Solid-Phase Synthesis of Oligo(triacetylene)s and Oligo(phenylenetriacetylene)s Employing *Sonogashira* and *Cadiot–Chodkiewicz*-Type Cross-Coupling Reactions

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We describe the first polymer-supported synthesis of poly(triacetylene)-derived monodisperse oligomers, utilizing Pd^0-catalyzed *Sonogashira* and *Cadiot–Chodkiewicz*-type cross-couplings as the key steps in the construction of the acetylenic scaffolds. For our investigations, *Merrifield* resin functionalized with a 1-(4-iodoaryl)triazene linker was chosen as the polymeric support (**R2**; *Figure* and *Scheme 3*). The linker selection was made based on the results of several model studies in the liquid phase (*Schemes 1* and *2*). For the solid-support synthesis of the oligo(phenylene triacetylene)s **7b** – **7d**, a set of only three reactions was required: *i*) Pd^0-catalyzed *Sonogashira* cross-coupling, *ii*) Me$_3$Si–alkyne deprotection by protodesilylation, and *iii*) cleavage of the linker with liberation of the generated oligomers (*Scheme 5*). The longest-wavelength absorption maxima of the oligo(phenylene triacetylene)s **7a** – **7d** shift bathochromically with increasing oligomeric length, from λ_{max} 337 nm (monomer **7a**) to 384 nm (tetramer **7d**; *Table 2*). Based on the electronic absorption data, the effective conjugation length (ECL) of the oligo(phenylene triacetylene)s is estimated to involve at least four monomer units and 40 C-atoms. π-Electron conjugation in these oligomers is less efficient than in the known oligo(triacetylene)s **14a** – **14d** (*Table 2*) due to poor transmittance of π-electron delocalization by the phenyl rings inserted into the oligomeric backbone. Similar conclusions were drawn from the electrochemical properties of the two oligomeric series as determined by cyclic (CV) and rotating-disk voltammetry (RDV; *Table 3*). In sharp contrast to **14b** – **14d**, the oligo(phenylene triacetylene)s **7b** – **7d** are strongly fluorescent, with the highest quantum yield $\Phi_F = 0.69$ measured for trimer **7c** (*Table 2*). Whereas the *Sonogashira* cross-coupling on solid support proceeded smoothly, optimal conditions for alkyne–alkyne cross-coupling reactions employing Pd^0-catalyzed *Cadiot–Chodkiewicz* conditions still remain to be developed, despite extensive experimentation (*Scheme 7* and *Table 1*).

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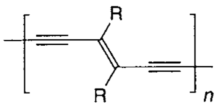
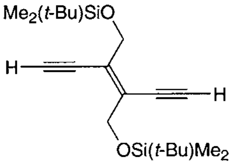
1. Introduction. – Monodisperse linearly π-conjugated oligomers of precise length and constitution have attracted considerable scientific interest. They have been recognized as valuable model systems for the corresponding infinite polymers, and their investigation has greatly benefitted the rational design of new functional polymers [1]. Furthermore, they have become integral to electronic and optical applications in emerging technologies such as organic light-emitting diodes [2], organic semiconductors [3], and nanoscale as well as single-molecule-based molecular electronics [4].

To explore structure–property relationships in oligo(triacetylene)s and extrapolate the properties of long-chain poly(triacetylene)s (PTAs), we had prepared several series of monodisperse PTA oligomers extending in length up to 17.8 nm (24-mer) by oxidative acetylenic coupling [5] of monomeric (*E*)-1,2-diethynylethene (DEE; (*E*)-hex-3-ene-1,5-diyne; *e.g.*, DEE derivative **1**) or higher oligomers [6]. This approach always generated oligomeric mixtures, and the separation and isolation of individual oligomers, formed in low-to-moderate yield, required tedious gravity and high-performance gel permeation chromatography (GPC).



trans-poly(triacetylene) (PTA)



1 (DEE derivative)

Solid-phase synthesis could offer a more efficient approach towards tailor-made PTA oligomers, potentially facilitating workup and purification protocols, and allowing flexible control of the oligomeric length. With the extensive development of solid-phase organic synthesis in the 1990s [7], monodisperse π-conjugated oligomers, in particular oligothiophenes [8] and oligo(phenylene ethynylene)s [9], have indeed increasingly been prepared on polymeric support, thereby overcoming the problems associated with solution-phase synthesis. Here, we present the development of a solid-phase synthesis on *Merrifield* resin (chloromethyl-substituted, 1% cross-linked poly(styrene divinylbenzene)) [10] for the construction of oligo(triacetylene)s and oligo(phenylene triacetylene)s, a new class of linearly π-conjugated oligomers, by means of Pd^0-catalyzed cross-coupling reactions (for a preliminary communication of parts of this work, see [11]).

