*). Removal of the Me_3Si groups in **55a** was accomplished with K_2CO_3 in MeOH to give PPA

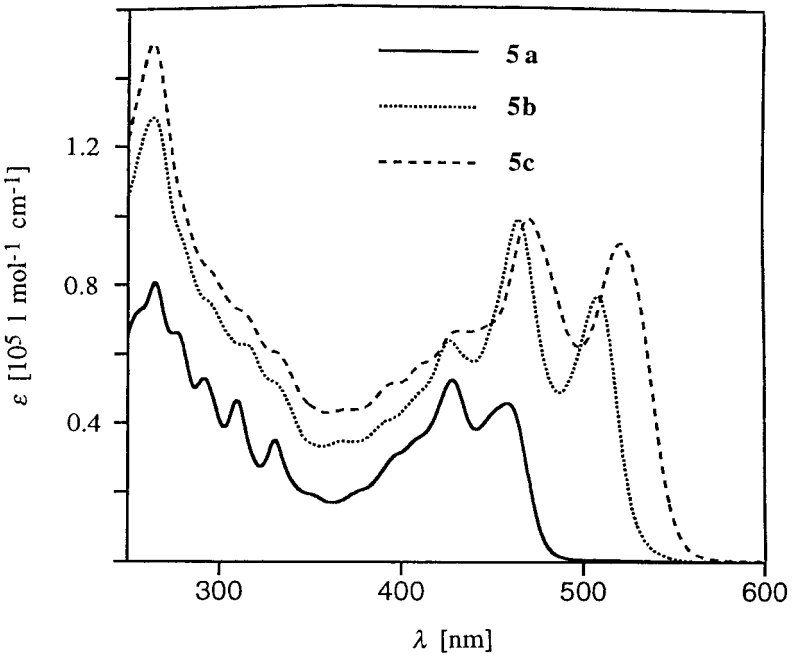
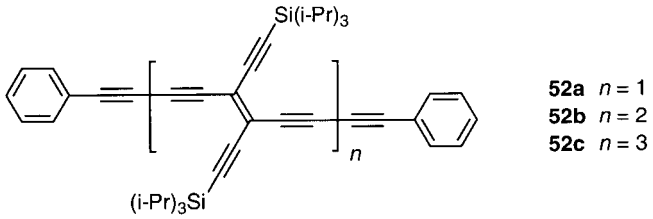
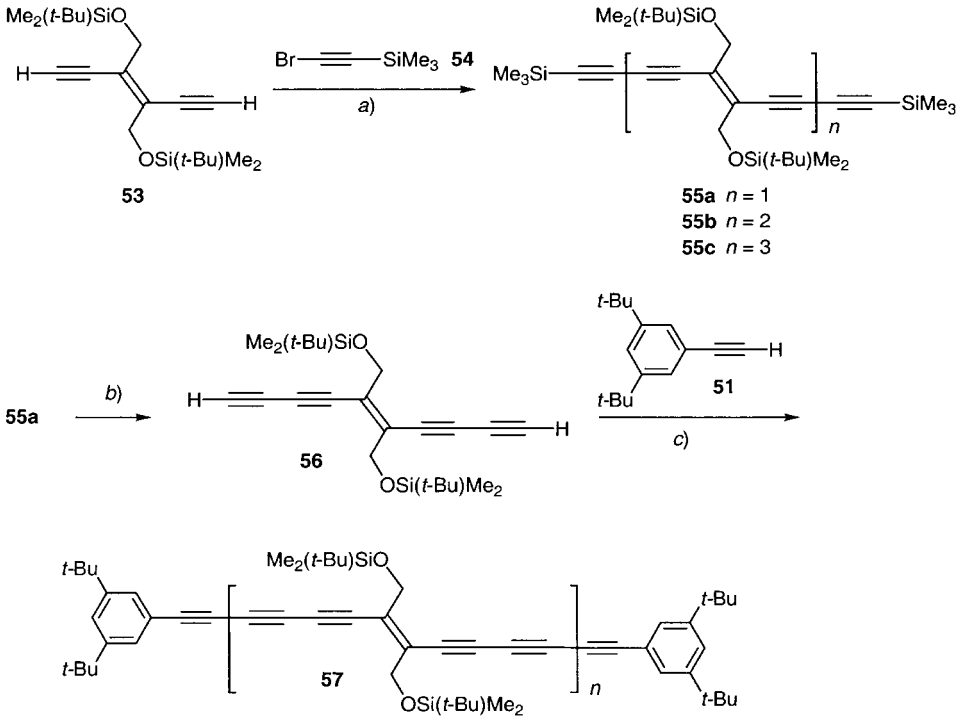


Fig. 11. *Electronic absorption spectra of* **5a–c** *in* $CHCl_3$ ($T = 298$ K)



monomer **56**, which proved to be very unstable. In contrast to PPA monomer **50**, enetetrayne **56** could not be isolated as a neat solid due to its instability. Oxidative oligomerization under *Hay* conditions in the presence of end-capping reagent **51**, however, was successful, leading to the dark-red unstable solid oligomeric mixture **57** with a degree of polymerization $X_n \approx 9$, as determined by end-group analysis. In this analysis, the ^{1}H-NMR integral of the *t*-Bu resonance of the end-capping moieties was compared to the integrals of the resonances in the lateral (*t*-Bu)Me_2SiOCH_2 side chains of the monomeric repeat units. The low isolated yield of **57** (11%) presumably was again a result of the instability of starting monomer **56**, since an insoluble, dark-red precipitate immediately formed after addition of CuCl and TMEDA.

Scheme 7. *Synthesis of the PPA Polymer* **57**

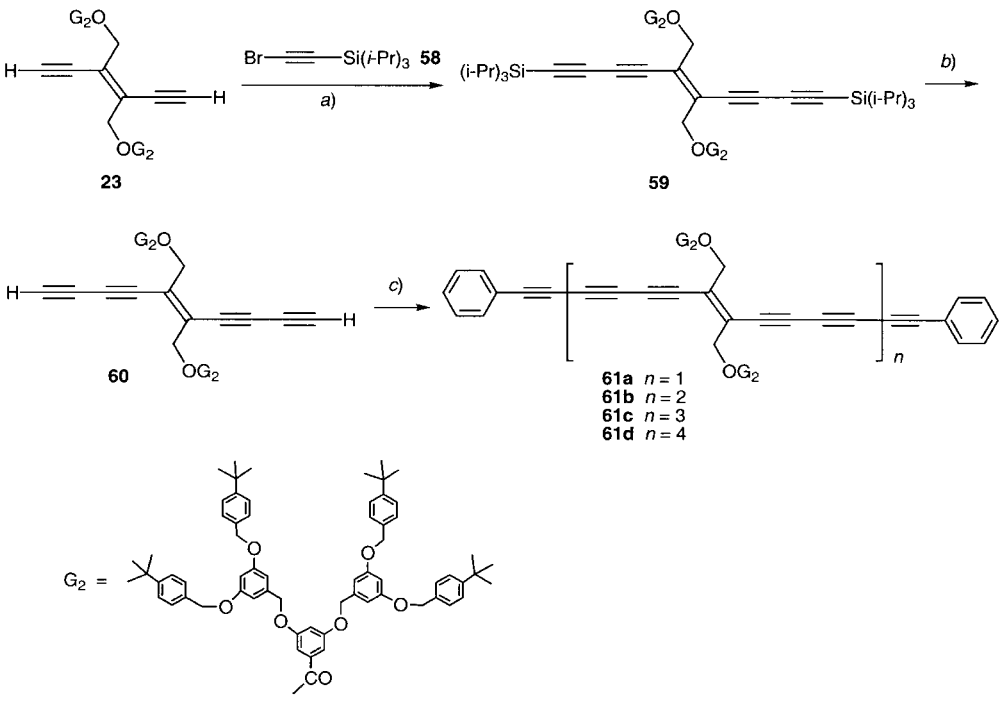


a) [$PdCl_2(PPh_3)_2$], CuI, (i-Pr)$_2$NH, THF, 0°, 2 h; 21% (**55a**), 18% (**55b**), 3% (**55c**). *b*) K_2CO_3, MeOH, 20°, 30 min; 90%. *c*) CuCl, TMEDA, air, CH_2Cl_2, 20°, 2 h; 11%.

PPA Oligomer **57** was found to be highly light-sensitive. Irradiation of a solution of **57** at $\lambda = 366$ nm led to a significant hypochromic effect already after 5 min. After 15 min, all characteristic absorption bands had disappeared. The nature of the chemical processes leading to this photo-bleaching remains to be investigated.

To circumvent the stability and solubility problems encountered in these first series of PPA oligomers, we decided to encapsulate these delicate chromophores into dendritic shells. For this purpose, (*E*)-enediyne **23**, which bears second-generation *Fréchet*-type dendrons, was transformed by *Cadiot-Chodkiewicz* heterocoupling with 1-bromo-3-(triisopropylsilyl)acetylene (**58**) [38] into (*E*)-enetetrayne **59**, which was deprotected with Bu_4NF to give monomer **60** (*Scheme 8*). The latter proved to be highly unstable and was used directly – without isolation – in the oxidative *Hay* oligomerization in the presence of PhC≡CH as end-capping reagent. According to GPC analysis, this reaction produced four main products, and analysis by MALDI-TOF-MS showed that monomeric to tetrameric oligomers **61a**–**d** had formed.

Scheme 8. *Synthesis of the Dendritic PPA Oligomers* **61a**–**d**



a) i-$PrNH_2$, CuCl, $NH_2OH \cdot HCl$, air, 20°, 1 h; 64%. *b*) Bu_4NF, wet THF, 20°, 5 min. *c*) CuCl, TMEDA, PhC≡CH, air, 20°, 1 h; yields not determined.

Monomer **61a** had a slightly higher retention time than the higher oligomers and was readily separated by GPC (CH_2Cl_2). Repeated preparative GPC finally also afforded pure fractions of dimer **61b**, as revealed by analytical GPC. The ^{1}H-NMR spectra, however, showed that monomer **61a** and dimer **61b** were present as mixtures of (*E*)- and (*Z*)-isomers: their *t*-Bu resonances were clearly doubled. Separation of the

(*E*)- and (*Z*)-isomers was achieved chromatographically (SiO_2); however, material quantities were too small to measure their ^{13}C-NMR spectra. It is unclear at present, whether this isomerization occurs thermally or photochemically, or even under both conditions. Trimer **61c** and tetramer **61d** could not be obtained in completely pure form; their MALDI-TOF-MS (matrix: 9-nitroanthracene) still showed the presence of compounds with higher molecular masses. In view of the ready (*E*) → (*Z*) isomerization, which again could be promoted by the dendritic branches (see *Sect. 2.1*), the preparation of PPA oligomers with *Fréchet*-type dendritic wedges was not further pursued.

2.5. *An Organometallic Approach to Dendritic Rods.* Here, we present initial studies towards the preparation of oligomers consisting of Pt-bridged tetraethynylethenes (TEEs, 3,4-diethynylhex-3-ene-1,5-diynes) with dendritic phosphane ligands coordinated to the metal centers to provide solubilization and encapsulation (*Fig. 12*). As ligands, we intended to use *Fréchet*-type dendritic phosphanes such as **62** and **63** (*Fig. 13*) introduced by *Catalano* and *Parodi* [43] (for P-containing dendrimers, see [8e][44]). Additionally, we prepared ligand **64** by reacting benzyl bromide **11** with $NaPPh_2$ (*Scheme 9*).

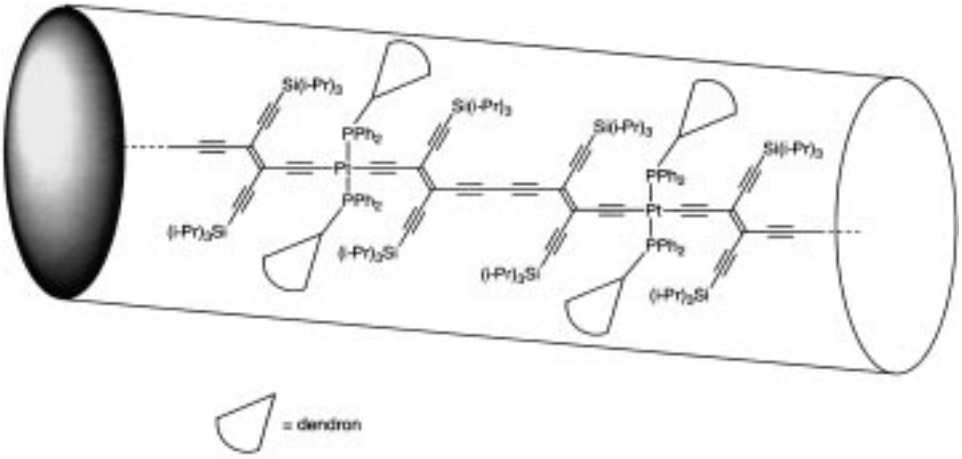


Fig. 12. *Schematic representation of dendritic oligomers made from Pt-bridged tetraethynylethenes*

To test the concept, we chose as the first target compounds *trans*-**65** and *trans*-**66**, two bis(*σ*-acetylene)platinum complexes of tetraethynylethenes [45] with phosphane dendrons ligated to the metal center (*Scheme 10*). Selective removal of their Me_3Si alkyne-protecting groups would provide direct monomeric precursors for oxidative oligomerization under formation of dendritically encapsulated molecular wires of the type shown in *Fig. 12*. For the construction of these systems, we needed the *trans*-dichloroplatinum(II) complexes *trans*-**67** and *trans*-**68** (*Scheme 11*), respectively, which were expected to react with mono-deprotected TEE **69** [46] according the *Hagihara* coupling [47].

For the synthesis of *trans*-**65** and *trans*-**66**, *trans*-[$Pt(NCPh)_2Cl_2$] was prepared by heating $PtCl_2$ in PhCN to 100° [48], and subsequent ligand exchange with **62** or **64**

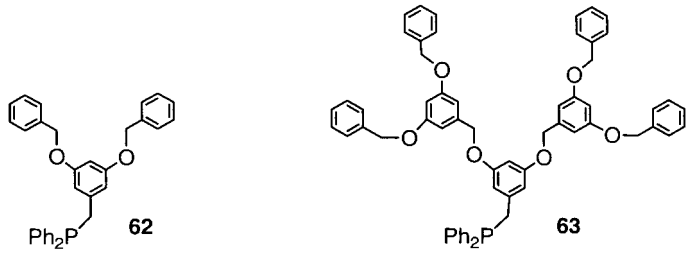
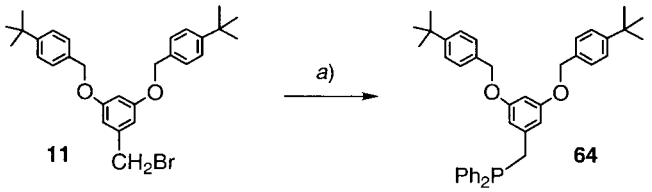


Fig. 13. *Dendritic phosphane ligands* **62** *and* **63** *introduced by* Catalano *and* Parodi [43]

Scheme 9. *Synthesis of the Dendritic Phosphane Ligand* **64**

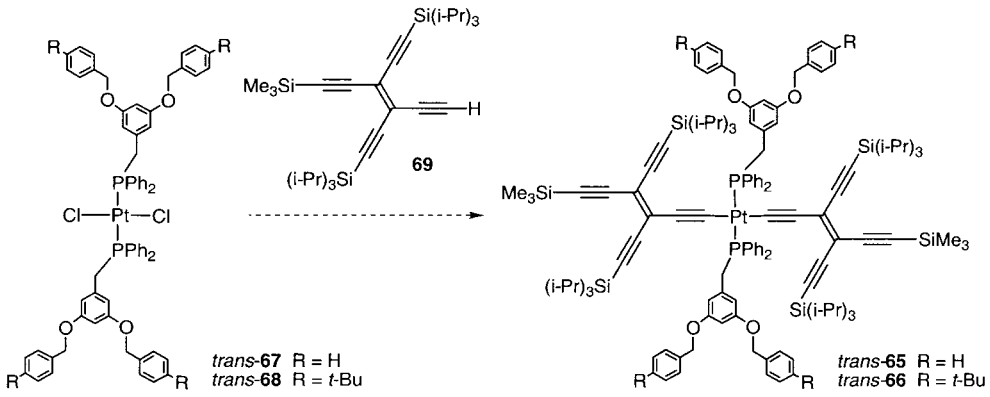


a) Na, NH_3, $ClPPh_2$, THF, $-78° \rightarrow 20°$, 3 h; 72%.

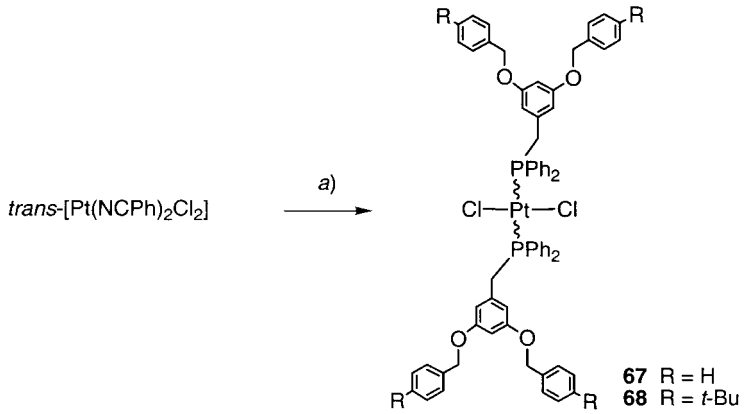
afforded **67** and **68**, respectively, as mixtures of *cis*- and *trans*-isomers (*Scheme 11*). While chromatographic separation of the isomers failed in both cases, fractional crystallization (CH_2Cl_2/EtOH 2 : 1; $-20°$) was successful for **67** and provided isomerically pure *trans*-**67**. Expectedly, the ^{31}P-NMR spectrum (202.5 MHz, $CHCl_3$) displayed only one resonance at 16.01 ppm ($^1J(^{195}Pt,^{31}P) = 2576$ Hz), whereas the ^{195}Pt-NMR spectrum (107.5 MHz, $CDCl_3$) showed one *triplet* at -4007.8 ppm ($^1J(^{195}Pt, ^{31}P) = 2582$ Hz).

The structure of *trans*-**67** was unambiguously revealed by X-ray structure analysis (*Fig. 14*) of crystals obtained at 20° from CH_2Cl_2/EtOH 4 : 1. The complex crystallized in the triclinic space group $P\bar{1}$ with Pt as the inversion center.

Scheme 10. *Projected Synthesis of the Dendritic Bis(σ-acetylene)platinum Complexes* **65** and **66**



Scheme 11. *Synthesis of the Dichloroplatinum(II) Complexes* **67** *and* **68**



a) **62** or **64**, $CHCl_3$, Δ, 45 min, 30% (*trans*-**67**); 60% (**68**).

We subsequently undertook the *Hagihara* coupling of *trans*-**67** with mono-deprotected TEE **69** under the conditions described by *Harriman et al.* and obtained the bis(σ-acetylene)platinum complex **65** in 41% yield (*Scheme 12*) [49]. However, the ^{31}P-NMR spectrum (121.5 MHz, $CDCl_3$) displayed two close resonances at 14.46 ppm

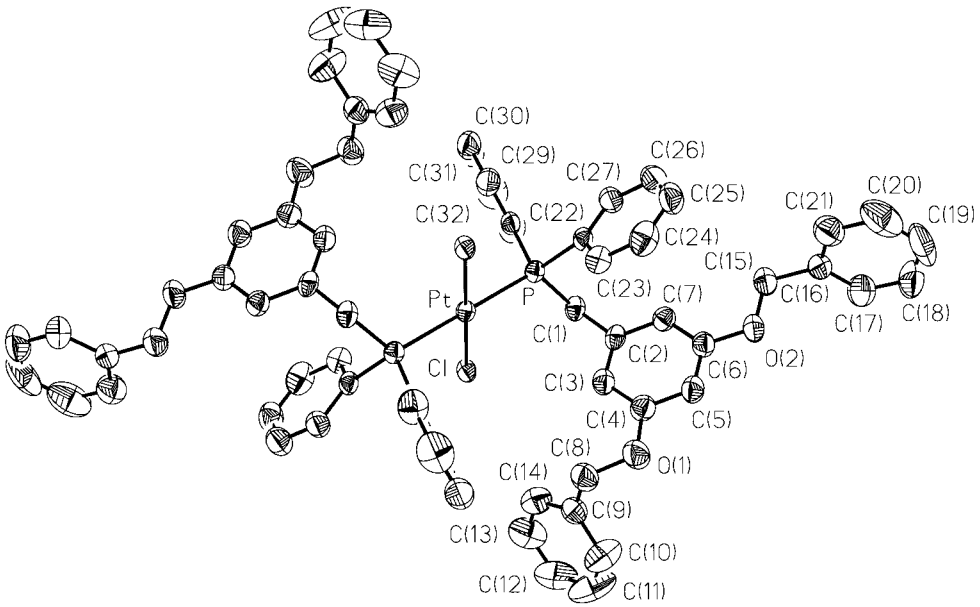
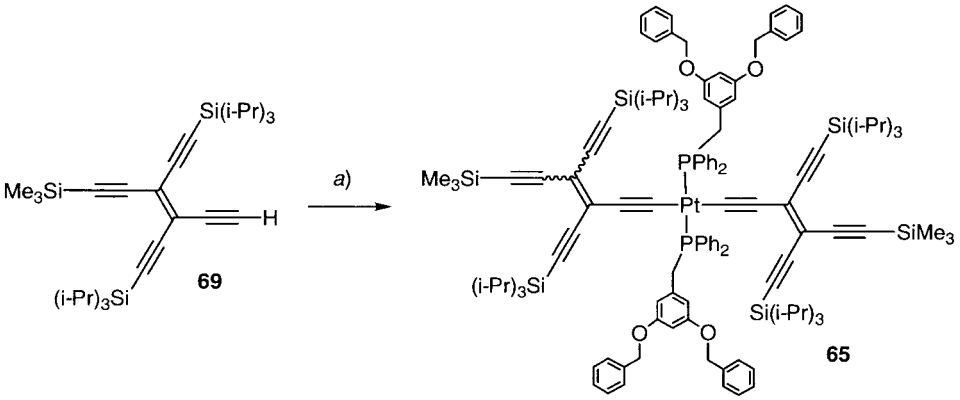


Fig. 14. *X-Ray crystal structure of* trans-**67**. Arbitrary numbering. Atomic displacement parameters obtained at 293 K are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: Pt–P 2.319(3), Pt–Cl 2.343(3), P–C(1) 1.840(7), P–C(22) 1.821(7), P–C(28) 1.816(8), P–Pt–P 180.0, P–Pt–Cl 90.33(11), Cl–Pt–Cl 180.0, C(28)–P–Pt 108.7(2), C(22)–P–Pt 118.6(2), C(1)–P–Pt 118.4(3), C(28)–P–C(22) 104.1(3), C(28)–P–C(1) 104.7(3), C(22)–P–C(1) 100.6(3)

Scheme 12. *The Synthesis of the Dendritic Bis(σ-acetylene)platinum Complex* **65** *Proceeds with (Z)/(E)-Isomerization of the TEE Moieties*



a) *trans*-**67**, CuI, $(i\text{-Pr})_2NH$, THF, 20°, 20 h; 41%.

($^1J(^{195}Pt,^{31}P) = 2540$ Hz) and 14.81 ppm ($^1J(^{195}Pt,^{31}P) = 2514$ Hz), indicating that isomerization had occurred during the coupling. The similar values of the chemical shifts and the coupling constants clearly indicated that both compounds had the same (*trans*) coordination geometry at the Pt center [50]. Indeed, we never had observed *trans* → *cis* isomerization during *Hagihara* couplings at Pt; furthermore, the *trans*-isomers are usually the thermodynamically more stable ones. To explain the formation of two isomers, we, therefore, had to assume that $(E) \rightarrow (Z)$ isomerization at one of the coordinating TEE moieties had occurred.

Photochemical [29][51] and electrochemical [52] $(E) \rightarrow (Z)$ isomerization of TEE and DEE (1,2-diethynylethene) derivatives coupled directly to substituted Ph or other aromatic rings has been well-established in our recent work. In some studies, we also observed this isomerization as an undesired side reaction in the presence of proton sources [23a]. Since we rigorously excluded light and proton sources in the *Hagihara* coupling of **69**, we must conclude that the observed TEE isomerization is a hitherto unobserved process, possibly induced by steric interactions between TEE and phosphane dendrons in **65**. Further investigations to shed light into this process are now underway.

3. Conclusions. – In this paper, the first comprehensive approach towards dendritic encapsulation of monodisperse oligomers with a π-conjugated backbone is described. Poly(triacetylene) (PTA) oligomers were laterally functionalized either with *Fréchet*-type dendrons of generation one (**1a**–**e**), two (**2a**–**c**), or three (**3a**,**b**) or with second-generation carbosilane dendrons (**4a**–**d**). During the course of this investigation, we also synthesized the first series of poly(pentaacetylene) (PPA) oligomers (**5a**–**c**) but found these compounds to be quite insoluble as well as rather unstable. To enhance solubility and stability, we prepared a series of dendritic PPA oligomers **61a**–**d** with laterally appended second-generation *Fréchet*-type wedges; these interesting novel oligomers, however, were not formed in isomerically pure form (see below).

In yet another approach towards dendritic encapsulation of chromophoric molecular rods, we explored the formation of Pt-bridged tetraethynylethene oligomers (*Fig. 12*) bearing solubilizing dendritic phosphane ligands at the metal centers. Our preliminary work demonstrated the synthetic feasibility, but again, isomerization of the monomeric precursor **65** to such rods caused problems that require further investigation.

Physical studies (UV/VIS, electrochemistry) with the PTA oligomers **1**–**4** demonstrated that, in these tubular macromolecules, the insulating layers created by the dendritic wedges protect and stabilize the central conjugated backbone, but do not alter its electronic properties. UV/VIS Spectroscopic measurements indicated that there is no loss of π-electron conjugation along the PTA backbone in the higher-generation compounds, despite their distortion from planarity due to steric overcrowding of the bulky dendritic wedges. Independent of the dendritic generation number, the longer-wavelength absorptions, which originate from electronic transitions within the conjugated PTA backbone, appear at almost the same positions, with nearly identical vibrational fine structure and molar extinction coefficients. π-Electron conjugation involving the acetylenic fragments in the PTA backbone is presumably best described as being cylindrical rather than resulting from orbital overlap within a distinct plane and is therefore fully maintained upon rotation about C(sp)–C(sp^2) and C(sp)–C(sp) single bonds. The observation that effective π-electron conjugation does not require full planarity of the molecule is an important finding for the rich field of acetylenic scaffolding [24b].

This study also raised challenging new questions concerning the $(E) \rightarrow (Z)$ isomerization of tetraethynylethenes (TEEs) and diethynylethenes (DEEs). While this isomerization under photochemical or electrochemical control is quite established through other work from this program [29][51][52], and while some members of these classes of molecules have been shown to undergo proton-induced isomerization [23a], the present study has revealed additional, potentially quite different mechanisms for this isomerization. First, we found that the *Fréchet*-type dendrons of generation three induce $(E) \rightarrow (Z)$ isomerization within the PTA backbone, possibly through photosensitization [30]. Subsequently, we found that the dendritic PPA oligomers **61a**–**d** readily underwent $(E) \rightarrow (Z)$ isomerization within the conjugated backbone, presumably in a thermal process. Finally, monomer **65** for the preparation of dendritic Pt-bridged tetraethynylethene oligomers surprisingly underwent isomerization within the TEE moieties during its preparation by *Hagihara* coupling. Possibly, steric interactions between the TEE moieties and the dendritic phosphane ligands at the Pt center are promoting this thermal process, the exact nature of which remains to be determined in future work. From one viewpoint, these isomerization processes hampered progress in some aspects of the described work, from another viewpoint, however, they could provide the basis for new molecular switches for use in molecular electronics and optical devices [51][53].

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Experimental Part

General. Solvents and reagents were reagent-grade and commercially available and used without further purification unless otherwise stated. Compounds **18** [4][21], **51** [39], **53** [41], **62** [43], and **69** [46] were prepared according to literature procedures. *Karstedt* catalyst ((divinyltetramethyldisiloxane)platinum complex in xylene) was obtained from *United Chemical Technologies, Inc.* 2731 Bartram Road, Bristol, PA 19007. CuI (99.999%) was purchased from *Aldrich*; Bu_3P (85%) from *Fluka*. THF and Et_2O were freshly distilled from sodium benzophenone ketyl. CH_2Cl_2 and $CHCl_3$ were distilled over CaH_2. All reactions were carried out under N_2 or Ar unless otherwise noted. Degassing of solvents for Pd- and Pt-mediated reactions as well as for conversions with three-valent phosphorus derivatives was done by three freeze-pump-thaw cycles. Evaporation *in vacuo* was conducted at H_2O-aspirator pressure. For anal. and spectroscopic characterization, compounds were dried at 10^{-2} Torr. Column chromatography (CC) and flash chromatography (FC): SiO_2 *60* (230–400 mesh, 0.040–0.063 mm) from *E. Merck*, SiO_2 (70–230 mesh, 0.05–0.2 mm) from *Macherey-Nagel*, or SiO_2-*H* (0.005–0.040 mm) from *Fluka*. TLC: glass sheets coated with SiO_2 *60* F_{254} from *E. Merck* or *Macherey-Nagel* glass plates *DURASIL-25 UV254*; visualization by UV light or staining with $KMnO_4$ (0.5 g $KMnO_4$ in 100 ml 1M NaOH) or with a 'mostain' soln. (400 ml 10% aq. H_2SO_4, 20 g $(NH_4)_6Mo_7O_{24} \cdot 6\,H_2O$, 0.6 g $Ce(SO_4)_2$). Prep. GPC: *Bio-Beads S-X1* (styrene-divinylbenzene copolymer, pore size 200–400 μm) from *BIO-RAD* at ambient pressure and temp.; mobile phase: PhMe or CH_2Cl_2; flow rate 5–10 drops min^{-1}. High-performance prep. and anal. GPC: *Merck-Hitachi* HPLC pump *L-7100*, UV detector *L-7400*, RI detector *L-7490,* and *Chromointegrator D-2500*. Anal. separations: two sequential *NovoGrom* columns (*GROM-SDV gel 1000*, 2 × 60 cm, pore diameter: 10 μm) from *GROM Analytik und HPLC*; or two *Shodex GPC KF-802.5* and *Shodex GPC KF-803L* columns, or two *TSK gel G2500 HR* columns (7.8 × 300 mm) from *TosoHaas*; eluent: PhMe, flow rate 0.5 ml min^{-1}. Anal. GPC for oligomeric mass determination: *Knauer GP* chromatograph with *KMX-6-LAALS* (*Low Angle Laser Light Scattering*) detector from *Chromatix* and *Viscotek H-502* differential viscosimeter; data sampling and evaluation with *TriSEC GPC-Software V. 2.7*; column *PL-Gel mixed-C5* from *Polymer Laboratories* (7.5 × 600 mm); calibration with polystyrene standards from *Polymer Laboratories*; eluent: THF, flow rate 1 ml min^{-1}. M.p.: *Büchi B-510* or *Büchi B-540*, uncorrected. UV/VIS Spectra: *Varian-CARY 5* spectrometer; ε [l mol^{-1} cm^{-1}]. IR Spectra (cm^{-1}): *Perkin-Elmer 1600-FT-IR*. NMR Spectra: *Bruker AMX-500* and *Varian Gemini-300* or *-200* at 293 K, with solvent peak (^1H, ^{13}C) or Na_2PtCl_6 (^{195}Pt) as reference. ^{31}P-NMR Spectra were measured with ^1H- and ^{13}C-broad-band decoupling. All NMR spectra were recorded in $CDCl_3$ unless noted otherwise. MS (*m/z* (%)); EI-MS: *VG TRIBRID* spectrometer at 70 eV; FAB-MS: *VG ZAB2-SEQ* spectrometer with 3-nitrobenzyl alcohol (NOBA) as matrix. MALDI-TOF-MS: *Bruker REFLEX* spectrometer; matrices: 9-nitroanthracene and 2,5-dihydroxybenzoic acid (DHB); positive-ion mode at 20-kV acceleration voltage, reflector mode. ESI-MS: *Finnigan TSQ 7000*. High-resolution (HR) MALDI-TOF-MS: *Ion Spec Ultima FT-ICR* mass spectrometer (DHB matrix, 4.7 Tesla) by the two-layer technique (analyte in CH_2Cl_2 is added *via* capillary to the matrix in MeOH/H2O). Elemental analyses were performed by the *Mikrolabor* at the *Laboratorium für Organische Chemie*, *ETH-Zürich.*

Electrochemistry. The electrochemical experiments were carried out at 20 ± 2° in CH_2Cl_2 containing 0.1M Bu_4NPF_6 in a classical three-electrode cell. The working electrode was a glassy C disk electrode used either motionlessly for CV (10 mV s^{-1} to 10 V s^{-1}) or as a rotating disk electrode (RDE). All potentials in the present study are referenced to the ferrocene/ferricinium (Fc/Fc^+) couple used as an internal standard. The auxiliary electrode was a Pt wire, and a Ag wire was used as a pseudo-reference electrode. The accessible range of potentials on the glassy carbon electrode in CH_2Cl_2 was + 1.4 to − 2.4 V *vs.* Fc/Fc^+.

*Methyl 3,5-Bis{[4-(*tert*-butyl)benzyl]oxy}benzoate* (**7**). K_2CO_3 (9.4 g, 68.0 mmol) was added to 4-(*tert*-butyl)benzyl bromide (10 ml, 54.4 mmol), **6** (4.57 g, 27.2 mmol), and [18]crown-6 (1.44 g, 5.4 mmol) in acetone (800 ml). After stirring at reflux for 2 d, filtration of insoluble materials, drying ($MgSO_4$), evaporation *in vacuo*, and recrystallization (PhMe/hexane) afforded **7** (11.38 g, 91%). White needles. M.p. 121°. IR (KBr): 2963, 1717, 1596, 1161, 1158. ^1H-NMR (200 MHz): 1.36 (*s*, 18 H); 3.94 (*s*, 3 H); 5.06 (*s*, 4 H); 6.84 (*t*, *J* = 2.3, 1 H); 7.34 (*d*, *J* = 2.3, 2 H); 7.39 (*d*, *J* = 8.7, 4 H); 7.46 (*d*, *J* = 8.7, 4 H). ^{13}C-NMR (50.8 MHz): 31.26; 34.53; 52.18; 70.18; 107.28; 108.33; 125.63; 127.63; 132.07; 133.50; 151.31; 160.04; 166.96. EI-MS: 460 (2, M^+), 429 (1, $[M - OMe]^+$), 313 (16, $[M - ((t\text{-Bu})C_6H_4CH_2)]^+$), 147 (100, $[(t\text{-Bu})C_6H_4CH_2]^+$). Anal. calc. for $C_{30}H_{36}O4$ (460.62): C 78.23, H 7.88; found: C 78.29, H 8.15.

*3,5-Bis{[4-(*tert*-butyl)benzyl]oxy}benzoic Acid* (**8**). A soln. of **7** (8.72 g, 18.9 mmol) in EtOH (370 ml) was stirred with solid KOH (2.01 g, 35.8 mmol) at reflux for 2 h. After concentration by half and acidification to pH of *ca.* 1 with 1N HCl, the resulting emulsion was extracted with CH_2Cl_2 (3 ×), and the combined org. layers were washed with sat. aq. NaCl soln. Drying ($MgSO_4$) and evaporation *in vacuo* provided **8** (8.45 g, 99%). White

solid. M.p. 195°. IR (KBr): 2963, 1694, 1595, 1162. ^{1}H-NMR (500 MHz): 1.37 (*s*, 18 H); 5.09 (*s*, 4 H); 6.90–6.91 (*m*, 1 H); 7.32–7.52 (*m*, 10 H); 11.8 (br. *s*, 1 H). ^{13}C-NMR (125.8 MHz): 31.33; 34.61; 70.24; 108.19; 108.82; 125.59; 127.58; 131.08; 133.33; 151.25; 159.98; 171.76. EI-MS: 446 (2, M^+), 299 (1, $[M-((t\text{-Bu})C_6H_4CH_2)]^+$, 147 (100, $[(t\text{-Bu})C_6H_4CH_2]^+$). Anal. calc. for $C_{29}H_{34}O_4$ (446.59): C 78.00, H 7.67; found: C 77.79, H 7.81.