2. Results and Discussion. – 2.1. *Evaluation of Suitable Linker Systems in Liquid-Phase Studies.* A prerequisite for a successful application of solid-support chemistry to oligomer synthesis is the choice of an appropriate linker moiety to attach the starting monomer onto the resin. 1-Aryltriazene linkers have been widely used in the preparation of oligo(phenylene ethynylene)s as well as phenylacetylene-based dendrimers [9]; they are compatible with Pd^0-catalyzed coupling reactions and can be cleaved from the resin under a variety of conditions [7c][9][12]. Thus, aromatic diazonium salts are accessible by cleaving the triazene with trifluoroacetic acid (TFA) [12b,c], whereas a cleavage utilizing MeI generates the corresponding aryl iodides [7c][9][12f]. Traceless cleavage replacing the triazene substituent with a C–H bond can be achieved by either using 10% HCl in THF [12a], H_3PO_2 in $Cl_2CHCOOH$ [12a], or $HSiCl_3$ in CH_2Cl_2 [12e].

We opted for the two resin-linker conjugates **R2** and **R3**, which were introduced by *Moore* and co-workers [9a–c] and differing only in the length of the spacer between the triazene moiety and the resin. In a first step, we investigated their applicability to the synthesis of oligo(triacetylene)s in liquid-phase test reactions by using the readily available, soluble counterparts **2** and **3** (*Figure*).

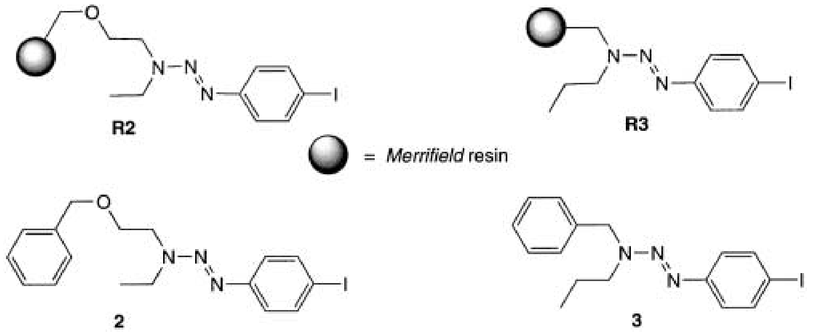


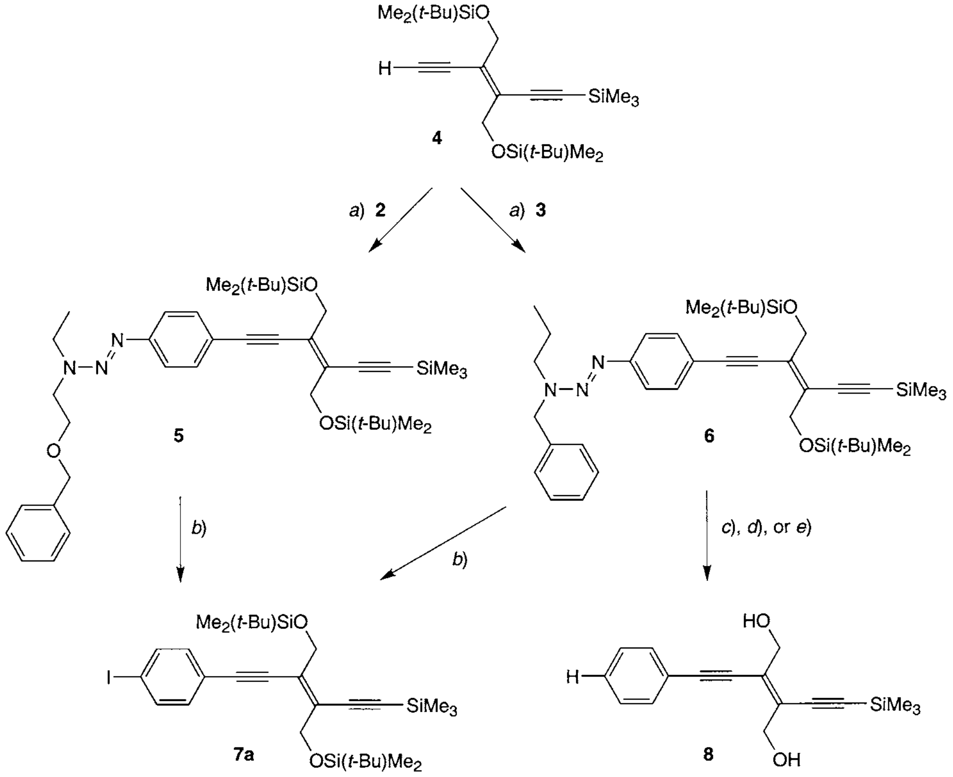
Figure. Merrifield *resin-linker conjugates* **R2** *and* **R3**, *and their soluble counterparts* **2** *and* **3**