*(3,5-Bis{[4-(*tert*-butyl)benzyl]oxy}phenyl)methanol* (**10**). K_2CO_3 (17.3 g, 125 mmol) was added to 4-(*tert*-butyl)benzyl bromide (18.5 ml, 0.100 mmol), **9** (7.00 g, 50.0 mmol), and [18]crown-6 (2.64 g, 10.0 mmol) in acetone (800 ml), and the mixture was heated to reflux for 2 d. Filtration through a plug (SiO_2) and washing with CH_2Cl_2, drying ($MgSO_4$), evaporation *in vacuo*, and recrystallization (EtOH/hexane) afforded **10** (14.48 g, 67%). White needles. M.p. 116–117°. IR ($CHCl_3$): 2967, 1594, 1156. ^{1}H-NMR (300 MHz): 1.38 (*s*, 18 H); 1.98 (*t*, $J=5.6$, 1 H); 4.64 (*d*, $J=5.6$, 2 H); 5.03 (*s*, 4 H); 6.61 (*t*, $J=2.2$, 1 H); 6.67 (*d*, $J=2.2$, 2 H); 7.40 (*d*, $J=8.4$, 4 H); 7.46 (*d*, $J=8.4$, 4 H). ^{13}C-NMR (75.5 MHz): 31.20; 34.45; 65.19; 69.97; 101.23; 105.60; 125.57; 127.57; 133.83; 143.49; 151.14; 160.37. EI-MS: 432 (M^+). Anal. calc. for $C_{29}H_{36}O_3$ (432.61): C 80.52, H 8.39; found: C 80.65, H 8.49.

*5-(Bromomethyl)-1,3-bis{[4-(*tert*-butyl)benzyl]oxy}benzene* (**11**). Ph_3P (5.38 g, 20.5 mmol) was added to **10** (7.09 g, 16.4 mmol) and CBr_4 (6.80 g, 20.5 mmol) in THF (20 ml), and the mixture was stirred for 30 min while a precipitate formed. After dilution with hexane (60 ml), the mixture was filtered through a plug (SiO_2; hexane), and evaporation *in vacuo* yielded a colorless oil that crystallized upon standing to give **11** (8.10 g, 99%). White needles. M.p. 100–101°. IR ($CHCl_3$): 2967, 1594, 1161. ^{1}H-NMR (200 MHz): 1.38 (*s*, 18 H); 4.46 (*s*, 2 H); 5.03 (*s*, 4 H); 6.60 (*t*, $J=2.2$, 1 H); 6.69 (*d*, $J=2.2$, 2 H); 7.42 (*d*, $J=8.1$, 4 H); 7.46 (*d*, $J=8.1$, 4 H). ^{13}C-NMR (75.5 MHz): 31.22; 33.51; 34.49; 70.01; 102.14; 108.05; 125.63; 127.64; 133.64; 139.79; 151.26; 160.30. EI-MS: 46 (M^+). Anal. calc. for $C_{29}H_{35}O_2Br$: C 70.30, H 7.12, Br 16.13; found: C 70.23, H 7.20, Br 15.89.

*Methyl 3,5-Bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]benzoate* (**12**). According to the procedure for **7**, **11** (3.18 g, 6.42 mmol), **6** (540 mg, 3.21 mmol), [18]crown-6 (170 mg, 0.64 mmol), and K_2CO_3 (1.11 g, 8.03 mmol) were reacted in acetone (100 ml) to give, after filtration (SiO_2 plug) and recrystallization (hexane), **12** (3.07 g, 96%). White needles. M.p. 120°. IR (KBr): 2961, 1723, 1597, 1158. ^{1}H-NMR (200 MHz): 1.39 (*s*, 36 H); 3.97 (br. *s*, 3 H); 5.06 (br. *s*, 12 H); 6.66–6.67 (*m*, 2 H); 6.76–6.77 (*m*, 6 H); 6.87–6.88 (*m*, 1 H); 7.34–7.49 (*m*, 16 H). ^{13}C-NMR (75.5 MHz): 31.26; 34.50; 52.21; 69.99; 70.18; 101.66; 106.33; 107.25; 108.46; 125.60; 127.66; 132.17; 133.79; 138.90; 151.18; 159.85; 160.45; 166.86. FAB-MS: 995 (7, $[M-1]^+$), 849 (9, $[M-((t\text{-Bu})C_6H_4CH_2)]^+$), 581 (17, $[M-((t\text{-Bu})C_6H_4CH_2O)_2C_6H_3CH_2]^+$), 415 (11, $[(t\text{-Bu})C_6H_4CH_2O)_2C_6H_3CH_2]^+$), 147 (100, $[(t\text{-Bu})C_6H_4CH_2]^+$). Anal. calc. for $C_{66}H_{76}O_8$ (997.34): C 79.49, H 7.68; found: C 79.51, H 8.01.

*3,5-Bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]benzoic Acid* (**13**). According to the procedure for **8**, **12** (505 mg, 0.51 mmol) and KOH (56 mg, 1.00 mmol) were reacted in EtOH (10 ml), and recrystallization (PhMe/hexane) gave **13** (487 mg, 97%). White needles. M.p. 172°. IR (KBr): 2961, 1692, 1597, 1161. ^{1}H-NMR (500 MHz): 1.33 (*s*, 36 H); 5.01 (*s*, 8 H); 5.03 (*s*, 4 H); 6.60 (*t*, $J=2.2$, 2 H); 6.70 (*d*, $J=2.2$, 4 H); 6.86 (*t*, $J=2.2$, 1 H); 7.36–7.42 (*m*, 18 H). ^{13}C-NMR (125.8 MHz): 31.3; 34.6; 70.0; 70.2; 101.7; 106.3; 108.0; 108.9; 125.5; 127.5; 131.2; 133.7; 138.7; 151.1; 159.8; 160.3 (C=O resonance not observed). FAB-MS: 1005 (21, $[M+Na]^+$); 835 (16, $[M-((t\text{-Bu})C_6H_4CH_2)]^+$), 567 (34, $[M-((t\text{-Bu})C_6H_4CH_2O)_2C_6H_3CH_2]^+$), 415 (22, $[((t\text{-Bu})C_6H_4O)_2C_6H_3CH_2]^+$), 147 (100, $[(t\text{-Bu})C_6H_5CH_2]^+$). Anal. calc. for $C_{65}H_{74}O_8$ (983.31): C 79.40, H 7.59; found: C 79.43, H 7.69.

*{3,5-Bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]phenyl}methanol* (**14**). According to the procedure for **10**, **11** (1.43 g, 2.89 mmol), **9** (203 mg, 1.45 mmol), K_2CO_3 (501 mg, 3.62 mmol), and [18]crown-6 (77 mg, 0.29 mmol) were reacted in acetone (45 ml) to give, after plug filtration (SiO_2; Et_2O) and recrystallization (PhMe/hexane), **14** (1.22 g, 87%). White solid. M.p. 142°. IR (KBr): 3550, 2961, 1597, 1162. ^{1}H-NMR (500 MHz): 1.35 (*s*, 36 H); 4.64 (*d*, $J=6.1$, 2 H); 5.00 (*s*, 4 H); 5.01 (*s*, 8 H); 6.57 (*t*, $J=2.2$, 1 H); 6.60 (*t*, $J=2.2$, 2 H); 6.64 (*d*, $J=2.2$, 2 H); 6.71 (*d*, $J=2.2$, 4 H); 7.38 (*d*, $J=8.4$, 8 H); 7.43 (*d*, $J=8.4$, 8 H). ^{13}C-NMR (125.8 MHz): 31.34; 34.58; 65.31; 70.00; 101.35; 101.50; 105.75; 106.27; 125.53; 127.58; 133.71; 139.20; 143.43; 151.08; 160.12; 160.29. FAB-MS: 968 (19, M^+), 821 (12, $[M-((t\text{-Bu})C_6H_4CH_2)]^+$), 553 (48, $[((t\text{-Bu})C_6H_4CH_2O)_2C_6H_3CH_2]^+$), 415 (30, $[((t\text{-Bu})C_6H_4CH_2O)_2C_6H_3CH_2]^+$), 147 (100, $[(t\text{-Bu})C_6H_4CH_2]^+$). Anal. calc. for $C_{65}H_{76}O_7$ (969.33): C 80.54, H 7.90; found: C 80.25, H 8.09.

*1,3-Bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]-5-(bromomethyl)benzene* (**15**). According to the procedure for **11**, **14** (9.80 g, 10.11 mmol), CBr_4 (4.36 g, 13.15 mmol), and Ph_3P (3.45 g, 13.15 mmol) were reacted in THF (15 ml) to provide, after CC (SiO_2; CH_2Cl_2), **15** (10.34 g, 99%). White solid. M.p. 171°. IR (KBr): 2961, 1596, 1158. ^{1}H-NMR (200 MHz): 1.37 (*s*, 36 H); 4.45 (*s*, 2 H); 5.01 (*s*, 4 H); 5.04 (*s*, 8 H); 6.59–6.73 (*m*, 9 H); 7.40 (*d*, $J=8.5$, 8 H); 7.46 (*d*, $J=8.5$, 8 H). ^{13}C-NMR (50.3 MHz): 31.32; 33.66; 34.56; 69.95; 70.05; 101.54; 102.21; 106.27; 108.14; 125.55; 127.57; 133.67; 138.94; 139.76; 151.06; 159.98; 161.30. FAB-MS: 415 (7, [(*t*-

Bu)$C_6H_4CH_2O)_2C_6H_3CH_2]^+$), 147 (100, [(*t*-Bu)$C_6H_4CH_2]^+$). Anal. calc. for $C_{65}H_{75}O_6Br \cdot H_2O$ (1050.24): C 74.34, H 7.39; found: C 74.25, H 7.43.

*Methyl 3,5-Bis({3,5-bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]benzyl}oxy)benzoate* (**16**). According to the procedure for **7**, **15** (4.041 g, 3.91 mmol), **6** (329 mg, 1.96 mmol), K_2CO_3 (676 mg, 4.89 mmol), and [18]crown-6 (103 mg, 0.39 mmol) were reacted in acetone (390 ml) to give, after filtration (SiO_2 plug; CH_2Cl_2) and CC (SiO_2; CH_2Cl_2/hexane 7:3), **16** (3.03 g, 74%). White solid. M.p. 77°. IR (KBr): 2960, 1723, 1596, 1156. ^{1}H-NMR (200 MHz): 1.37 (*s*, 72 H); 3.90 (*s*, 3 H); 5.00 (br. *s*, 28 H); 6.60 (*m*, 6 H); 6.70 (br. *s*, 12 H); 6.82–6.83 (*m*, 1 H); 7.32 (*d*, *J* = 2.1, 2 H); 7.37 (*d*, *J* = 8.5, 16 H); 7.43 (*d*, *J* = 8.5, 16 H). ^{13}C-NMR (50.3 MHz): 31.17; 34.31; 51.96; 69.74; 101.45; 106.17; 125.41; 127.54; 132.01; 133.75; 138.93; 130.19; 150.87; 159.69; 160.10; 160.26; 166.55. FAB-MS: 2068 (<1, $[M-1]^+$), 1922 (<2, $[M-((t\text{-Bu})C_6H_4CH_2)]^+$), 147 (100, [(*t*-Bu)$C_6H_4CH_2]^+$). Anal. calc. for $C_{138}H_{156}O_{16}$ (2070.77): C 80.04, H 7.59; found: C 80.07, H 7.67.

*3,5-Bis({3,5-bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]benzyl}oxy)benzoic Acid* (**17**). According to the procedure for **8**, **16** (609 mg, 0.29 mmol) and KOH (33 mg, 0.59 mmol) were reacted in EtOH/THF 1:1 (12 ml) containing one drop of H_2O to give **17** (605 mg, 99%). Slightly yellow solid. M.p. 103°. IR (KBr): 2961, 1714, 1596, 1157. ^{1}H-NMR (300 MHz): 1.30 (br. *s*, 72 H); 4.97 (br. *s*, 28 H); 6.57 (br. *s*, 6 H); 6.68 (br. *s*, 12 H); 6.84–6.85 (*m*, 1 H); 7.24–7.38 (*m*, 34 H). ^{13}C-NMR (50.3 MHz): 31.26; 34.50; 69.99; 101.60; 106.36; 125.60; 127.66; 133.79; 138.86; 139.18; 151.15; 159.10; 160.26; 160.42 (C=O resonance not observed). FAB-MS: 2078 (9, $[M\text{H}+\text{Na}]^+$), 147 (100, [(*t*-Bu)$C_6H_4CH_2]^+$). Anal. calc. for $C_{137}H_{154}O_{16} \cdot H_2O$ (2074.76): C 79.31, H 7.58; found: C 79.46, H 7.49.

*[(*E*)-1,6-Bis(triisopropylsilyl)hex-3-ene-1,5-diyne-3,4-diyl]dimethylene Bis(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzoate)* (**19**). Bu_3P (2.4 ml, 8.29 mmol) and TMAD (1.42 g, 8.22 mmol) were sequentially added to a degassed soln. of **18** (1.47 g, 3.28 mmol) and **8** (3.67 g, 8.22 mmol) in THF (20 ml), and the mixture was heated to reflux under N_2 for 1 d. Evaporation *in vacuo* and CC (SiO_2; CH_2Cl_2/hexane 1:1) afforded **19** (3.49 g, 81%). White solid. M.p. 184°. FT-IR (KBr): 2960, 2143, 1725, 1596, 1161. ^{1}H-NMR (200 MHz): 1.00 (*s*, 42 H); 1.34 (*s*, 36 H); 5.03 (*s*, 8 H); 5.24 (*s*, 4 H); 6.82–6.83 (*m*, 2 H); 7.27–7.46 (*m*, 20 H). ^{13}C-NMR (50.3 MHz): 11.00; 18.43; 31.25; 34.52; 64.39; 70.17; 101.34; 107.07; 107.21; 108.67; 125.59; 127.62; 127.66; 131.87; 133.56; 151.27; 159.97; 165.90. FAB-MS: 859 (6, $[M-((t\text{-Bu})C_6H_4CH_2O)_2C_6H_3CO_2]^+$), 429 (100, $[((t\text{-Bu})C_6H_4CH_2O)_2C_6H_3CO]^+$), 147 (97, [(*t*-Bu)$C_6H_4CH_2]^+$). Anal. calc. for $C_{84}H_{112}O_8Si_2$ (1306.00): C 77.25, H 8.64; found: C 77.21, H 8.74.

*[(*E*)-1,6-Bis(triisopropylsilyl)hex-3-ene-1,5-diyne-3,4-diyl]dimethylene Bis{3,5-bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]benzoate}* (**20**). According to the procedure for **19**, **18** (1.01 g, 2.23 mmol), **13** (5.49 g, 5.58 mmol), PBu_3 (1.6 ml, 5.64 mmol), and TMAD (0.966 g, 5.59 mmol) were reacted in THF (20 ml) to give, after CC (SiO_2; CH_2Cl_2/hexane 1:1), **20** (3.25 g, 61%). White solid. M.p. 139°. IR (KBr): 2958, 2143, 1728, 1596, 1160. ^{1}H-NMR (200 MHz): 0.97 (*s*, 42 H); 1.31 (*s*, 72 H); 4.99 (*s*, 24 H); 5.23 (*s*, 4 H); 6.58 (*t*, *J* = 2.3, 4 H); 6.70 (*d*, *J* = 2.3, 8 H); 6.80–6.81 (*m*, 2 H); 7.33–7.44 (*m*, 36 H). ^{13}C-NMR (50.3 MHz): 11.09; 18.55; 31.32; 34.59; 64.49; 70.05; 70.27; 101.66; 106.40; 106.84; 107.19; 108.77; 125.54; 127.57; 127.85; 131.92; 133.76; 138.84; 151.09; 159.76; 160.36. MALDI-TOF-MS (9-nitroanthracene): 2403 ($[M+\text{Na}]^+$). Anal. calc. for $C_{156}H_{192}O_{16}Si_2$ (2379.43): C 78.75, H 8.13; found: C 78.77, H 8.02.

*[(*E*)-1,6-Bis(triisopropylsilyl)hex-3-ene-1,5-diyne-3,4-diyl]dimethylene Bis(3,5-bis({3,5-bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]benzyl}oxy)benzoate)* (**21**). According to the procedure for **19**, **18** (0.10 g, 0.223 mmol), **17** (1.23 g, 0.599 mmol), Bu_3P (0.16 ml, 0.553 mmol), and TMAD (0.098 g, 0.569 mmol) were reacted in THF (20 ml) to give, after GPC (CH_2Cl_2), **21** (39 mg, 4%). White solid. M.p. 94°. IR (KBr): 2952, 2369, 1726, 1596, 1157. ^{1}H-NMR (300 MHz): 0.98 (br. *s*, 42 H); 1.32 (br. *s*, 144 H); 4.98 (br. *s*, 56 H); 5.24 (*s*, 4 H); 6.58 (br. *s*, 12 H); 6.70 (*m*, 24 H); 6.82–6.83 (*m*, 2 H); 7.24–7.38 (*m*, 68 H). ^{13}C-NMR (75.5 MHz): 10.96; 18.45; 31.20; 31.25; 34.47; 64.55; 69.96; 70.24; 101.30; 101.67; 106.35; 106.56; 106.91; 108.84; 125.13; 125.58; 125.64; 127.86; 132.02; 133.83; 138.98; 139.22; 151.16; 159.88; 160.30; 160.45; 165.82. MALDI-TOF-MS (9-nitroanthracene): 4564 (70, $[M+\text{K}]^+$), 4549 (100, $[M+\text{Na}]^+$). Anal. calc. for $C_{300}H_{352}O_{32}Si_2$ (4526.30): C 79.61, H 7.84; found: C 79.90, H 7.64.

*[(*E*)-Hex-3-ene-1,5-diyne-3,4-diyl]dimethylene Bis(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzoate)* (**22**). A soln. of **19** (2.10 g, 1.61 mmol) and Bu_4NF (2 ml of a 1M soln. in THF, 2.0 mmol) in wet THF was stirred for 1 h. CH_2Cl_2 was added, and the mixture was washed with sat. aq. NH_4Cl soln. and dried ($MgSO_4$). Evaporation *in vacuo* and recrystallization (Et_2O) provided **22** (1.75 g, 99%). Off-white crystals. M.p. 162°. IR (KBr): 3258, 2962, 1717, 1592, 1159. ^{1}H-NMR (300 MHz): 1.33 (*s*, 36 H); 3.59 (*s*, 2 H); 5.03 (*s*, 8 H); 5.17 (*s*, 4 H); 6.82 (*t*, *J* = 2.4, 2 H); 7.35–7.44 (*m*, 20 H). ^{13}C-NMR (75.5 MHz): 32.21; 34.52; 64.20; 70.17; 78.42; 90.85; 107.43; 108.56; 122.66; 127.67; 128.16; 131.67; 133.48; 151.35; 160.06; 166.01. FAB-MS: 992 (<2, M^+), 429 (100, $[((t\text{-Bu})C_6H_4CH_2O)_2C_6H_3CO]^+$), 147 (87, [(*t*-Bu)$C_6H_4CH_2]^+$). Anal. calc. for $C_{66}H_{72}O_8 \cdot 0.5\,H_2O$ (1002.31): C 79.09, H 7.34; found: C 79.12, H 7.35.

*[(*E*)-Hex-3-ene-1,5-diyne-3,4-diyl]dimethylene Bis{3,5-bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]-benzoate}* (**23**). According to the procedure for **22**, **20** (2.02 g, 0.849 mmol) and Bu_4NF (2.0 ml of a 1M soln. in THF, 2.0 mmol) were reacted in wet THF to give, after precipitation from Et_2O, **23** (1.70 g, 97%). White solid. M.p. 107°. IR (KBr): 3286, 2961, 1726, 1597, 1158. ^{1}H-NMR (200 MHz): 1.30 (*s*, 72 H); 3.58 (*s*, 2 H); 4.96 (*s*, 24 H); 5.16 (*s*, 4 H); 6.58–6.59 (*m*, 4 H); 6.68 (*d*, *J* = 2.2, 8 H); 6.80–6.81 (*m*, 2 H); 7.24–7.44 (*m*, 36 H). ^{13}C-NMR (50.3 MHz): 31.27; 34.48; 64.09; 69.91; 70.10; 78.38; 90.95; 101.59; 106.28; 107.42; 108.61; 125.46; 127.52; 127.97; 128.16; 129.03; 131.62; 133.65; 138.76; 150.95; 159.71; 160.25; 165.65. MALDI-TOF-MS (9-nitroanthracene): 2091 ([*M* + Na]$^+$). Anal. calc. for $C_{138}H_{154}O_{16}$ (2066.74): C 80.20, H 7.41; found: C 79.86, H 7.46.

*[(*E*)-Hex-3-ene-1,5-diyne-3,4-diyl]dimethylene Bis[3,5-bis({3,5-bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}ben-zyl)oxy]benzyl}oxy)benzoate]* (**24**). According to the protocol for **22**, **21** (0.2 g, 0.04 mmol) and Bu_4NF (0.1 ml of a 1M soln. in THF, 0.1 mmol) were reacted in wet THF (20 ml) to give, after precipitation from Et_2O, **24** (152 mg, 90%). White solid. M.p. 89°. IR (KBr): 3286, 2961, 1726, 1596, 1156. ^{1}H-NMR (200 MHz): 1.33 (br. *s*, 144 H); 3.62 (*s*, 2 H); 4.98 (br. *s*, 56 H); 5.16 (*s*, 4 H); 6.62 (*t*, *J* = 2.2, 12 H); 6.73 (*d*, *J* = 2.2, 24 H); 6.86 (*t*, *J* = 2.2, 2 H); 7.24–7.45 (*m*, 68 H). ^{13}C-NMR (75.5 MHz): 29.58; 30.23; 31.22; 34.11; 34.45; 64.20; 69.46; 70.04; 70.17; 78.41; 90.78; 101.62; 101.75; 106.36; 106.56; 107.45; 108.73; 125.57; 127.64; 133.78; 133.82; 138.96; 139.20; 151.14; 159.86; 160.28; 160.43; 165.85. MALDI-TOF-MS (9-nitroanthracene): 4238 ([*M* + Na]$^+$). Anal. calc. for $C_{282}H_{312}O_{32}$ (4213.61): C 80.21, H 7.66; found: C 79.92, H 7.70.

Oxidative Oligomerization of **22**. TMEDA (80 mg, 0.10 ml, 0.69 mmol) and CuCl (22 mg, 0.02 mmol) were added to **22** (200 mg, 0.202 mmol) and PhC≡CH (41 mg, 0.402 mmol) in dry CH_2Cl_2 (10 ml) over molecular sieves (4 Å), and the mixture was stirred in air for 2 h. After addition of sat. aq. NH_4Cl soln., the mixture was exhaustively extracted with CH_2Cl_2. The combined org. phases were washed with sat. aq. NaCl soln. and dried ($MgSO_4$). GPC (CH_2Cl_2) and FC (SiO_2; CH_2Cl_2/hexane 1:1), followed by precipitation from MeOH, gave the pure oligomers **1a**–**e**.

*[(*E*)-1,10-Diphenyldec-5-ene-1,3,7,9-tetrayne-5,6-diyl]dimethylene Bis(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}-benzoate)* (**1a**). Yield: 41 mg (17%). M.p. 199°. UV/VIS ($CHCl_3$): 259 (68 000), 324 (29 600), 361 (46 500), 388 (35 400). IR (KBr): 2956, 2200, 1722, 1594, 1161. ^{1}H-NMR (200 MHz): 1.33 (*s*, 36 H); 5.06 (*s*, 8 H); 5.25 (*s*, 4 H); 6.85 (*t*, *J* = 2.4, 2 H); 7.26–7.44 (*m*, 30 H). ^{13}C-NMR (50.3 MHz): 31.19; 34.56; 64.40; 70.17; 73.41; 76.52; 87.67; 88.75; 107.76; 108.43; 121.06; 125.54; 127.63; 128.43; 129.22; 129.67; 131.51; 132.56; 133.35; 151.13; 159.92; 165.82. MALDI-TOF-MS (9-nitroanthracene): 1216 ([*M* + Na]$^+$). Anal. calc. for $C_{82}H_{80}O_8$ (1193.55): C 82.52, H 6.76; found: C 82.66, H 6.73.

*[(5*E*,11*E*)-1,16-Diphenylhexadeca-5,11-diene-1,3,7,9,13,15-hexayne-5,6,11,12-tetrayl]tetramethylene Tetra-kis(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzoate)* (**1b**). Yield: 26 mg (6%). M.p. 98°. UV/VIS ($CHCl_3$): 264 (143 000), 362 (60 000), 387 (72 000), 422 (51 500). IR (KBr): 2960, 2200, 1728, 1595, 1158. ^{1}H-NMR (300 MHz): 1.31 (*s*, 36 H); 1.32 (*s*, 36 H); 4.98 (*s*, 12 H); 5.01 (*s*, 8 H); 5.09 (*s*, 4 H); 6.76 (*t*, *J* = 2.4, 2 H); 6.81 (*t*, *J* = 2.4, 2 H); 7.26–7.43 (*m*, 50 H). ^{13}C-NMR (75.5 MHz): 31.22; 34.47; 63.94; 64.06; 70.14; 73.41; 76.37; 82.45; 87.53; 88.23; 89.68; 107.72; 108.26; 108.43; 121.10; 125.58; 125.61; 127.70; 127.81; 128.53; 129.82; 130.32; 131.44; 132.54; 132.67; 133.38; 133.43; 151.22; 152.29; 160.03; 160.06; 165.67; 165.77. MALDI-TOF-MS (9-nitroanthracene): 2209 ([*M* + Na]$^+$). Anal. calc. for $C_{148}H_{150}O_{16}$ (2184.84): C 81.36, H 6.92; found: C 81.17, H 6.78.

*[(5*E*,11*E*,17*E*)-1,22-Diphenyldocosa-5,11,17-triene-1,3,7,9,13,15,19,21-octayne-5,6,11,12,17,18-hexayl]hexa-methylene Hexakis(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzoate)* (**1c**). Yield: 19 mg (3%). M.p. 96°. UV/VIS (CHCl3): 266 (164 500), 397 (71 300), 420 (71 200). IR (KBr): 2960, 2203, 1724, 1595, 1159. ^{1}H-NMR (500 MHz): 1.29 (*s*, 36 H); 1.30 (*s*, 36 H); 1.31 (*s*, 36 H); 4.87 (*s*, 4 H); 4.94 (*s*, 8 H); 4.96 (*s*, 8 H); 4.98 (*s*, 4 H); 5.00 (*s*, 8 H); 5.08 (*s*, 4 H); 6.72 (*t*, *J* = 2.3, 2 H); 6.75 (*t*, *J* = 2.3, 2 H); 6.81 (*t*, *J* = 2.3, 2 H); 7.26–7.43 (*m*, 70 H). ^{13}C-NMR (125.8 MHz): 29.69; 31.32; 34.56; 63.78; 64.06; 70.22; 73.46; 76.43; 82.34; 83.06; 87.37; 88.29; 88.33; 89.81; 107.72; 107.84; 108.37; 108.42; 108.52; 121.10; 125.49; 125.51; 127.59; 127.66; 128.08; 128.43; 128.85; 129.54; 129.71; 130.86; 130.99; 131.35; 131.40; 131.56; 132.59; 133.38; 133.42; 151.11; 151.12; 151.15; 159.96; 159.99; 165.35; 165.56. MALDI-TOF-MS (9-nitroanthracene): 3199 ([*M* + Na]$^+$). Anal. calc. for $C_{214}H_{220}O_{24}$ (3176.13): C 80.93, H 6.98; found: C 80.92, H 6.97.

*[(5*E*,11*E*,17*E*,23*E*)-1,28-Diphenyloctacosa-5,11,17,23-tetraene-1,3,7,9,13,15,19,21,25,27-decayne-5,6,11,12,17,18,23,24-octayl]octamethylene Octakis(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzoate)* (**1d**). Yield: 8 mg (1%). M.p. 94°. UV/VIS ($CHCl_3$): 269 (278 000), 397 (85 900), 423 (89 000). IR (KBr): 2955, 2200, 1728, 1594, 1156. ^{1}H-NMR (500 MHz): 1.27 (*s*, 36 H); 1.28 (*s*, 36 H); 1.29 (*s*, 36 H); 1.30 (*s*, 36 H); 4.87 (*s*, 8 H); 4.92 (*s*, 8 H); 4.93 (*s*, 12 H); 4.95 (*s*, 12 H); 5.06 (*s*, 8 H); 6.71 (*t*, *J* = 2.4, 2 H); 6.72 (*t*, *J* = 2.4, 2 H); 6.74 (*t*, *J* = 2.4, 2 H); 6.80 (*t*, *J* = 2.4, 2 H); 7.24–7.41 (*m*, 90 H). ^{13}C-NMR (125.8 MHz): 29.70; 31.32; 31.58; 34.55; 34.56; 63.76; 63.85; 64.04; 70.20; 70.24; 73.47; 76.41; 82.28; 82.83; 83.11; 87.35; 88.12; 88.29; 88.45; 89.84; 107.71; 107.84; 108.42; 108.51; 121.10; 125.49; 125.51; 127.60; 127.66; 128.02; 128.43; 129.17; 129.71; 130.16; 131.09; 131.31; 131.36;

131.39; 131.56; 132.59; 133.38; 133.42; 151.11; 141.15; 159.96; 159.99; 165.33; 165.39; 165.56. MALDI-TOF-MS (9-nitroanthracene): 4189.6 ([$M+Na$]$^+$). Anal. calc. for $C_{280}H_{290}O_{32}\cdot 4\,H_2O$ (4239.48): C 79.33, H 7.09; found: C 79.48, H 7.38.

*[(5*E*,11*E*,17*E*,23*E*,29*E*)-1,34-Diphenyltetratriaconta-5,11,17,23,29-pentaene-1,3,7,9,13,15,19,21,25,27,31,33-dodecayne-5,6,11,12,17,18,23,24,29,30-decayl]decamethylene Decakis(3,5-bis{[4-(*tert-*butyl)benzyl]oxy}benzoate)* (**1e**). Yield: 4 mg (0.4%). M.p. 93°. UV/VIS ($CHCl_3$): 272 (320000), 397 (80800), 462 (95000). IR (KBr): 2957, 2199, 1726, 1594, 1156. ^{1}H-NMR (500 MHz): 1.26 (*s*, 36 H); 1.27 (*s*, 36 H); 1.28 (*s*, 36 H); 1.29 (*s*, 36 H); 1.30 (*s*, 36 H); 4.85 (*s*, 8 H); 4.90 (*s*, 16 H); 4.92 (*s*, 8 H); 4.94 (*s*, 12 H); 4.98 (*s*, 12 H); 5.05 (*s*, 4 H); 6.71 – 6.72 (*m*, 6 H); 6.73 (*t*, $J=2.4$, 2 H); 6.80 (*t*, $J=2.4$, 2 H); 7.24 – 7.47 (*m*, 110 H). ^{13}C-NMR (75.5 MHz): 29.60; 31.22; 34.45; 63.78: 64.01; 70.12; 73.42; 76.35; 82.23; 82.73; 82.82; 83.07; 87.32; 88.08; 88.20; 88.29; 88.45; 89.85; 107.69; 107.82; 108.39; 108.48; 121.11; 125.58; 127.70; 127.77; 128.06; 128.53; 129.14; 129.84; 130.32; 131.16; 131.34; 131.41; 131.60; 132.68; 133.41; 133.46; 151.24; 160.06; 165.48; 165.72. MALDI-TOF-MS (9-nitroanthracene): 5198 ([$M+K$]$^+$), 5182 ([$M+Na$]$^+$). Anal. calc. for $C_{346}H_{360}O_{40}$ (5158.70): C 80.56, H 7.03; found: C 80.33, H 7.28.

Oxidative Oligomerization of **23**. According to the procedure for **1a** – **e**, **23** (200 mg, 0.097 mmol), PhC≡CH (20 mg, 0.196 mmol), CuCl (1 mg, 0,01 mmol), and TMEDA (4 mg, 0.005 ml, 0.035 mmol) were reacted in dry CH_2Cl_2 over molecular sieves (4 Å) in the air to give, after GPC (CH_2Cl_2), FC (SiO_2; CH_2Cl_2/hexane 1:1), and precipitation from MeOH, the pure oligomers **2a** – **c**.

*[(*E*)-1,10-Diphenyldec-5-ene-1,3,7,9-tetrayne-5,6-diyl]dimethylene Bis{3,5-bis[(3,5-bis{[4-(*tert-*butyl)benzyl]oxy}benzyl)oxy]benzoate}* (**2a**). Yield: 20 mg (9%). M.p. 98°. UV/VIS ($CHCl_3$): 260 (56000), 323 (28100), 361 (45800), 390 (37200). IR (KBr): 2956, 2204, 1729, 1594, 1158. ^{1}H-NMR (200 MHz): 1.32 (*s*, 72 H); 4.98 (*s*, 16 H); 5.04 (*s*, 8 H); 5.24 (*s*, 4 H); 6.58 (*t*, $J=2.4$, 4 H); 6.70 (*d*, $J=2.4$, 8 H); 6.84 (*t*, $J=2.4$, 2 H); 7.24 – 7.41 (*m*, 46 H). ^{13}C-NMR (50.3 MHz): 29.61; 31.23; 34.47; 64.34; 69.92; 70.24; 73.41; 76.52; 87.79; 88.87; 101.76; 106.43; 107.82; 108.55; 121.03; 125.56; 127.63; 128.46; 129.22; 129.72; 131.69; 132.58; 133.79; 138.77; 151.15; 159.91; 160.39; 165.85. MALDI-TOF-MS (9-nitroanthracene): 2290 ([$M+Na$]$^+$). Anal. calc. for $C_{154}H_{160}O_{16}$ (2266.98): C 81.59, H 7.11; found: C 81.32, H 6.87.

*[(5*E*,11*E*)-1,16-Diphenylhexadeca-5,11-diene-1,3,7,9,13,15-hexayne-5,6,11,12-tetrayl]tetramethylene Tetrakis{3,5-bis[(3,5-bis{[4-(*tert-*butyl)benzyl]oxy}benzyl)oxy]benzoate}* (**2b**). Yield: 25 mg (6%). M.p. 79°. UV/VIS ($CHCl_3$): 314 (83000), 361 (50800), 390 (69000), 423 (52500). IR (KBr): 2952, 2214, 1738, 1596, 1158. ^{1}H-NMR (300 MHz): 1.29 (*s*, 72 H); 1.31 (*s*, 72 H); 4.93 (*s*, 48 H); 5.09 (*s*, 8 H); 6.54 – 6.56 (*m*, 8 H); 6.64 – 6.66 (*m*, 16 H); 6.73 (*t*, $J=2.3$, 2 H); 6.79 (*t*, $J=2.3$, 2 H); 7.20 – 7.40 (*m*, 82 H). ^{13}C-NMR (50.8 MHz): 29.57; 31.18; 31.25; 34.41; 34.44; 64.02; 69.88; 70.14; 73.46; 76.39; 82.61; 87.71; 88.31; 89.77; 101.70; 106.40; 108.45; 120.97; 125.53; 127.65; 128.33; 128.48; 129.77; 130.50; 131.49; 131.63; 132.62; 133.82; 133.83; 151.03; 151.11; 159.86; 159.90; 160.38; 165.62; 165.67. MALDI-TOF-MS (9-nitroanthracene): 4353 ([$M+Na$]$^+$). Anal. calc. for $C_{292}H_{310}O_{32}$ (4331.71): C 80.97, H 7.21; found: C 80.71, H 7.13.