Attachment of mono-deprotected DEE **4** [6a] to both linker systems **2** and **3** by *Sonogashira* cross-coupling [13] proceeded smoothly, providing the DEE-linker conjugates **5** and **6**, respectively, in high yield (*ca.* 90%; *Scheme 1*). In contrast, **5** and **6** differed substantially in their reactivity during linker cleavage using MeI at 110° for 6 h. (Benzyloxyethyl)triazene **5** was more reactive and provided aryl iodide **7a** in 85% yield, whereas cleavage of benzyl derivative **6** only proceeded in 66% yield, demonstrating the steric advantage of the longer spacer connecting the triazene moiety to the aryl ring in **2** (and to the *Merrifield* resin in **R2**; *Figure*). We also examined the DEE-linker conjugate **6** under the conditions of traceless cleavage (*Scheme 1*) [12a,e]. Unfortunately, all applied experimental conditions turned out to be too acidic, and, in each experiment, diol **8** was obtained by cleavage of the *O*-protecting silyl groups.

Protodesilylation of **5** and **6** with 2N NaOH in MeOH/THF provided the terminally deprotected alkynes **9** and **10**, respectively (*Scheme 2*). Besides unproblematic *Sonogashira* cross-couplings with aryl halides [14], acetylenic hetero-couplings under *Hay* [15] and *Cadiot – Chodkiewicz*-type conditions [16] were explored with the two alkynes. In the latter conversion, the original protocol (CuCl, Et_2NH, $NH_2OH \cdot HCl$, $EtOH/H_2O$ 95 : 5) [16] was not used, since the *Merrifield* resin (in the subsequent solid-supported reactions) swells poorly in alcoholic solutions [17]. To circumvent this problem, we switched to the alternative Pd^0-catalyzed alkyne cross-coupling in benzene developed by *Vasella* and co-workers for the synthesis of acetylenosaccharides [18]. [(Benzyloxy)ethyl]triazene **9** was found superior in both the *Hay* coupling with **4** (4 equiv.) and the *Cadiot–Chodkiewicz*-type coupling with bromoalkyne **11** (1 equiv.) [19], providing **12** in 58 and 56% yield, respectively. The yields of **13** in the corresponding coupling with benzyltriazene **10** were markedly lower (47 and 43%, resp.). DEE Dimer **14b**, resulting from oxidative homo-coupling of **4**, was an important side-product under the *Hay*-coupling conditions, but was also formed in small quantities in the Pd^0-catalyzed cross-coupling of **10** with **11**.

Finally, the triazene linkers were cleaved with MeI at 110° for 6 h to yield (4-iodophenyl)-substituted DEE dimer **15**. Again, the yield for cleavage of the (benzyloxy)ethyl derivative **12** was much higher (60%) compared with only 21% for benzyl derivative **13**. The moderate cleavage yields for both linker systems are in

Scheme 1. *Liquid-Phase Test Reactions with Linkers* **2** *and* **3**



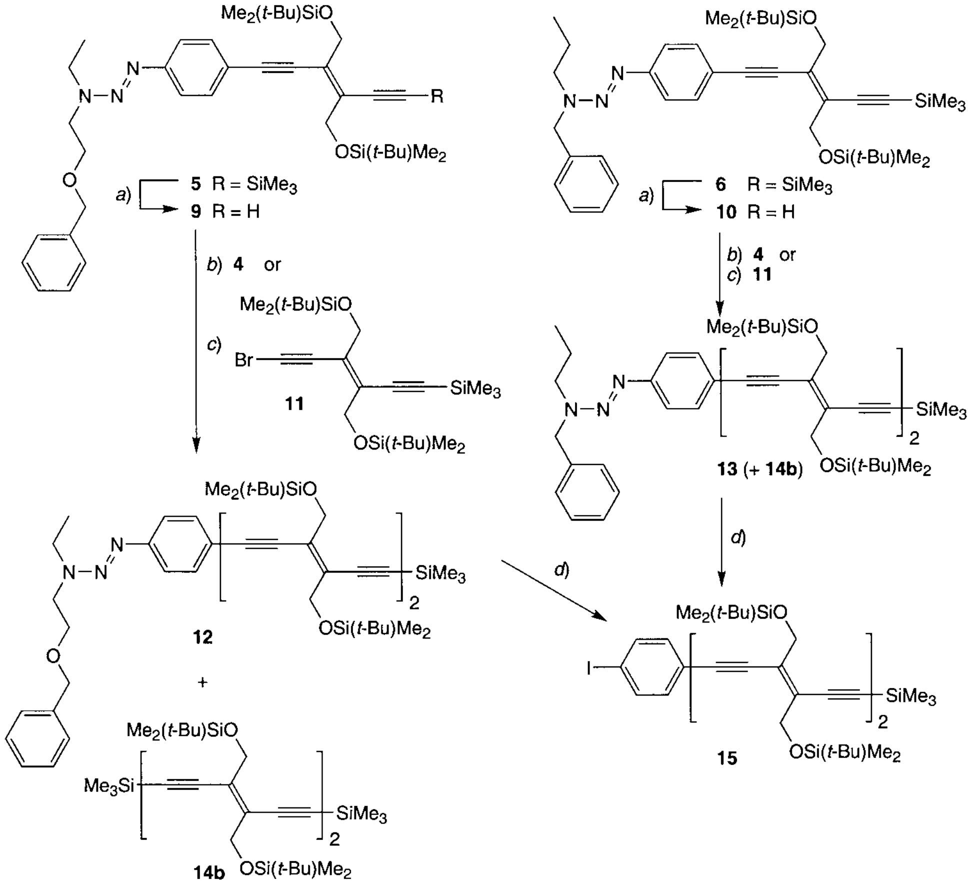
a) $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, 25°, 20 h; 89% (**5**); 90% (**6**). *b*) MeI, 110°, 6 h; 85% (from **5**); 66% (from **6**). *c*) 1N HCl/THF 1:10, ultrasound, 50°, 10 min; 43%. *d*) H_3PO_2, $Cl_2CHCOOH$, 25°, 4 h; 37%. *e*) $HSiCl_3$, CH_2Cl_2, 40°, 15 min; 52%.

agreement with previous reports, which show that electron-withdrawing groups in the *para*-position of the aromatic ring, such as the DEE dimer fragments in **12** and **13** [14b], slow down the conversion to the aryl iodide [9f][20].

Clearly, the (benzyloxyethyl)triazene linker system with the longer spacer between triazene moiety and aryl ring shows, certainly for steric reasons, substantial advantages over the benzyltriazene analog in terms of alkyne coupling yields and cleavage efficiency. Therefore, the resin-linker combination **R2** (*Figure*) was used in the development of a solid-phase synthesis of oligo(triacetylene)-derived oligomers.

2.2. *Solid-Phase Synthesis of Oligo(phenylene Triacetylene)s by* Sonogashira *Cross-Coupling*. In a first step, polymer-supported triazene **R2** was obtained by etherification of *Merrifield* resin (0.9 mmol Cl/g resin) with (2-hydroxyethyl)triazene **16** with NaH in THF [9b] (*Scheme 3*). Elemental analysis showed a resin loading of 0.57 mmol I/g resin. Thus, a comparison of this value with the theoretical maximum loading of 0.72 mmol I/g resin provides a yield of 79% [9d] (see also *Exper. Part*). The resin-bound linker was subsequently coupled under *Sonogashira* conditions with DEE

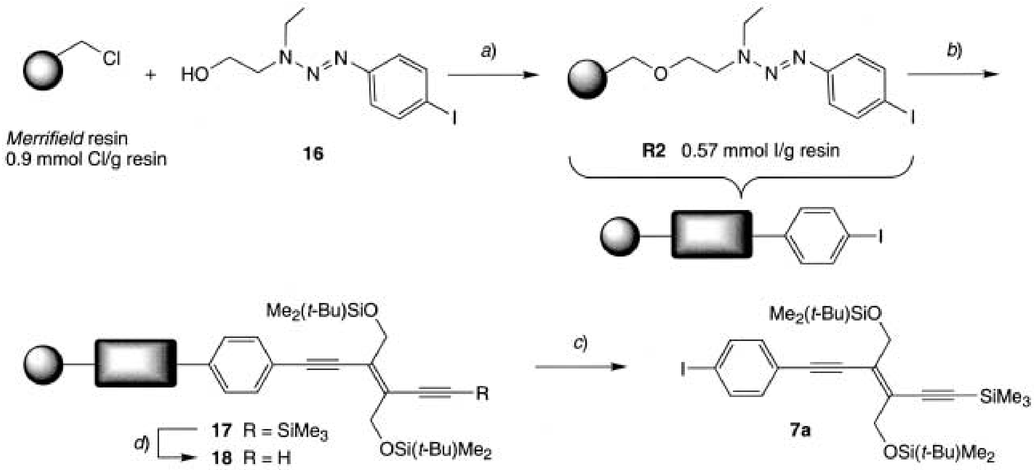
Scheme 2. *Alkyne Coupling and Linker-Cleavage Test Reactions in the Liquid Phase*



a) 2N NaOH, MeOH/THF 1:1, 25°, 45 min; quant. *b*) CuCl, TMEDA, O_2, CH_2Cl_2, 25°, 3.5 h; 58% (**12**) and 27% (**14b**); 47% (**13**) and 50% (**14b**). *c*) [$Pd_2(dba)_3$], CuI, PMP, LiI, C_6H_6, 25°, 7 h; 56% (**12**); 43% (**13**) and 17% (**14b**). *d*) MeI, 120°, 6 h; 60% (from **12**); 21% (from **13**). TMEDA = *N,N,N′,N′*-Tetramethylethylenediamine; dba = dibenzylideneacetone; PMP = 1,2,2,6,6-pentamethylpiperidine.