*[(5*E*,11*E*,17*E*)-1,22-Diphenyldocosa-5,11,17-triene-1,3,7,9,13,15,19,21-octayne-5,6,11,12,17,18-hexayl]hexamethylene Hexakis{3,5-bis[(3,5-bis{[4-(*tert-*butyl)benzyl]oxy}benzyl)oxy]benzoate}* (**2c**). Yield: 12 mg (2%). M.p. 80°. UV/VIS ($CHCl_3$): 313 (60200), 397 (69700), 420 (69500). IR (KBr): 2956, 2200, 1728, 1594, 1156. ^{1}H-NMR (500 MHz): 1.26 (*s*, 72 H); 1.27 (*s*, 72 H); 1.31 (*s*, 72 H); 4.86 (*s*, 8 H); 4.87 (*s*, 8 H); 4.88 (*s*, 16 H); 4.90 (*s*, 16 H); 4.91 (*s*, 8 H); 4.92 (*s*, 16 H); 5.00 (*s*, 4 H); 5.01 (*s*, 4 H); 5.03 (*s*, 4 H); 6.51 (*t*, $J=2.3$, 4 H); 6.53 (*t*, $J=2.3$, 4 H); 6.55 (*t*, $J=2.3$, 4 H); 6.60 – 6.64 (*m*, 24 H); 6.69 (*t*, $J=2.3$, 2 H); 6.70 (*t*, $J=2.3$, 2 H); 6.77 (*t*, $J=2.3$, 2 H); 7.23 – 7.38 (*m*, 118 H). ^{13}C-NMR (100.6 MHz): 29.68; 31.29; 34.47; 34.49; 34.52; 64.02; 69.85; 70.08; 70.57; 73.46; 76.43; 82.46; 83.15; 87.54; 88.29; 88.35; 89.86; 101.69; 106.30; 106.39; 107.56; 108.36; 120.99; 125.40; 125.42; 125.45; 127.54; 128.34; 128.48; 129.74; 130.53; 131.32; 131.56; 132.50; 133.72; 138.69; 150.82; 150.87; 150.95; 159.68; 160.19; 165.33. MALDI-TOF-MS (9-nitroanthracene): 6415 ([$M+Na$]$^+$). Anal. calc. for $C_{430}H_{460}O_{48}$ (6396.43): C 80.75, H 7.25; found: C 80.73, H 7.29.

Oxidative Oligomerization of **24**. According to the procedure for **1a** – **e**, **24** (100 mg, 0.024 mmol), PhC≡CH (5.1 mg, 0.050 mmol), CuCl (1 mg, 0.01 mmol), and TMEDA (2.5 mg, 0.02 mmol) were reacted in dry CH_2Cl_2 over molecular sieves (4 Å) in the air to give, after GPC (CH_2Cl_2), FC (SiO_2; CH_2Cl_2/hexane 1:1), and precipitation from MeOH, the pure oligomers **3a**, **b**.

*[(*E*)-1,10-Diphenyldec-5-ene-1,3,7,9-tetrayne-5,6-diyl]dimethylene Bis(3,5-bis({3,5-bis[(3,5-bis{[4-(*tert-*butyl)benzyl]oxy}benzyl)oxy]benzyl}oxy)benzoate)* (**3a**). Yield: 14 mg (13%). M.p. 91°. UV/VIS ($CHCl_3$): 323 (25800), 363 (45200), 389 (38100). IR (KBr): 2955, 2211, 1728, 1594, 1156. ^{1}H-NMR (200 MHz): 1.29 (br. *s*, 144 H); 4.91 (*s*, 16 H); 4.96 (br. *s*, 32 H); 4.99 (br. *s*, 8 H); 5.19 (*s*, 4 H); 6.55 (*t*, $J=2.1$, 12 H); 6.66 (*d*, $J=2.1$, 24 H); 6.82 (*t*, $J=2.1$, 2 H); 7.15 – 7.41 (*m*, 78 H). ^{13}C-NMR (100.6 MHz): 29.69; 30.91; 31.12; 31.32; 34.55; 64.31; 69.96; 70.02; 70.24; 73.44; 76.51; 87.83; 88.94; 101.56; 101.79; 106.30; 106.55; 107.69; 108.51; 120.90; 125.50; 127.24;

127.56; 128.41; 129.09; 129.68; 131.63; 132.47; 133.71; 138.74; 139.08; 151.01; 159.78; 160.09; 160.25; 165.65. MALDI-TOF-MS (9-nitroanthracene): 4436 ($[M+Na]^+$). Anal. calc. for $C_{298}H_{320}O_{32}$ (4413.85): C 81.09, H 7.31; found: C 80.83, H 7.33.

*[(5*E*,11*E*)-1,16-Diphenylhexadeca-5,11-diene-1,3,7,9,13,15-hexayne-5,6,11,12-tetrayl]tetramethylene Tetrakis[3,5-bis({3,5-bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]benzyl}oxy)benzoate]* (**3b**): Yield: 6 mg (3%). UV/VIS ($CHCl_3$): 310 (82600), 362 (69600), 391 (77500), 425 (53000). ^{1}H-NMR (500 MHz): 1.23 (*s*, 144 H); 1.26 (*s*, 144 H); 4.82–5.03 (*m*, 120 H); 6.40–6.65 (*m*, 72 H); 7.20–7.40 (*m*, 146 H). MALDI-TOF-MS (9-nitroanthracene): 8650 ($[M+K]^+$).

4-(Prop-2-enyl)phenol (**27**). 1M BBr_3 in CH_2Cl_2 (100 ml, 0.1 mol) was added to a soln. of **25** (15.36 ml, 0.1 mol) in dry CH_2Cl_2 (250 ml) cooled to $-70°$. The mixture was slowly warmed over 2 h to $+15°$, and ice water was carefully added. The org. phase was extracted with 5% aq. NaOH soln., the aq. phase was acidified to pH 6 with 1N HCl and extracted with Et_2O. Drying (Na_2SO_4), evaporation *in vacuo*, and bulb-to-bulb distillation gave **27** (9.5 g, 70%). Clear oil. IR ($CHCl_3$): 3598, 3341, 3014, 1730, 1613, 1513, 1253. ^{1}H-NMR (200 MHz): 3.32 (*d*, *J* = 6.6, 2 H); 4.71 (*s*, 1 H); 5.00–5.02 (*m*, 1 H); 5.03–5.11 (*m*, 1 H); 5.85–6.05 (*m*, 1 H); 6.77 (*d*, *J* = 8.7, 2 H); 7.06 (*d*, *J* = 8.7, 2 H). ^{13}C-NMR (75.5 MHz): 39.14; 115.36; 115.50; 129.79; 132.47; 137.86; 153.51. EI-MS: 134 (100, M^+).

*1-(*tert*-Butoxy)-4-(prop-2-enyl)benzene* (**26**). Dry CH_2Cl_2 (25 ml) was added into a 100-ml flask and cooled to $-78°$. Gaseous isobutene was bubbled into the solvent at that temp. until the volume had increased by 20 ml. After addition of **27**, the reaction was started by syringe injection of CF_3SO_3H (0.180 ml, 2 mmol) and the mixture was stirred for 3 h at $-78°$. After addition of Et_3N (0.384 ml, 2.75 mmol), the mixture was slowly warmed to 20°, then evaporated *in vacuo*. Pentane was added to the residue, and the mixture was filtered, dried (Na_2SO_4), and evaporated *in vacuo*. Bulb-to-bulb distillation afforded **26** (3.66 g, 96%). Clear oil. IR ($CHCl_3$): 2979, 1638, 1607, 1504, 1366, 1160, 893. ^{1}H-NMR (200 MHz): 1.33 (*s*, 9 H); 3.35 (*d*, *J* = 6.7, 2 H); 5.01–5.05 (*m*, 1 H); 5.07–5.12 (*m*, 1 H); 5.87–6.08 (*m*, 1 H); 6.91 (*d*, *J* = 8.3, 2 H); 7.08 (*d*, *J* = 8.3, 2 H). ^{13}C-NMR (75 MHz): 28.71; 39.45; 78.13; 115.62; 124.26; 128.93; 134.98; 137.78; 153.62. EI-MS: 190 (M^+). Anal. calc. for $C_{13}H_{18}O$ (190.28): C 82.06, H 9.53; found: C 82.18, H 9.39.

1-Methoxy-4-{3-[tri(prop-2-enyl)silyl]propyl}benzene (**30**). Allyl bromide (23.36 ml, 0.27 mol) in dry Et_2O (300 ml) was added to a suspension of Mg chips (6.56 g, 0.27 mol) in dry Et_2O (200 ml) at a rate to maintain the mixture at reflux. After complete addition, the mixture was heated to reflux for 1 h. A mixture of $HSiCl_3$ (70 ml, 0.67 mol), **25** (10 g, 0.067 mol), and *Karstedt* catalyst (3% soln. in xylene; 0.03 ml, 1.425 mmol) was stirred for 2 h, until ^{1}H-NMR monitoring indicated completion of the hydrosilylation. Excess $HSiCl_3$ was evaporated *in vacuo* and recovered in a cooling trap. The oily residue was dissolved in dry THF (30 ml), and the soln. was added dropwise with a syringe over 1 h at 20° to the pre-prepared *Grignard* soln. After 6 h, the mixture was filtered and the precipitate washed exhaustively with Et_2O. Ice-water and sat. aq. NH_4Cl soln. were added to the combined org. liquors. The aq. layer was washed with Et_2O (2×), and the combined org. phases were washed with H_2O and sat. aq. NaCl soln. Drying (Na_2SO_4), evaporation *in vacuo*, and FC (SiO_2; hexane/AcOEt 100:1), followed by bulb-to-bulb distillation afforded **30** (12.5 g, 61%). Clear oil. IR ($CHCl_3$): 3078, 2921, 1628, 1512, 1248, 1176, 1036, 899, 811. ^{1}H-NMR (300 MHz): 0.58–0.66 (*m*, 2 H); 1.51–1.70 (*m*, 8 H); 2.55 (*t*, *J* = 7.5, 2 H); 3.79 (*s*, 3 H); 4.82–4.91 (*m*, 6 H); 5.66–5.87 (*m*, 3 H); 6.82 (*d*, *J* = 8.7, 2 H); 7.08 (*d*, *J* = 8.7, 2 H). ^{13}C-NMR (75.5 MHz): 11.12; 19.44; 25.72; 38.87; 55.16; 113.61; 113.72; 129.38; 134.45; 134.56; 157.86. ^{29}Si-NMR (79.5 MHz): −0.3. EI-MS: 300 (M^+). Anal. calc. for $C_{19}H_{28}OSi$ (300.51): C 75.94, H 9.39; found: C 75.74, H 9.45.

*1-(*tert*-Butoxy)-4-{3-[tri(prop-2-enyl)silyl]propyl}benzene* (**31**). According to the procedure for **30**, the *Grignard* reagent was prepared from Mg chips (511 mg, 21 mmol) in dry Et_2O (25 ml) and allyl bromide (1.82 ml, 27 mmol) in dry Et_2O (25 ml). Hydrosilylation occurred with $HSiCl_3$ (5.3 ml, 0.52 mmol), **26** (1 g, 5.25 mmol), and *Karstedt* catalyst (0.01 ml, 0,475 mmol). The crude hydrosilylated product was dissolved in dry THF (40 ml), and allylation and workup as described for **30** yielded **31** (896 mg, 49%). Clear oil. IR ($CHCl_3$): 3078, 2978, 2927, 1628, 1505, 1366, 1160, 897. ^{1}H-NMR (200 MHz): 0.58–0.66 (*m*, 2 H); 1.33 (*s*, 9 H); 1.55–1.72 (*m*, 8 H); 2.57 (*t*, *J* = 7.5, 2 H); 4.82–4.92 (*m*, 6 H); 5.66–5.87 (*m*, 3 H); 6.90 (*d*, *J* = 8.7, 2 H); 7.05 (*d*, *J* = 8.7, 2 H). ^{13}C-NMR (75.5 MHz): 11.00; 19.42; 25.47; 28.73; 39.05; 78.05; 113.61; 124.14; 128.80; 134.43; 137.34; 153.31. ^{29}Si-NMR (79.5 MHz): −0.3. EI-MS: 342 (M^+). Anal. calc. for $C_{22}H_{34}OSi$ (342.60): C 77.13, H 10.00; found: C 77.11, H 10.01.

1-Methoxy-4-[3-(tris{3-[tri(prop-2-enyl)silyl]propyl}silyl)propyl]benzene (**34**). To **30** (300 mg, 1 mmol) in dry THF (1 ml), $HSiCl_3$ (0.378 ml, 1 mmol) and 3% *Karstedt* catalyst in xylene (0.5 ml, 2.375 mmol) were added, and the mixture was stirred for 3 h (^{1}H-NMR monitoring of conversion). Excess $HSiCl_3$ was evaporated *in vacuo* and recovered in a cooling trap. The residue was dissolved in THF (20 ml), and the soln. was dropped *via* syringe

pump during 30 min. to pre-prepared (see protocol for **30**) 1M soln. of allylmagnesium bromide (11.25 ml, 11.25 mmol) in THF. After stirring for 48 h at 20°, ice water and 1N HCl were added, and the mixture was extracted with Et_2O. The org. phase was washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln. Drying (Na_2SO_4), evaporation *in vacuo*, FC (SiO_2, hexane/AcOEt 50:1), and GPC (CH_2Cl_2) afforded **34** (202 mg, 26%). Clear oil. IR ($CHCl_3$): 3070, 2909, 2871, 1625, 1510, 1159, 1035, 898, 808. ^{1}H-NMR (500 MHz): 0.54–0.55 (*m*, 2 H); 0.55–0.57 (*m*, 6 H); 0.65–0.66 (*m*, 6 H); 1.31–1.34 (*m*, 6 H); 1.52–1.55 (*m*, 2 H); 1.57–1.59 (*m*, 18 H); 2.56 (*t*, *J* = 7.5, 2 H); 3.78 (*s*, 3 H); 4.85–4.91 (*m*, 18 H); 5.74–5.83 (*m*, 9 H); 6.83 (*d*, *J* = 8.7, 2 H); 7.08 (*d*, *J* = 8.7, 2 H). ^{13}C-NMR (125.8 MHz): 12.28; 16.55; 17.43; 18.19; 19.68; 26.44; 39.21; 55.14; 113.49; 113.65; 129.23; 134.38; 157.66. ^{29}Si-NMR (79.5 MHz): −1.1; 1.2. EI-MS: 757 (M^+). Anal. calc. for $C_{46}H_{72}OSi_4$ (757.46): C 72.94, H 10.11; found: C 72.79, H 10.17.

1-(Methoxy)-4-[3-(triethenylsilyl)propyl]benzene (**35**). *Karstedt* catalyst (3% in xylene; 0.03 ml, 1.425 mmol) was added to $HSiCl_3$ (74 ml, 0.73 mol) and **25** (10 g, 0.067 mol), and exothermic reaction induced refluxing of the soln. After stirring for 2 h at 20°, excess $HSiCl_3$ was evaporated *in vacuo* (see protocol for **30**), and the residue was dissolved in dry THF (30 ml) and added dropwise over 1 h *via* syringe pump under water bath cooling to a freshly prepared 1.3M soln. of vinylmagnesium bromide in Et_2O (195 ml, 0.25 mol). After stirring for 12 h, ice water and 1N HCl were added, and the mixture was extracted with Et_2O. The org. phase was washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln. Drying (Na_2SO_4), evaporation *in vacuo*, FC (hexane/AcOEt 50:1), and bulb-to-bulb distillation provided **35** (11.6 g, 66%). Clear oil. IR ($CHCl_3$): 3051, 3007, 2934, 1610, 1512, 1403, 1248, 1176, 1036, 1009, 959, 824, 702. ^{1}H-NMR (300 MHz): 0.75–0.81 (*m*, 2 H); 1.61–1.71 (*m*, 2 H); 2.59 (*t*, *J* = 7.5, 2 H); 3.79 (*s*, 3 H); 5.74 (*dd*, *J* = 18.0, 6.0, 3 H); 6.07 (*dd*, *J* = 15.0, 6.0, 3 H); 6.15 (*dd*, *J* = 18, 15, 3 H); 6.83 (*d J* = 8.7, 2 H); 7.09 (*d*, *J* = 8.7, 2 H). ^{13}C-NMR (75.5 MHz): 12.26; 25.81; 38.66; 55.14; 113.69; 129.42; 134.50; 134.64; 134.76; 157.83. ^{29}Si-NMR (79.5 MHz): −19.7. EI-MS: 258 (M^+). Anal. calc. for $C_{16}H_{22}OSi$ (258.44): C 74.36, H 8.58; found: C 74.35, H 8.38.

1-Methoxy-4-(3-{tris[2-(triethenylsilyl)ethyl]silyl}propyl)benzene (**36**). *Karstedt* catalyst (3% in xylene; 0.3 ml, 14.25 mmol) was added to $HSiCl_3$ (55 ml, 0.54 mol) and **35** (10.34 g, 0.04 mol), and the mixture started to reflux. After heating at 20° for 2 h, excess $HSiCl_3$ was evaporated *in vacuo* (see protocol for **30**). The residue was dissolved in dry THF (40 ml) and added dropwise *via* syringe pump over 1 h under cooling with a water-bath to a freshly prepared 1.3M soln. of vinylmagnesium bromide in Et_2O (346 ml, 0.45 mol). After stirring for 12 h, ice water and 1N HCl were added, and the mixture was extracted with Et_2O. The org. phase was washed with sat. $NaHCO_3$ soln. and sat. aq. NaCl soln, dried (Na_2SO_4), and evaporated *in vacuo*. FC (SiO_2; hexane/AcOEt 50:1) and GPC (PhMe) gave **36** (15.91 g, 67%). Clear oil. IR ($CHCl_3$): 3050, 3007, 2911, 1610, 1590, 1511, 1403, 1247, 1131, 1009, 958, 703. ^{1}H-NMR (500 MHz): 0.48–0.61 (*m*, 14 H); 1.57 (*m*, 2 H); 2.57 (*t*, *J* = 7.5, 2 H); 3.81 (*s*, 3 H); 5.79 (*dd*, *J* = 18.9, 5.3, 9 H); 6.11 (*dd*, *J* = 14.7, 5.3, 9 H); 6.17 (*dd*, *J* = 18.9, 14.7, 9 H); 6.85 (*d*, *J* = 8.6, 2 H); 7.10 (*d*, *J* = 8.6, 2 H). ^{13}C-NMR (125.8 MHz): 3.03; 4.79; 10.63; 26.17; 39.11; 55.18; 113.64; 129.32; 134.45; 134.60; 134.66; 157.66. ^{29}Si-NMR (79.5 MHz): −18.4; 8.6. EI-MS: 589 (M^+). Anal. calc. for $C_{34}H_{52}OSi_4$ (589.13): C 69.32, H 8.90; found: C 69.36, H 8.72.

1-Methoxy-4-[3-(triethylsilyl)propyl]benzene (**37**). Compound **35** (1.29 g, 5 mmol) in pentane (30 ml) was hydrogenated (1 bar H_2) in the presence of Pd/C (10%, 531 mg, 10 mol%) for 2 h. Filtration and evaporation *in vacuo* afforded **37** (1.2 g, 90%). *Warning:* **37** is quite volatile even under water-aspirator pressure. Clear oil. IR ($CHCl_3$): 3007, 2954, 2912, 2874, 1610, 1511, 1247, 1176, 1036, 1016, 823. ^{1}H-NMR (300 MHz): 0.49 (*q*, *J* = 8.0, 6 H); 0.55 (*m*, 2 H); 0.91 (*t*, *J* = 8.0, 9 H); 1.50–1.62 (*m*, 2 H); 2.56 (*t*, *J* = 7.5, 2 H); 3.79 (*s*, 3 H); 6.83 (*d*, *J* = 8.7, 2 H); 7.09 (*d*, *J* = 8.7, 2 H). ^{13}C-NMR (75.5 MHz): 3.15; 7.29; 11.11; 26.15; 39.21; 55.16; 113.69; 129.37; 134.98; 157.76. ^{29}Si-NMR (79.5 MHz): 6.7. EI-MS: 264 (5, M^+), 235 (100, $[M - C_2H_5]^+$).

4-[3-(Triethylsilyl)propyl]phenol (**38**). 1M Br_3B in CH_2Cl_2 (0.472 ml, 3.78 mmol) was added to **37** (1.0 g, 3.78 mmol) in dry CH_2Cl_2 (50 ml) at −78°. The soln. was slowly warmed to 15°, and ice water and sat. aq. $NaHCO_3$ soln. were carefully added. The mixture was extracted with CH_2Cl_2, and the org. phase was washed with sat. aq. NaCl soln., dried (Na_2SO_4), and evaporated *in vacuo*. FC (SiO_2; hexane/AcOEt 10:1) provided **38** (942 mg, 99%). Clear oil. IR ($CHCl_3$): 3599, 3333, 3011, 2953, 2874, 1612, 1513, 1456, 1170, 1015, 828. ^{1}H-NMR (200 MHz): 0.51 (*q*, *J* = 8.0, 6 H); 0.56 (*m*, 2 H); 0.93 (*t*, *J* = 8.0, 9 H); 1.50–1.67 (*m*, 2 H); 2.56 (*t*, *J* = 7.0, 2 H); 4.86 (*s*, 1 H); 6.77 (*d*, *J* = 8.5, 2 H); 7.06 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR (75.5 MHz): 3.15; 7.29; 11.06; 26.12; 39.18; 115.12; 129.59; 135.19; 153.47. EI-MS: 250 (1, M^+), 221 (100, $[M - C_2H_5]^+$).

1-Methoxy-4-(3-{tris[2-(triethylsilyl)ethyl]silyl}propyl)benzene (**39**). A mixture of **35** (500 mg, 1.93 mmol), Et_3SiH (3.68 ml, 23.16 mmol), and 3% *Karstedt* catalyst in xylene (0.04 ml, 1.9 mmol) in dry THF (10 ml) was heated to reflux for 48 h. Evaporation *in vacuo*, FC (SiO_2; hexane/AcOEt 100:1), and GPC (PhMe) provided **39** (1.15 g, 97%). Clear oil. IR ($CHCl_3$): 2953, 2898, 2874, 1610, 1581, 1511, 1464, 1416, 1300, 1245, 1176, 1130, 1015, 826, 703. ^{1}H-NMR (500 MHz): 0.30–0.42 (*m*, 12 H); 0.50 (*q*, *J* = 8.0, 18 H); 0.52–0.56 (*m*, 2 H); 0.91 (*t*,

$J = 8.0$, 27 H); 1.50–1.60 (*m*, 2 H); 2.55 (*t*, $J = 7.5$, 2 H); 3.77 (*s*, 3 H); 6.81 (*d*, $J = 8.7$, 2 H); 7.07 (*d*, $J = 8.7$, 2 H). ^{13}C-NMR (125.8 MHz): 2.90; 3.08; 3.15; 7.51; 10.80; 26.48; 39.32; 55.21; 113.66; 129.36; 134.91; 157.67. ^{29}Si-NMR (79.5 MHz): 6.3; 20.0. EI-MS: 607 (M^+).

4-(3-{Tris[2-(triethylsilyl)ethyl]silyl}propyl)phenol (**40**). According to the procedure for **38**, **39** (500 mg, 0.823 mmol) and Br_3B (0.077 ml, 0.823 mmol) in dry CH_2Cl_2 (10 ml) reacted to give, after FC (SiO_2; hexane/AcOEt 10:1), **40** (350 mg, 71%). Clear oil. IR ($CHCl_3$): 3599, 3344, 2953, 2898, 2874, 1612, 1513, 1457, 1416, 1130, 1057, 1015, 972, 828, 703. ^{1}H-NMR (300 MHz): 0.30–0.42 (*m*, 12 H); 0.52 (*q*, $J = 7.8$, 18 H); 0.56–0.60 (*m*, 2 H); 0.94 (*t*, $J = 7.8$, 27 H); 1.57–1.60 (*m*, 2 H); 2.57 (*t*, $J = 7.5$, 2 H); 4.82 (*s*, 1 H); 6.76 (*d*, $J = 8.5$, 2 H); 7.05 (*d*, $J = 8.5$, 2 H). ^{13}C-NMR (75.5 MHz): 2.71; 2.89; 2.95; 7.34; 10.62; 26.32; 39.19; 115.10; 129.62; 135.16; 153.56. EI-MS: 592 (MH$^+$). Anal. calc. for $C_{33}H_{68}OSi_4$ (593.24): C 66.81, H 11.55; found: C 66.70, H 11.35.

1-Methoxy-4-{3-[tris(2-{tris[2-(triethylsilyl)ethyl]silyl}ethyl)silyl]propyl}benzene (**41**). A mixture of **36** (33 mg, 0.056 mmol), Et_3SiH (0.9 ml, 5.66 mmol), and 3% *Karstedt* catalyst in xylene (0.01 ml, 0.475 mmol) in dry THF (2 ml) was heated to reflux for 48 h. The mixture was filtered over a short plug (SiO_2; Et_2O), and GPC (CH_2Cl_2) provided **41** (76 mg, 82%). Amorphous solid. M.p. 77–80°. IR ($CHCl_3$): 2952, 2906, 2874, 1611, 1511, 1464, 1415, 1243, 1128, 1015. ^{1}H-NMR (500 MHz): 0.34–0.43 (*m*, 48 H); 0.51 (*q*, $J = 8.0$, 54 H); 0.55–0.60 (*m*, 2 H); 0.92 (*t*, $J = 8.0$, 81 H); 1.57 (*m*, 2 H); 2.56 (*t*, $J = 7.5$, 2 H); 3.78 (*s*, 3 H); 6.80 (*d*, $J = 8.6$, 2 H); 7.06 (*d*, $J = 8.6$, 2 H). ^{13}C-NMR (125.8 MHz): 2.41; 2.85; 3.17; 7.50; 11.02; 26.17; 39.36; 55.17; 113.58; 129.18; 134.74; 157.63. ^{29}Si-NMR (79.5 MHz): 7.4; 8.2; 9.6. Anal. calc. for $C_{88}H_{196}OSi_{13}$ (1635.65): C 64.62, H 12.08; found: C 64.33, H 12.21.

1-Methoxy-4-(3-{tris[2-(triphenylsilyl)ethyl]silyl}propyl)benzene (**42**). A mixture of **35** (500 mg, 1.93 mmol), Ph_3SiH (2.16 g, 8.32 mmol), and 3% *Karstedt* catalyst in xylene (0.02 ml, 0.95 mmol) in dry THF (10 ml) was heated to reflux for 7 h. After evaporation *in vacuo*, the crude product was purified by FC (SiO_2; hexane/AcOEt 50:1) to give **42** (421 mg, 27%). Amorphous colorless solid. IR ($CHCl_3$): 3069, 3007, 2911, 1610, 1511, 1486, 1427, 1300, 1247, 1176, 1132, 1110, 703. ^{1}H-NMR (500 MHz): 0.52–0.55 (*m*, 2 H); 0.56–0.60 (*m*, 6 H); 1.05–1.08 (*m*, 6 H); 1.40–1.43 (*m*, 2 H); 2.46 (*t*, $J = 7.4$, 2 H); 3.74 (*s*, 3 H); 6.76 (*d*, $J = 8.7$, 2 H); 6.95 (*d*, $J = 8.7$, 2 H); 7.25–7.50 (*m*, 45 H). ^{13}C-NMR (125.8 MHz): 3.25; 5.43; 10.32; 25.93; 38.88; 55.21; 113.63; 127.81; 129.11; 129.32; 134.48; 135.09; 135.64; 157.63. ^{29}Si-NMR (79.5 MHz): −9.7; 9.4. ESI-MS: 1077 (12, $[M + K]^+$), 1061 (28, $[M + Na]^+$), 1056 (100, $[M + NH_4]^+$). Anal. calc. for $C_{70}H_{70}OSi_4$ (1039.67): C 80.87, H 6.79; found: C 80.76, H 6.85.

4-(3-{Tris[2-(triphenylsilyl)ethyl]silyl}propyl)phenol (**43**). According to the procedure for **38**, **42** (522 mg, 0.502 mmol) and Br_3B (0.047 ml, 0.502 mmol) in dry CH_2Cl_2 (10 ml) reacted to give, after FC (SiO_2; hexane/AcOEt 5:1), **43** (360 mg, 70%). Amorphous white solid. IR ($CHCl_3$): 3597, 3345, 3069, 3007, 2911, 1612, 1588, 1513, 1486, 1427, 1257, 1132, 1110, 703. ^{1}H-NMR (300 MHz): 0.50–0.55 (*m*, 2 H); 0.57–0.60 (*m*, 6 H); 1.02–1.24 (*m*, 6 H); 1.27–1.43 (*m*, 2 H); 2.44 (*t*, $J = 8.7$, 2 H); 4.50 (*s*, 1 H); 6.67 (*d*, $J = 8.7$, 2 H); 6.90 (*d*, $J = 8.7$, 2 H); 7.25–7.50 (*m*, 45 H). ^{13}C-NMR (75.5 MHz): 3.18; 5.27; 10.06; 25.80; 38.76; 115.10; 127.90; 129.42; 129.58; 134.69; 135.19; 135.74; 153.60. ESI-MS: 1064 (12, $[M + K]^+$), 1047 (32, $[M + Na]^+$), 1041 (100, $[M + H_2O]^+$). Anal. calc. for $C_{69}H_{68}OSi_4$ (1025.65): C 80.80, H 6.68; found: C 80.32, H 6.73.

*(*E*)-3,4-Bis[({4-[3-(triethylsilyl)propyl]phenyl}oxy)methyl]-1,6-bis(triisopropylsilyl)hex-3-ene-1,5-diyne* (**44**). DEAD (0.322 ml, 2.05 mmol) was added dropwise to a soln. of **18** (448 mg, 1 mmol), **38** (525 mg, 2.1 mmol), and Ph_3P (550 mg, 2.1 mmol) in dry THF. After stirring for 6 h at 20°, Et_2O (150 ml) was added and the org. phase was washed with 1N HCl, sat. aq. $NaHCO_3$ soln, and sat. aq. NaCl soln. Drying (Na_2SO_4), evaporation *in vacuo*, and FC (SiO_2; hexane/AcOEt 10:1) gave **44** (626 mg, 68%). Clear oil. IR ($CHCl_3$): 2946, 2867, 2148, 1609, 1582, 1509, 1462, 1016, 882. ^{1}H-NMR (300 MHz): 0.50 (*q*, $J = 8.0$, 12 H); 0.54–0.58 (*m*, 4 H); 0.91 (*t*, $J = 8.0$, 18 H); 1.05 (*s*, 42 H); 1.50–1.62 (*m*, 4 H); 2.55 (*t*, $J = 7.2$, 4 H); 4.89 (*s*, 4 H); 6.83 (*d*, $J = 8.7$, 4 H); 7.03 (*d*, $J = 8.7$, 4 H). ^{13}C-NMR (75.5 MHz): 3.18; 7.31; 11.04; 11.16; 18.47; 26.15; 39.27; 67.97; 102.22; 106.48; 114.76; 129.24; 129.45; 135.13; 156.60. ^{29}Si-NMR (79.5 MHz): −1.2; 6.8. ESI-MS: 951 ($[M + K]^+$), 935 ($[M + Na]^+$), 913 (MH$^+$). Anal. calc. for $C_{56}H_{96}O_2Si_4$ (913.72): C 73.61 H 10.59; found: C 73.62, H 10.33.

*(*E*)-3,4-Bis[({4-[3-(triethylsilyl)propyl]phenyl}oxy)methyl]hex-3-ene-1,5-diyne* (**45**). 1M Bu_4NF in THF (1.94 ml, 1.94 mmol) was added at 0° to a soln. of **44** (444 mg, 0.486 mmol) in dry THF (10 ml). After 2 min, Et_2O was added and the org. phase was washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln. After drying (Na_2SO_4), evaporation *in vacuo*, and FC (SiO_2; hexane/AcOEt 10:1) provided **45** (259 mg, 88%). Dark-red oil. IR ($CHCl_3$): 2201, 2953, 2874, 1609, 1509, 1458, 1177, 1016, 827, 657. ^{1}H-NMR (300 MHz): 0.52 (*q*, $J = 8.0$, 12 H); 0.54–0.60 (*m*, 4 H); 0.93 (*t*, $J = 8.0$, 18 H); 1.55–1.65 (*m*, 4 H); 2.58 (*t*, $J = 7.5$, 4 H); 3.66 (*s*, 2 H); 4.89 (*s*, 4 H); 6.89 (*d*, $J = 8.7$, 4 H); 7.10 (*d*, $J = 8.7$, 4 H). ^{13}C-NMR (75.5 MHz): 3.18; 7.31; 11.14; 26.10; 39.27; 68.12; 79.09; 90.49; 114.89; 129.42; 129.56; 135.68; 156.60.

*(*E*)-1,6-Bis(triisopropylsilyl)-3,4-bis({[4-(3-{tris[2-(triethylsilyl)ethyl]silyl}propyl)phenyl]oxy}methyl)hex-3-ene-1,5-diyne* (**46**). A soln. of **18** (300 mg, 0.668 mmol), **40** (991 mg, 1.67 mmol), and Bu_3P (0.477 ml, 1.68 mmol) was degassed by three freeze-pump-thaw cycles. ADDP (421 mg, 1.67 mmol) in dry THF (3 ml) was added at 20° over a period of 24 h *via* syringe pump. After stirring for 10 h, Et_2O was added, and the mixture was washed with 1N HCl, sat. aq. $NaHCO_3$ soln, and sat. aq. NaCl soln. After drying (Na_2SO_4), evaporation *in vacuo*, FC (SiO_2; hexane/AcOEt 10:1), and GPC (PhMe) afforded **46** (695 mg, 65%). Highly viscous clear oil. IR ($CHCl_3$): 2951, 2906, 2871, 2146, 1609, 1581, 1509, 1462, 1416, 1129, 1015, 882, 703. ^{1}H-NMR (500 MHz): 0.35–0.43 (*m*, 24 H); 0.51 (*q*, *J* = 8.0, 36 H); 0.57–0.60 (*m*, 4 H); 0.93 (*t*, *J* = 8.0, 54 H); 1.06 (*s*, 42 H); 1.54–1.57 (*m*, 4 H); 2.56 (*t*, *J* = 7.6, 4 H); 4.89 (*s*, 4 H); 6.84 (*d*, *J* = 8.5, 4 H); 7.04 (*d*, *J* = 8.5, 4 H). ^{13}C-NMR (125.8 MHz): 2.86; 3.07; 3.14; 7.48; 11.05; 11.18; 18.58; 26.50; 39.48; 68.03; 102.23; 106.36; 114.65; 129.13; 129.38; 135.07; 156.53. ^{29}Si-NMR (79.5 MHz): −1.2; 7.7; 8.2. ESI-MS: 1637 (28, $[M+K]^+$), 1621 (100, $[M+Na]^+$).

*(*E*)-3,4-Bis({[4-(3-{tris[2-(triethylsilyl)ethyl]silyl}propyl)phenyl]oxy}methyl)hex-3-ene-1,5-diyne* (**47**). According to the procedure for **45**, **46** (125 mg, 0.078 mmol) and 1M Bu_4NF in THF (0.0032 ml, 0.313 mmol) in dry THF (6 ml) reacted to give, after GPC (CH_2Cl_2), **47** (83 mg, 82%). Highly viscous clear oil. IR ($CHCl_3$): 3301, 2952, 2903, 2864, 1609, 1583, 1509, 1458, 1416, 1377, 1299, 1176, 1129, 1057, 1015, 703. ^{1}H-NMR (300 MHz): 0.32–0.44 (*m*, 24 H); 0.53 (*q*, *J* = 8.0, 36 H); 0.58–0.61 (*m*, 4 H); 0.94 (*t*, *J* = 8.0, 54 H); 1.50–1.64 (*m*, 4 H); 2.58 (*t*, *J* = 7.5, 4 H); 3.64 (*s*, 2 H); 4.88 (*s*, 4 H); 6.90 (*d*, *J* = 8.5, 4 H); 7.09 (*d*, *J* = 8.5, 4 H). ^{13}C-NMR (75 MHz): 2.70; 2.90; 2.96; 7.35; 10.70; 26.28; 39.25; 68.12; 79.12; 90.35; 114.81; 129.44; 129.49; 135.67; 156.64. ESI-MS: 1325 (24, $[MH+K]^+$), 1309 (100, $[MH+Na]^+$).