monomer **4** (1.5 equiv.) to afford polymer-bound DEE **17** in 91% yield. Conditions were chosen (see *Exper. Part*) to minimize – by rigorous degassing – homo-coupling of **4**, and to allow recovery and recycling of excess starting material. At the end of the coupling reaction, resin-bound DEE **17** was isolated by filtration, washed, and dried *in vacuo*. Treatment with MeI at 120° for 24 h led to linker cleavage, providing iodoarylated DEE **7a** in a satisfying yield of 83% over three steps (including the attachment of linker **16** to the *Merrifield* resin). Also, protodesilylation of **17** (2N NaOH, MeOH/THF) proceeded smoothly, providing the terminally deprotected alkyne **18** in quantitative yield. The progress of the deprotection was analyzed by infrared (IR) spectroscopy, monitoring the disappearance of the band at 2133 cm^{-1} ($C{\equiv}C{-}SiMe_3$ stretch) and the appearance of the bands at 3311 cm^{-1} ($C{\equiv}C{-}H$

Scheme 3. *Synthesis of Resin-Bound DEE*



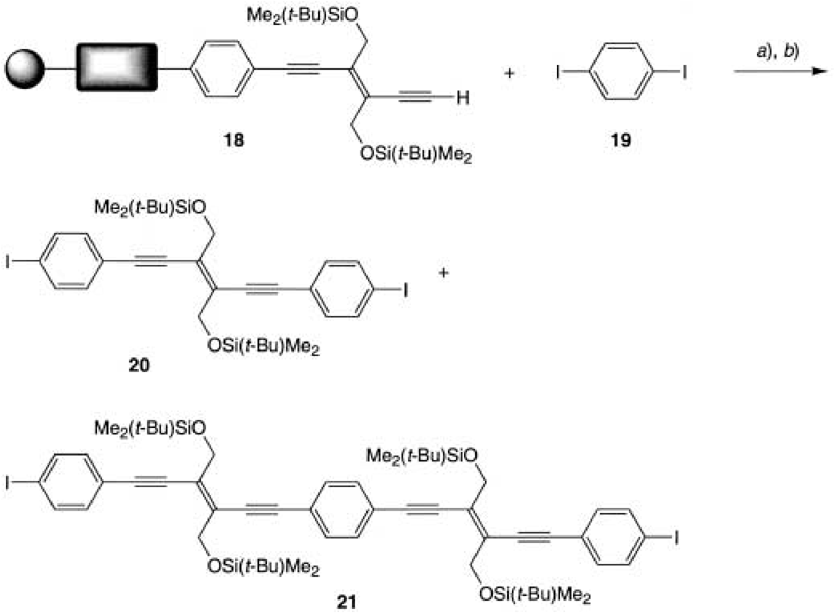
a) NaH, THF, $-78° \rightarrow 45°$, 5 d; 79%. *b*) **4**, $[Pd_2(dba)_3]$, CuI, PPh_3, Et_3N, 70°, 24 h; 91%. *c*) MeI, 120°, 24 h; 83% (3 steps). *d*) 2N NaOH, MeOH/THF 1 : 1, 70°, 3 h; quant. Yields are given starting from the attachment of **16** to the *Merrifield resin* (see also the *Exper. Part*).

stretch) and 2109 cm^{-1} ($C{\equiv}C{-}H$ stretch). IR Analysis was also useful for monitoring the progress of the subsequent cross-coupling reactions.

Initially, we wanted to build up oligo(phenylene triacetylene)s by mono-cross-coupling of resin-bound DEE **18** to 1,4-diiodobenzene **19**, followed by a repetitive sequence of *i*) cross-coupling with DEE monomer **4**, *ii*) alkyne desilylation, and *iii*) mono-coupling to **19** (*Scheme 4*). Product analysis after each step would be done by both elemental analysis and IR spectroscopy. Regrettably, substantial site–site interactions were already observed during the first coupling between **18** and **19** despite using a large excess of **19** (5 equiv.). After executing the *Sonogashira* cross-coupling, cleavage of the linker with MeI provided the desired bis(4-iodophenyl)-substituted DEE **20** (19% over five steps) in addition to the bis-DEE derivative **21** (27% over five steps). This undesired side-product is formed by the reaction of two adjacent resin-bound DEEs **18** with 1 equiv. of diiodide **19**. Site–site interactions are of frequent concern in solid-phase chemistry, even in highly cross-linked resins with low loading levels [21]. The pseudo-dilution effect provided by the *Merrifield* support has been shown to be rather limited, largely due to its conformational flexibility [22].