Oxidative Oligomerization of **47**. A suspension of CuCl (1.75 mg, 0.178 mmol) and TMEDA (0.04 ml) in CH_2Cl_2 (0.5 ml) was stirred for 10 min in the air and then added to **47** (114 mg, 0.089 mmol), powdered molecular sieves (4 Å; 40 mg), and PhC≡CH (0.019 ml, 0.178 mmol) in CH_2Cl_2 (0.5 ml). After stirring for 1 h in the air, additional PhC≡CH (0.038 ml, 0.356 mmol) was added. After stirring for 3 h, the mixture was evaporated *in vacuo* and subjected to GPC (PhMe). Enriched fractions were further purified by HP-GPC to give **4a–d** as orange-to-red solids.

*(*E*)-1,10-Diphenyl-5,6-bis({[4-(3-{tris[2-(triethylsilyl)ethyl]silyl}propyl)phenyl]oxy}methyl)dec-5-ene-1,3,7,9-tetrayne* (**4a**). Yield: 17 mg (13%). UV/VIS ($CHCl_3$): 360 (41 700). IR ($CHCl_3$): 2953, 2908, 2872, 2212, 1603, 1509, 1238, 1180, 1120, 1013, 830, 693. ^{1}H-NMR (500 MHz, CD_2Cl_2): 0.37–0.44 (*m*, 24 H); 0.51 (*q*, *J* = 8.0, 36 H); 0.57–0.61 (*m*, 4 H); 0.92 (*t*, *J* = 8.0, 54 H); 1.55–1.62 (*m*, 4 H); 2.58 (*t*, *J* = 7.5, 4 H); 4.90 (*s*, 4 H); 6.90 (*d*, *J* = 8.7, 4 H); 7.12 (*d*, *J* = 8.7, 4 H); 7.34–7.41 (*m*, 6 H); 7.51–7.53 (*m*, 4 H). ^{13}C-NMR (125.8 MHz, CD_2Cl_2): 3.21; 3.42; 3.46; 7.67; 26.84; 39.69; 68.79; 73.58; 77.59; 87.56; 88.37; 115.11; 121.54; 128.94; 129.82; 130.20; 131.20; 132.90; 136.35; 156.76. HR-MALDI-TOF-MS (DHB): 1507.9542 (100, $[M+Na]^+$, calc. 1507.9526).

*(5*E*,11*E*)-1,16-Diphenyl-5,6,11,12-tetrakis({[4-(3-{tris[2-(triethylsilyl)ethyl]silyl}propyl)phenyl]oxy}methyl)-hexadeca-5,11-diene-1,3,7,9,13,15-hexayne* (**4b**). Yield: 13 mg (7%). UV/VIS ($CHCl_3$): 386 (61 700). IR ($CHCl_3$): 2952, 2908, 2874, 2201, 1607, 1509, 1458, 1176, 1129, 1015, 828. ^{1}H-NMR (500 MHz): 0.32–0.42 (*m*, 48 H); 0.501 (*q*, *J* = 8.0, 36 H); 0.505 (*q*, *J* = 8.0, 36 H); 0.56–0.59 (*m*, 8 H); 0.917 (*t*, *J* = 8.0, 54 H); 0.920 (*t*, *J* = 8.0, 54 H); 1.56–1.62 (*m*, 8 H); 2.56 (*t*, *J* = 7.5, 8 H); 4.86 (*s*, 4 H); 4.87 (*s*, 4 H); 6.89 (*d*, *J* = 8.6, 8 H); 7.08 (*d*, *J* = 8.6, 8 H); 7.31–7.40 (*m*, 6 H); 7.48–7.51 (*m*, 4 H). ^{13}C-NMR (125.8 MHz): 2.87; 3.05; 3.12; 7.50; 10.94; 26.44; 39.43; 68.21; 68.35; 73.61; 77.15; 82.72; 87.38; 87.50; 88.87; 114.84; 114.90; 121.32; 128.46; 129.37; 129.66; 129.89; 131.78; 132.52; 135.73; 135.74; 156.33; 156.37. HR-MALDI-TOF-MS (DHB): 2791.8420 ($[M+Na]^+$, calc. 2791.8410).

*(5*E*,11*E*,17*E*)-1,22-Diphenyl-5,6,11,12,17,18-hexakis({[4-(3-{tris[2-(triethylsilyl)ethyl]silyl}propyl)phenyl]-oxy}methyl)docosa-5,11,17-triene-1,3,7,9,13,15,19,21-octayne* (**4c**). Yield: 5 mg (2%). UV/VIS ($CHCl_3$): 405 (73 900). IR ($CHCl_3$): 2952, 2908, 2874, 2202, 1607, 1509, 1458, 1416, 1129, 1015, 829. ^{1}H-NMR (500 MHz): 0.32–0.41 (*m*, 72 H); 0.494 (*q*, *J* = 8.0, 36 H); 0.498 (*q*, *J* = 8.0, 36 H); 0.501 (*q*, *J* = 8.0, 36 H); 0.55–0.59 (*m*, 12 H); 0.910 (*t*, *J* = 8.0, 54 H); 0.913 (*t*, *J* = 8.0, 54 H); 0.917 (*t*, *J* = 8.0, 54 H); 1.53–1.55 (*m*, 12 H); 2.55 (*t*, *J* = 8.0, 12 H); 4.82 (*s*, 4 H); 4.84 (*s*, 4 H); 4.86 (*s*, 4 H); 6.85 (*d*, *J* = 8.7, 4 H); 6.88 (*d*, *J* = 8.6, 8 H); 7.05 (*d*, *J* = 8.7, 4 H); 7.08 (*d*, *J* = 8.6, 8 H); 7.31–7.38 (*m*, 6 H); 7.48–7.50 (*m*, 4 H). ^{13}C-NMR (125.8 MHz): 2.69; 3.04; 3.12; 7.49; 10.94; 11.01; 26.44; 39.43; 39.47; 68.19; 68.33; 73.60; 77.12; 82.59; 83.04; 87.28; 87.55; 87.94; 88.97; 114.82; 114.84; 114.89; 121.31; 128.46; 129.36; 129.67; 129.74; 130.96; 131.98; 132.52; 135.73; 135.74; 135.79; 156.26; 156.32; 156.36. MALDI-TOF-MS (DHB): 4074 ($[M+Na]^+$).

*(5*E*,11*E*,17*E*,23*E*)-1,28-Diphenyl-5,6,11,12,17,18,23,24-octakis({[4-(3-{tris[2-(triethylsilyl)ethyl]silyl}propyl)phenyl]oxy}methyl)octacosa-5,11,17,23-tetraene-1,3,7,9,13,15,19,21,25,27-decayne* (**4d**). Yield: 2 mg (1%). UV/VIS ($CHCl_3$): 420 (90 000). IR ($CHCl_3$): 2952, 2908, 2874, 2200, 2603, 2509, 1458, 1129, 1015, 823. ^{1}H-NMR (500 MHz): 0.32–0.42 (*m*, 96 H); 0.46–0.52 (*m*, 144 H); 0.55–0.59 (*m*, 16 H); 0.88–0.93 (*m*, 216 H); 1.50–1.55 (*m*, 16 H); 2.51–2.56 (*m*, 16 H); 4.81 (*s*, 8 H); 4.84 (*s*, 4 H); 4.85 (*s*, 4 H); 6.84 (*d*, *J* = 8.6, 8 H); 6.87 (*d*, *J* = 8.6, 8 H); 7.04 (*d*, *J* = 8.6, 8 H); 7.07 (*d*, *J* = 8.6, 8 H); 7.30–7.40 (*m*, 6 H); 7.47–7.50 (*m*, 4 H). ^{13}C-NMR (125.8 MHz):

2.87; 3.04; 3.12; 7.50; 10.94; 11.00; 26.45; 39.43; 39.48; 68.15; 68.18; 68.32; 73.60; 77.12; 82.70; 82.90; 83.10; 87.25; 87.55; 87.82; 88.02; 88.98; 114.82; 114.88; 121.31; 128.46; 129.35; 129.71; 130.80; 131.12; 132.03; 132.52; 135.74; 135.79; 156.24; 156.31; 156.36.

*(*E*)-5,6-[Bis(triisopropylsilyl)ethynyl]dec-5-ene-1,3,7,9-tetrayne* (**50**). A mixture of **49** (100 mg, 0.159 mmol) and Bu_4NF on SiO_2 (5 mg, 0.005 mmol) in THF/H_2O 100:1 (4 ml) was stirred for 5 min at 20°. Hexane (100 ml) was added, and the mixture was extracted with H_2O (4 × 15 ml) and sat. aq. NaCl soln. (15 ml). Drying ($MgSO_4$), evaporation *in vacuo*, and filtration over a short plug (SiO_2; hexane) provided **50** (69 mg, 90%). Yellow oil. IR (neat): 3303, 2943, 2865, 2211, 2180, 2140, 1618, 1463, 1089, 850. ^{1}H-NMR (200 MHz): 1.12 (*s*, 42 H); 2.74 (*s*, 2 H). ^{13}C-NMR (50.3 MHz): 11.2; 18.6; 67.9; 71.9; 76.4; 83.8; 101.4; 105.1; 120.1. EI-MS: 484 (1, M^+), 441 (2, $[M-(\text{i-Pr})]^+$), 73 (100, Me_3Si^+). HR-EI-MS: 484.2945 (M^+, $C_{32}H_{44}Si_2^+$; calc. 484.2981).

Oxidative Oligomerization of **50**. CuCl (1.00 g, 10.20 mmol), **51** (0.0025 g, 0.117 mmol), and TMEDA (2.0 ml, 13.45 mmol) were added to **50** (69 mg, 0.142 mmol) in CH_2Cl_2 (200 ml), and the mixture was stirred for 2 h in the air. Filtration over *Celite* (CH_2Cl_2) gave a soln., which was extracted with 0.7M aq. EDTA (ethylenediaminetetraacetic acid) soln. (pH 8, 2 × 50 ml), H_2O (2 × 50 ml), and sat. aq. NaCl soln (50 ml). Drying ($MgSO_4$), evaporation *in vacuo*, and GPC (PhMe) provided oligomers **5a–c**.

*(*E*)-1,14-Bis[3,5-di(*tert*-butyl)phenyl]-7,8-bis[(triisopropylsilyl)ethynyl]tetradec-7-ene-1,3,5,9,11,13-hexayne* (**5a**). Yield: 14 mg (10%). Yellow Solid. M.p. 104–107° (dec.). UV/VIS ($CHCl_3$): 264 (80400), 277 (66300), 291 (52900), 310 (46300), 330 (35000), 352 (19100), 377 (sh, 20500), 396 (sh, 30600), 410 (sh, 36100), 428 (52600), 450 (sh, 43300), 458 (45900). IR (neat): 2956, 2856, 2167, 2100, 1120, 881. ^{1}H-NMR (200 MHz): 1.12 (*s*, 42 H); 1.33 (*s*, 36 H); 7.38 (*d*, *J* = 1.9, 4 H); 7.47 (*d*, *J* = 1.9, 2 H). ^{13}C-NMR (50.3 MHz): 11.2; 18.6; 31.2; 34.9; 68.1; 72.8; 73.2; 75.4; 83.1; 85.7; 101.4; 105.2; 120.2; 124.7; 127.3; 128.8; 151.2. FAB-MS: 909 (86, M^+), 154 (100). Anal. calc. for $C_{64}H_{84}Si_2$ (909.5): C 84.52, H 9.31; found: C 84.50, H 9.42.

*(7*E*,17*E*)-1,24-Bis[3,5-di(*tert*-butyl)phenyl]-7,8,17,18-tetrakis[(triisopropylsilyl)ethynyl]tetracosa-7,17-diene-1,3,5,9,11,13,15,19,21,23-decayne* (**5b**). Yield: 12 mg (6%). Orange solid. M.p. 145–149° (dec.). UV/VIS ($CHCl_3$): 263 (128500), 296 (73900), 316 (62400), 333 (50400), 366 (34700), 393 (sh, 41000), 409 (sh, 48700), 426 (64200), 464 (99300), 508 (76800). IR (neat): 2942, 2865, 2153, 2093, 1589, 1458, 1123, 878. ^{1}H-NMR (200 MHz): 1.13 (*s*, 84 H); 1.32 (*s*, 36 H); 7.40 (*d*, *J* = 1.9, 4 H); 7.48 (*d*, *J* = 1.9, 2 H). ^{13}C-NMR (125.8 MHz): 11.2; 18.5; 18.6; 31.2; 34.9; 65.7; 66.2; 72.6; 73.2; 73.4; 75.3; 76.2; 83.6; 85.0; 86.6; 100.9; 101.4; 105.9; 106.0; 119.5; 119.6; 121.7; 124.8; 127.3; 151.2. FAB-MS: 1392 (29, M^+), 136 (100). Anal. calc. for $C_{96}H_{126}Si_4$ (1392.4): C 82.81, H 9.12; found: C 82.72; H 9.31.

*(5*E*,17*E*,27*E*)-1,34-Bis[3,5-di(*tert*-butyl)phenyl]-7,8,17,18,27,28-hexakis[(triisopropylsilyl)ethynyl]tetratriaconta-7,17,27-triene-1,3,5,9,11,13,15,19,21,23,25,29,31,33-tetradecayne* (**5c**). Yield: 9 mg (3%). Red solid. M.p. 165–168° (dec.). UV/VIS ($CHCl_3$): 262 (149600), 294 (sh, 84600), 315 (sh, 71000), 333 (sh, 60000), 368 (43900), 393 (sh, 51200), 410 (sh, 57300), 428 (sh, 66500), 470 (99500), 519 (92300). IR (neat): 2944, 2866, 2190, 2152, 2092, 1588, 1459, 1364, 1236, 1085, 882. ^{1}H-NMR (200 MHz): 1.13 (*s*, 126 H); 1.32 (*s*, 36 H); 7.40 (*d*, *J* = 1.9, 4 H); 7.48 (*d*, *J* = 1.9, 2 H). ^{13}C-NMR (125.8 MHz): 11.1; 11.2; 18.5; 18.6; 18.7; 31.2; 34.9; 65.6; 66.0; 66.5; 69.5; 72.5; 73.2; 73.5; 75.3; 76.0; 76.4; 83.6; 84.9; 85.8; 86.7; 100.8; 100.9; 101.4; 105.9; 106.0; 106.6; 119.4; 119.6; 120.9; 121.8; 124.8; 127.3; 151.2. FAB-MS: 1876 (0.2, M^+), 136 (100). Anal. calc. for $C_{128}H_{168}Si_6$ (1875.3): C 81.98, H 9.03; found: C 81.82, H 9.07.

Heterocoupling of **53**. To a degassed soln. of **53** (1.00 g, 2.75 mmol) in THF (20 ml), **54** (1.00 g, 5.65 mmol), $[PdCl_2(PPh_3)_2]$ (0.100 g, 0.142 mmol), and CuI (0.030 g, 0.158 mmol) were added. After cooling to 0°, $(\text{i-Pr})_2NH$ (0.70 ml, 0.158 mmol) was slowly added, and the mixture was stirred for 2 h at 0°. Evaporation *in vacuo* and CC (SiO_2; hexane/CH_2Cl_2 2:1) provided **55a–c**.

*(*E*)-5,6-Bis({[(*tert*-butyl)dimethylsilyl]oxy}methyl)-1,10-bis(trimethylsilyl)dec-5-ene-1,3,7,9-tetrayne* (**55a**). Yield: 0.237 g (21%). Colorless solid. M.p. 62°. UV/VIS (hexane): 212 (22300), 222 (45300), 232 (78700), 252 (18600), 306 (20500), 322 (38400), 343 (44500). IR (neat): 2957, 2857, 2198, 2096, 1460, 1252, 1110, 850. ^{1}H-NMR (200 MHz): 0.10 (*s*, 12 H); 0.21 (*s*, 18 H); 0.92 (*s*, 18 H); 4.41 (*s*, 4 H). ^{13}C-NMR (50.3 MHz): −5.5; −0.7; 18.1; 25.6; 63.6; 73.2; 87.3; 87.5; 95.3; 132.1. EI-MS: 556 (0.1, M^+), 541 (1, $[M-\text{Me}]^+$), 499 (24, $[M-(t\text{-Bu})]^+$), 73 (100, $SiMe_3^+$). Anal. calc. for $C_{30}H_{52}O_2Si_4$ (557.1): C 64.68, H 9.41; found: C 64.51, H 9.22.

*(5*E*,11*E*)-5,6,11,12-Tetrakis({[(*tert*-butyl)dimethylsilyl]oxy}methyl)-1,16-bis(trimethylsilyl)hexadeca-5,11-diene-1,3,7,9,13,15-hexayne* (**55b**). Yield: 180 mg (18%). Yellow solid. M.p. 103–105°. UV/VIS (hexane): 232 (52400), 290 (sh, 18000), 309 (sh, 23000), 322 (sh, 29300), 348 (47800), 372 (57300), 400 (52900). IR (neat): 2956, 2857, 2189, 2120, 2094, 1462, 1253, 1112, 837, 777. ^{1}H-NMR (200 MHz): 0.10 (*s*, 24 H); 0.22 (*s*, 18 H); 0.91 (*s*, 36 H); 4.41 (*s*, 4 H); 4.44 (*s*, 4 H). ^{13}C-NMR (50.3 MHz): −5.5; −0.7; 18.1; 25.6; 63.5; 73.3; 82.6; 86.8; 87.2; 87.7; 95.6; 131.9; 132.2. FAB-MS: 920 (90, MH^+), 862 (100, $[M-(t\text{-Bu})]^+$). Anal. calc. for $C_{50}H_{86}O_4Si_6$ (919.7): C 65.30, H 9.42; found: C 65.46, H 9.59.