In view of the encountered site–site interactions, the synthetic strategy was changed to the successful one shown in *Scheme 5*. The oligo(phenylene triacetylene)s **7b**–**7d** were prepared in a short period of time starting from **17** (*Scheme 3*) by repetitive cycles of three conversions: *i*) deprotection of the resin-bound alkyne, *ii*) *Sonogashira* cross-coupling with iodoarylated DEE **7a**, and *iii*) liberation of the formed oligomer from the solid support with MeI. The solvent mixture used in the cross-coupling step was changed from Et_3N to THF/Et_2NH 4 : 1 to take advantage of the better swelling properties of *Merrifield* beads in THF [17].

Scheme 4. *Site–Site Interactions in the* Sonogashira *Cross-Coupling between Resin-Bound DEE* **18** *and 1,4-Diiodobenzene* (**19**)



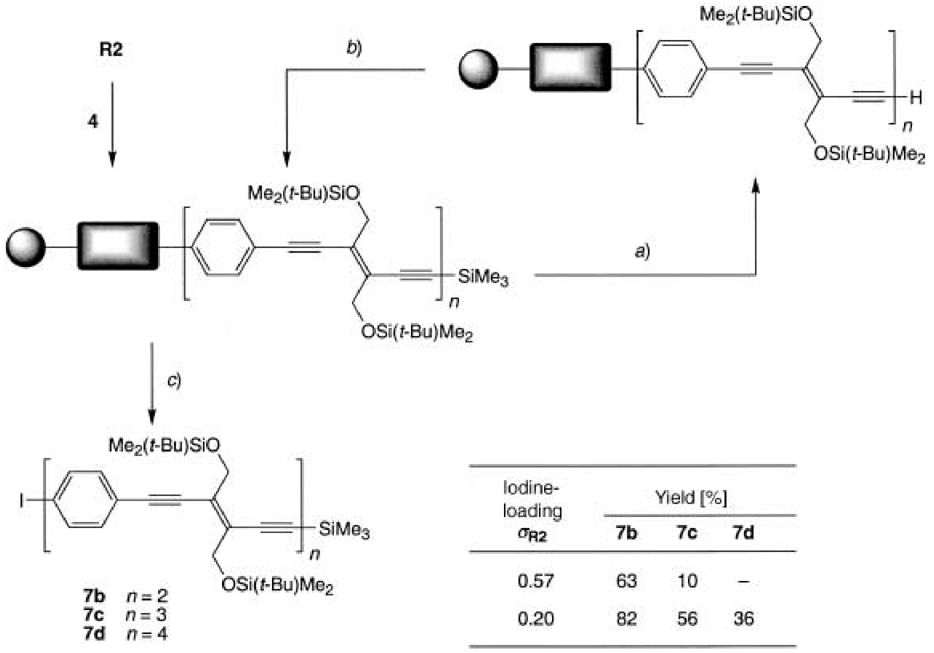
a) [$Pd_2(dba)_3$], CuI, PPh_3, Et_3N, 70°, 24 h. *b*) MeI, 120°, 24 h; 19% (**20**, 5 steps); 27% (**21**, 5 steps).

The oligomeric yields exhibited a significant dependence upon the iodine-loading level σ of resin **R2**. At a loading of 0.57 mmol/g resin, only dimer **7b** was obtained in good yield (63% over five steps), whereas trimer **7c** was formed in only 10% yield (over seven steps), and tetramer **7d** could not be isolated at all (*Scheme 5*). Apparently, a high concentration of reactive sites functionalized with the oligomers leads to overcrowding of the resin pores, thereby preventing further conversions. The use of solid support **R2** containing a lower iodine-loading of 0.20 mmol/g resin, indeed, provided significantly better results. Whereas monomer **7a** (*Scheme 3*) was obtained in identical yield at both resin loadings, the reduced loading substantially increased the yield of dimer **7b** (82% over five steps), trimer **7c** (56% over seven steps), and tetramer **7d** (36% over nine steps).

The oligo(phenylene triacetylene)s **7b**–**7d** are yellow, air- and light-stable solids that melt, apart from tetramer **7d**, without decomposition. Solubility decreases rapidly with increasing oligomeric length. Whereas monomer **7a** and dimer **7b** are soluble in all common solvents, trimer **7c** and especially tetramer **7d** are only poorly soluble in CH_2Cl_2.