*(5*E*,11*E*,17*E*)-5,6,11,12,17,18-Hexakis{[[(*tert*-butyl)dimethylsilyl]oxy}methyl)-1,22-bis(trimethylsilyl)docosa-5,11,17-triene-1,3,7,9,13,15,19,21-octayne* (**55c**). Yield: 35 mg (3%). Orange solid. M.p. 134–135°. UV/VIS (hexane): 257 (sh, 28300), 302 (26700), 330 (sh, 29700), 355 (sh, 40500), 387 (sh, 60900), 406 (69200), 432 (sh, 47700). IR (neat): 2956, 2929, 2856, 2094, 1596, 1473, 1253, 1114, 836. ^{1}H-NMR (200 MHz): 0.11 (*s*, 36 H); 0.23 (*s*, 18 H); 0.92 (*s*, 54 H); 4.42 (*s*, 4 H); 4.45 (*s*, 8 H). ^{13}C-NMR (50.3 MHz): −5.2; −0.4; 18.4; 25.9; 63.8; 63.9; 73.6; 83.0; 83.1; 87.1; 87.3; 87.5; 88.0; 95.9; 132.2; 132.3; 132.6. EI-MS: 1282 (41, M^+), 1224 (33, $[M-(t\text{-Bu})]^+$), 73 (100, Me_3Si^+). Anal. calc. for $C_{70}H_{120}O_6Si_8$ (1282.4): C 65.56, H 9.43; found: C 65.83, H 9.56.

*(*E*)-5,6-Bis([[(*tert*-butyl)dimethylsilyl]oxy}methyl)dec-5-ene-1,3,7,9-tetrayne* (**56**). K_2CO_3 (20 mg, 0.145 mmol) was added to a soln. of **55a** (185 mg, 0.332 mmol) in MeOH (3 ml), and the mixture was stirred for 30 min. Pentane (20 ml) was added, and the mixture was extracted with H_2O (4 × 15 ml) and sat. aq. NaCl soln. (15 ml). The org. phase was dried ($MgSO_4$) and evaporated *in vacuo*. Filtration through a short plug (SiO_2; pentane/CH_2Cl_2 1:1) provided **56** (123 mg, 90%). Unstable yellow oil. IR (neat): 3243, 2928, 2856, 2150, 2059, 1461, 1110, 850. ^{1}H-NMR (200 MHz): 0.12 (*s*, 12 H); 0.92 (*s*, 18 H); 2.72 (*s*, 2 H); 4.44 (*s*, 4 H). ^{13}C-NMR (50.3 MHz): −5.5; 18.1; 25.6; 63.4; 67.6; 71.6; 75.4; 86.6; 132.3. EI-MS: 412 (0.1, M^+), 397 (1, $[M-Me]^+$), 355 (32, $[M-(t\text{-Bu})]^+$, 73 (100, Me_3Si^+). HR-EI-MS: 412.2258 (M^+, $C_{24}H_{36}O_2Si_2^+$; calc. 412.2254).

Oxidative Oligomerization of **56**. *α,ω-Bis{[3,5-di(*tert*-butyl)phenyl]ethynyl}poly[(*E*)-5,6-bis([[(*tert*-butyl)dimethylsilyl]oxy}methyl)dec-5-ene-1,3,7,9-tetrayne-1,10-diyl]* (**57**). To **56** (120 mg, 0.291 mmol) in CH_2Cl_2 (50 ml), **51** (0.2 mg, 0.001 mmol), CuCl (30 mg, 0.306 mmol), and TMEDA (1.0 ml, 6.72 mmol) were added, and the dark mixture was stirred in the air for 2 h at 20°. The mixture was poured into MeOH (50 ml) and, after 5 min, the precipitate obtained was isolated by filtration. Digestion in $CHCl_3$ followed by filtration provided a dark-red, insoluble solid (105 mg). Evaporation of the filtrate *in vacuo* gave **57** (13 mg, 11%). Red solid. UV/VIS: 303 (sh, 14600); 326 (sh, 17600), 344 (19400), 361 (sh, 18600), 400 (16200), 443 (20100), 487 (19100). IR (KBr): 2929, 2857, 2190, 2096, 1640, 1472, 1362, 1257, 1120, 1023, 837, 776. ^{1}H-NMR (500 MHz): 0.07 (*s*, 12 H); 0.92 (*s*, 18 H); 4.43 (*s*, 4 H). ^{13}C-NMR (125.8 MHz): −5.3; 25.8; 63.8; no additional resonances observed.

*[(*E*)-1,10-Bis(triisopropylsilyl)dec-5-ene-1,3,7,9-tetrayne-5,6-diyl]dimethylene Bis{3,5-bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]benzoate}* (**59**). A soln. of **23** (376 mg, 0.18 mmol) and **58** (198 mg, 0.75 mmol) in THF (8 ml) was cooled to 0°. Propan-2-amine (2 ml), CuCl (0.2 g, 0.20 mmol), and $NH_2OH\cdot HCl$ (0.02 g, 0.28 mmol) were added, and the mixture was stirred for 1 h at 20° in the air. Sat. aq. NH_4Cl soln. was added, and the org. phase was extracted with CH_2Cl_2. CC (SiO_2, hexane/CH_2Cl_2 1:1 → 1:2) afforded **59** (293 mg, 64%). Pale-yellow solid. M.p. 84°. IR: 2960, 2142, 1728, 1596, 1158. ^{1}H-NMR (200 MHz): 1.04 (*s*, 42 H); 1.34 (*s*, 72 H); 5.02 (*s*, 24 H); 5.29 (*s*, 4 H); 6.61 (*t*, *J* = 2.3, 4 H); 6.72 (*d*, *J* = 2.3, 8 H); 6.82–6.83 (*m*, 2 H); 7.35–7.46 (*m*, 36 H). ^{13}C-NMR (50.3 MHz): 11.16; 18.41; 31.23; 34.47; 64.40; 69.95; 70.21; 88.55; 89.41; 95.29; 101.70; 106.43; 107.63; 108.55; 125.56; 127.63; 129.70; 131.63; 133.79; 138.77; 151.13; 159.88; 160.42; 165.88. MALDI-TOF-MS (9-nitroanthracene): 2451 ($[M+Na]^+$). Anal. calc. for $C_{160}H_{192}O_{16}Si_2\cdot H_2O$ (2445.49): C 78.58, H 8.00; found: C 78.49, H 7.83.

Preparation and Oligomerization of **60**: Bu_4NF (1.0M soln. in THF, 0.2 ml, 0.2 mmol) was added to **59** (0.2 g, 0.082 mmol) in wet THF (10 ml). The color of the soln. became immediately dark red, and after 5 min all starting material was consumed (TLC). CH_2Cl_2 was added, and the mixture was washed with sat. aq. NH_4Cl soln. and dried ($MgSO_4$). The volume was reduced *in vacuo* to 10 ml, and PhC≡CH (22 mg, 0.21 mmol), molecular sieves (4 Å), TMEDA (8 mg, 0.001 ml, 0.07 mmol), and CuCl (2 mg, 0.02 mmol) were added. After stirring in the air for 1 h at 20°, sat. aq. NH_4Cl soln. was added, and the mixture was exhaustively extracted with CH_2Cl_2. The org. phase was washed with sat. aq. NaCl soln. and dried ($MgSO_4$). GPC (CH_2Cl_2), FC (SiO_2; hexane/CH_2Cl_2 1:1), and precipitation from MeOH afforded **61a–d**.

*(*E*)-1,14-Diphenyltetradec-7-ene-1,3,5,9,11,13-hexayne-7,8-diyl Bis{3,5-bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]benzoate}* (**61a**). ^{1}H-NMR (500 MHz): 1.31 (*s*, 72 H); 4.97 (*s*, 16 H); 5.03 (*s*, 8 H); 5.16 (*s*, 4 H); 6.55 (*t*, *J* = 2.2, 4 H); 6.71 (*d*, *J* = 2.2, 8 H); 6.83 (*t*, *J* = 2.2, 2 H); 7.23–7.39 (*m*, 45 H). MALDI-TOF-MS (9-nitroanthracene): 2354 ($[M+K)^+$), 2338 ($[M+Na]^+$), 2313 (M^+).

*(7*E*,17*E*)-1,24-Diphenyltetracosa-7,17-diene-1,3,5,9,11,13,15,19,21,23-decayne-7,8,17,18-tetrayl Tetrakis{3,5-bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)oxy]benzoate}* (**61b**). ^{1}H-NMR (500 MHz): 1.29 (*s*, 72 H); 1.30 (*s*, 72 H); 4.94 (*s*, 16 H); 4.95 (*s*, 16 H); 4.96 (*s*, 8 H); 4.99 (*s*, 8 H); 5.04 (*s*, 4 H); 5.08 (*s*, 4 H); 6.55 (*m*, 8 H); 6.66 (*d*, *J* = 2.2, 8 H); 6.69 (*d*, *J* = 2.2, 8 H); 6.78 (*t*, *J* = 2.2, 2 H); 6.81 (*t*, *J* = 2.2, 2 H); 7.22–7.38 (*m*, 90 H). MALDI-TOF-MS (9-nitroanthracene): 4467 ($[M+K]^+$), 4451 ($[M+Na]^+$).

*(7*E*,17*E*,27*E*)-1,34-Diphenyltetratriaconta-7,17,27-triene-1,3,5,9,11,13,15,19,21,23,25,29,31,33-tetradecayne-7,8,17,18,27,28-hexayl Hexakis{3,5-bis[(3,5-bis{[4-(tert-butyl)benzyl]oxy}benzyl)oxy]benzoate}* (**61c**). MALDI-TOF-MS (9-nitroanthracene): 6815 ($[M+264]^+$), 6668 ($[M+127]^+$), 6564 ($[M+Na]^+$).

*(7E,17E,27E,37E)-1,44-Diphenyltetratetraconta-7,17,27,37-tetraene-1,3,5,9,11,13,15,19,21,23,25,29,31,33,35,39,41,43-octadecayne-7,8,17,18,27,28,37,38-octayl Octakis{3,5-bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)-oxy]benzoate}* (**61d**). MALDI-TOF-MS (9-nitroanthracene): 8780 ([$M+126$]$^+$), 8677 ([$M+$Na]$^+$ (very weak).

*(3,5-Bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)(diphenyl)phosphane* (**64**). Dry NH_3 (100 ml) was condensed under Ar at $-78°$, and Na (92 mg, 4.70 mmol) was added. $ClPPh_2$ (0.36 ml, 2.4 mmol) was added to the stirred deep-blue soln., and the color changed to orange. Compound **11** (1.00 g, 2.02 mmol) in dry degassed THF was added at $-78°$, and the mixture was slowly warmed to 20°. After evaporation of NH_3, the solvent was removed *in vacuo*. The residue was filtered over *Celite* (CH_2Cl_2) yielding **64** (811 mg, 72%). Colorless amorphous solid. M.p. 108°. ^{1}H-NMR (200 MHz): 1.35 (*s*, 18 H); 3.38 (*s*, 2 H); 4.85 (*s*, 4 H); 6.33 (*t*, $J=1.9$, 2 H); 6.43 (br. *s*, 1 H); 7.28–7.55 (*m*, 18 H). ^{31}P-NMR (121.5 MHz): -9.65.

trans-*Bis{[3,5-bis(benzyloxy)benzyl](diphenyl)phosphane}dichloroplatinum(II)* (*trans*-**67**). A soln. of **62** (180 mg, 370 μmol) in dry $CHCl_3$ (20 ml) was added to a degassed soln. of *trans*-[Pt(NCPh)$_2$Cl$_2$] (80 mg, 169 μmol), and the mixture was heated to reflux for 45 min. Filtration (SiO_2) and evaporation *in vacuo* yielded a weakly yellow solid. Fractional crystallization (CH_2Cl_2/EtOH) afforded *trans*-**67** (64 mg, 30%). Pale-yellow crystals. M.p. 211–212°. IR ($CHCl_3$): 3064, 3036, 3005, 1594, 1498, 1453, 1436, 1377, 1343, 1318, 1295, 1152, 1103, 1056, 1028, 850, 836, 694. ^{1}H-NMR (500 MHz): 3.92 (*t*, $J(^{31}P,^1H)=4.1$, 4 H); 4.71 (*s*, 8 H); 6.32 (*t*, $J=1.0$, 4 H); 6.39 (*s*, 2 H); 7.27–7.41 (*m*, 32 H); 7.54–7.61 (*m*, 8 H). ^{13}C-NMR (125.8 MHz): 31.06; 69.87; 101.47; 109.61; 127.68; 127.93; 127.98; 128.03; 128.40; 128.52; 130.58; 134.16; 135.56; 136.95; 159.44. ^{31}P-NMR (202.5 MHz): 16.01 ($^1J(^{195}Pt,^{31}P)=2576$). ^{195}Pt-NMR (107.5 MHz): -4007.8 (*t*, $^1J(^{195}Pt,^{31}P)=2582$). FAB-MS: 1246/1245/1244/1243/1242 (10/8/13/10/9, M^+), 1211/1210/1209/1208/1207/1206 (9/25/45/70/74/56, [$M-$Cl]$^+$), 1175/1174/1173/1172/1171 (10/26/39/100/90, [$M-2$ Cl]$^+$). Anal. calc. for $C_{66}H_{58}Cl_2O_4P_2Pt \cdot 0.5\ CH_2Cl_2$ (1285.57): C 62.13, H 4.63; found: C 62.34, H 4.74. X-Ray: see *Fig. 14*.

cis/trans-*Bis[(3,5-bis{[4-(*tert*-butyl)benzyl]oxy}benzyl)(diphenyl)phosphane]dichloroplatinum(II)* (**68**). According to the procedure for *trans*-**67**, **64** (222 mg, 370 μmol) in dry $CHCl_3$ (20 ml) was reacted with *trans*-[Pt(NCPh)$_2$Cl$_2$] (100 mg, 212 μmol) to give **68** (186 mg, 60%) as a *cis/trans*-mixture. Yellow needles. M.p. 114–115°. IR ($CHCl_3$): 3061, 3005, 2965, 2909, 2869, 1602, 1595, 1516, 1461, 1436, 1365, 1343, 1316, 1295, 1268, 1154, 1104, 1055, 850, 838, 821, 692. ^{1}H-NMR (300 MHz): 1.34 (*s*, 36 H); 3.95 (*t*, $J(^{31}P,^1H)=4.1$, 4 H); 4.68 (*s*, 8 H); 6.30 (*t*, $J=0.9$, 4 H); 6.43 (*s*, 2 H); 7.24–7.42 (2*m*, 28 H); 7.56–7.65 (*m*, 8 H). ^{13}C-NMR (75.5 MHz): 31.38; 34.60; 69.68; 77.26; 101.34; 109.37; 125.46; 127.68; 127.97; 128.65; 130.56; 133.81; 134.12; 134.20; 134.26; 135.42; 150.96; 159.47. ^{31}P-NMR (121.5 MHz): 14.22 ($^1J(^{195}Pt,^{31}P)=2526$); 16.17 ($^1J(^{195}Pt,^{31}P)=2570$). FAB-MS: 1434/1433/1432/1431/1430 (19/30/45/31/12, [$M-$Cl]$^+$), 1398/1397/1396/1395/1394 (11/33/88/61/28, [$M-2$ Cl]$^+$), 147 (100, $C_{11}H_{15}^+$). Anal. calc. for $C_{82}H_{90}Cl_2O_4P_2Pt$ (1467.54): C 67.11, H 6.18; found: C 66.92; H 6.36).

trans-*Bis{[3,5-bis(benzyloxy)benzyl](diphenyl)phosphane}bis{(*E*,E/Z)-3,4-bis[(triisopropylsilyl)ethynyl]-6-(trimethylsilyl)hex-3-en-1,5-diynyl}platinum(II)* (**65**). A soln. of **69** (30 mg, 58.9 μmol), *trans*-**67** (36 mg, 29.0 μmol), CuI (1 mg, 5 μmol), and (i-Pr)$_2$NH (1 ml) in dry THF (5 ml) was reacted in the dark in a *Schlenk* apparatus for 20 h at 20°. Workup in the dark proceeded by filtration of the brown mixture over SiO_2, evaporation *in vacuo*, FC (SiO_2; hexane/CH_2Cl_2 2:1), and GPC (PhMe) to give **65** (26 mg, 41%). Dark-yellow, highly viscous unstable oil, which slowly decomposed even at $-20°$. IR ($CHCl_3$): 2944, 2867, 2078, 1600, 1461, 1433, 1367, 1150, 857, 667. ^{1}H-NMR (500 MHz): -0.01, 0.12 (2*s*, 18 H); 0.88–1.00 (3*m*, 84 H); 4.15–4.29 (*m*, 4 H); 4.62–4.63 (2*s*, 8 H); 6.20 (br. *s*, 1 H); 6.28 (br. *s*, 2 H); 6.30–6.35 (*m*, 3 H); 7.14–7.38 (*m*, 32 H); 7.50–7.62 (*m*, 8 H). ^{31}P-NMR (121.5 MHz): 14.46 ($^1J(^{195}Pt,^{31}P)=2540$); 14.81 ($^1J(^{195}Pt,^{31}P)=2514$). FAB-MS: 2188 (73, M^+), 2114 (12, [$M-$SiMe$_3$]$^+$), 1700 (17, [$M-C_{33}H_{29}O_2P$]$^+$), 1679 (61, [$M-C_{31}H_{51}Si_3$]$^+$), 1172 (100, [$M-2$ $C_{31}H_{51}Si_3$]$^+$).

X-Ray Crystal Structure of trans-**67**. Single crystals were grown by slow evaporation from CH_2Cl_2/EtOH 4:1 at 20°. X-Ray crystal data for $C_{66}H_{58}Cl_2O_4P_2Pt$ ($M_r=1243.05$): triclinic space group $P\bar{1}$, $D_c=1.493$ g cm^{-3}, $Z=1$, $a=10.188(14)$, $b=12.695(15)$, $c=13.083(18)$ Å, $\alpha=112.39(10)$, $\beta=108.51(10)$, $\gamma=101.35(10)°$, $V=1383(3)$ Å^3, CuK_α radiation, $4.04 \le \theta \le 49.99°$, 2841 unique reflections, $T=293$ K. The structure was solved by direct methods (*SHELXTL PLUS*) and refined by full-matrix least-squares analysis based on 2841 independent F^2 data and 341 parameters using experimental weights; heavy atoms anisotropic, H-atoms fixed isotropic with positions calculated from stereochemical considerations. Final $R(F)=0.0422$ for 2841 observed reflections with $I>2\sigma(I)$ and $wR(F^2)=0.1137$ for all independent data. *Cambridge Crystallographic Data Centre* Deposition No. CCDC-149056. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

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