Dimer **7b** and tetramer **7d** were also prepared by an iterative divergent/convergent strategy (*Scheme 6*) utilizing a resin with an iodine-loading of 0.31 mmol/g resin. In general, this binomial approach provides higher yields of longer oligomers due to the reduction in the number of transformations [9b,c,d][23]. However, in this study, we observed the opposite. Dimer **7b** was formed in only 50% yield (over five steps), and

Scheme 5. *Solid-Phase Synthesis of Oligo(phenylene triacetylene)s* **7b** – **7d**



7b $n = 2$
7c $n = 3$
7d $n = 4$

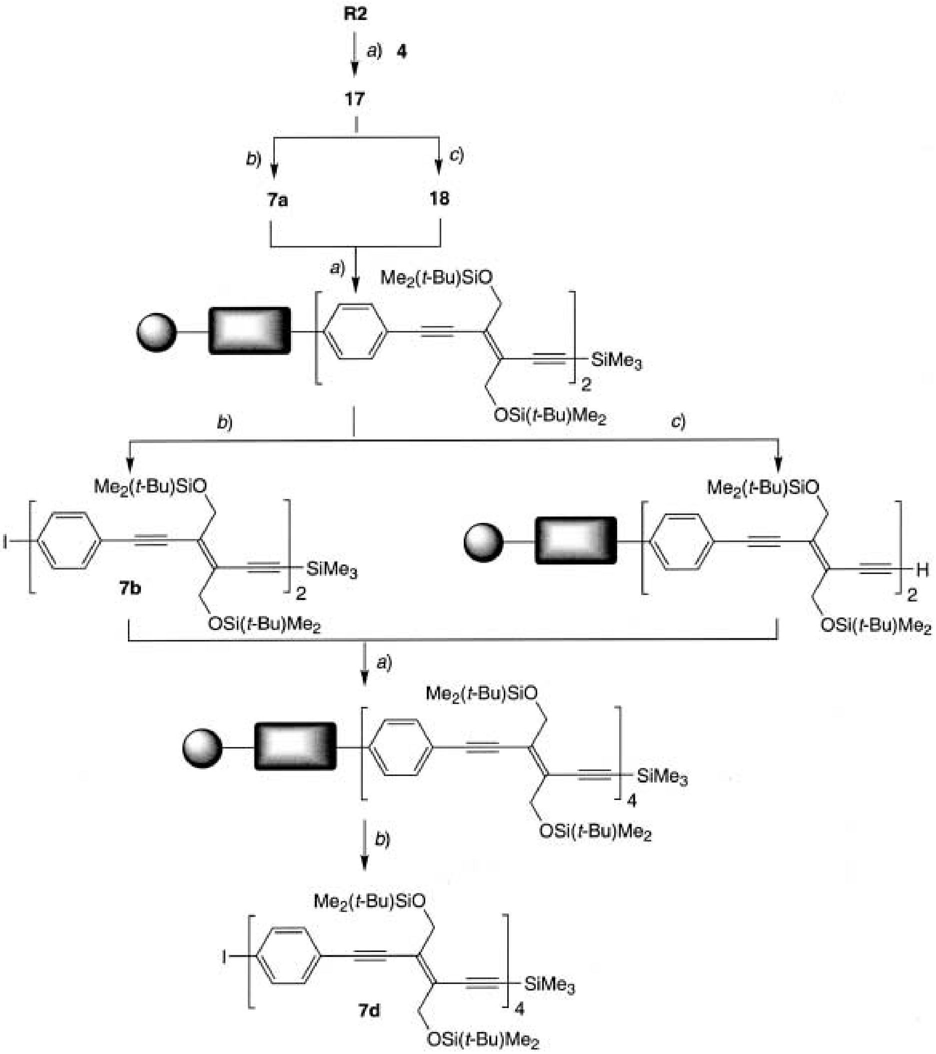
Iodine-loading σ_{R2}	Yield [%]		
	7b	**7c**	**7d**
0.57	63	10	–
0.20	82	56	36

a) 2N NaOH, MeOH/THF 1:1, 70°, 3 h. *b*) **7a**, [$Pd_2(dba)_3$], CuI, PPh_3, Et_2NH/THF 1:4, 70°, 24 h. *c*) MeI, 120°, 24 h. Iodine loading $\sigma_{\mathbf{R2}}$ in mmol/g resin.

tetramer **7d** was obtained in just 19% yield (over seven steps), which is less than the yields obtained in the stepwise synthesis (*Scheme 5*). We tentatively explain these results that contrast some of those obtained by others on similar resins with similar loadings [9a–d] [22] [23a–c] with the steric hindrance in the resin pores, caused by the bulky (*t*-Bu)Me_2SiOCH_2 substituents on the oligomeric backbones, as well as the limited solubility of the formed oligo(phenylene triacetylene)s.

2.3. *Solid-Phase Synthesis of Oligo(triacetylene)s by* Cadiot–Chodkiewicz-*Type Cross-Coupling.* In contrast to the large number of published *Sonogashira* cross-coupling reactions on solid phase [1a] [9] [22] [23a–c], only one report has appeared on solid-supported *Cadiot–Chodkiewicz* couplings [24]. Following the test reactions in solution (*Scheme 2*), we reacted resin-supported DEE **18** (iodine-loading of precursor resin **R2**: $\sigma = 0.20$ mmol/g resin) with bromoderivative **11** under various conditions (*Table 1*) in degassed benzene or THF at 45°. After 20–24 h, IR analysis still showed incomplete conversion. Cleavage of the linker with MeI at 120° provided in each run a mixture of three compounds, namely the desired hetero-coupled dimer **15**, uncoupled monomer **22**, and homo-coupled dimer **23**, resulting from site–site interactions. While rather unstable, oily **22** was readily isolated by chromatography (SiO_2; hexanes/CH_2Cl_2 2:1), separation of the two yellow, stable dimers **15** and **23** was unsuccessful, even by preparative high-performance liquid chromatography (HPLC). The yields of the two dimers, however, could be determined by analytical HPLC. For a complete character-

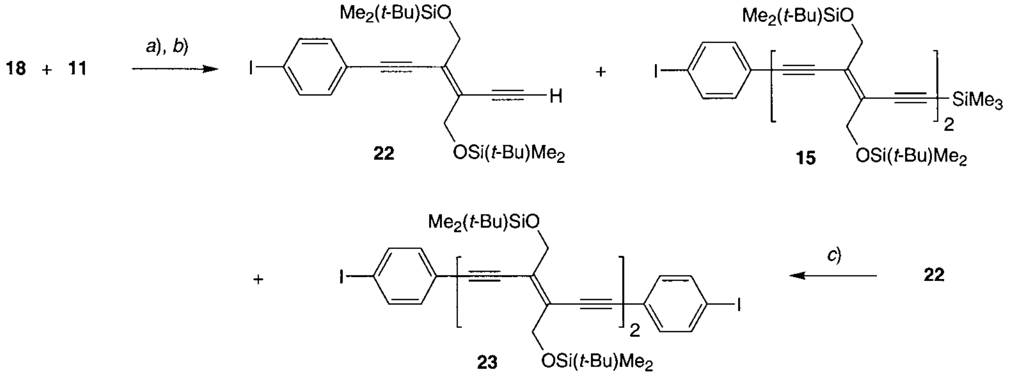
Scheme 6. *Binomial Synthesis of Oligo(phenylene Triacetylene)s*



a) [$Pd_2(dba)_3$], CuI, PPh_3, Et_2NH/THF 1:4, 70°, 24 h. *b*) MeI, 120°, 24 h; 83% (**7a**, 3 steps); 50% (**7b**, 5 steps); 19% (**7d**, 7 steps). *c*) 2N NaOH, MeOH/THF 1:1, 70°, 3 h.

ization, dimer **23** was independently prepared by oxidative *Hay* coupling of **22** (*Scheme 7*), obtained by deprotection of **7a**.

The Pd^0-catalyzed *Cadiot–Chodkiewicz* coupling on solid support was investigated in further detail (*Table 1*). Benzene was found to be superior to THF as the solvent, providing slightly higher product yields and selectivities. Omitting Cu^I ions, while at the same time raising the amount of Pd catalyst, leads to preferential formation of the desired dimer **15** (*Table 1, Entry 4 vs. 1*). The best result was obtained when, Scheme 7. Cadiot–Chodkiewicz *Cross-Coupling on Solid Support*



a) [$Pd_2(dba)_3$], CuI, LiI, PMP, C_6H_6 or THF, 45°, 20–24 h. *b*) MeI, 120°, 24 h (for yields, see *Table 1*). *c*) CuCl, TMEDA, O_2, CH_2Cl_2, 25°, 12 h; 19%.

Table 1. *Optimization of the Pd^0-Catalyzed* Cadiot–Chodkiewicz *Cross-Coupling on Solid Support.* Solvent: benzene.

Entry	Equiv. of **11**	Equiv. of [$Pd_2(dba)_3$]	Equiv. of CuI	Yield [%]	
				22[a])	**15**/**23**[b])
1	1.5	0.03	0.02	27	21:4
2	1.5	0.03	–	35	16:5
3	1.5	0.20	0.10	8	27:13
4	1.5	0.20	–	20	36:8
5	5.0	0.03	–	28	23:7
6	5.0	0.20	–	2	37:10

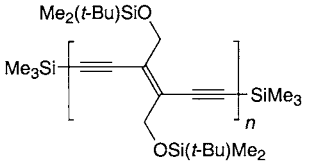
[a]) Isolated yields. [b]) Determined by calibrated HPLC.

additionally, the amount of bromoderivative **11** was raised to 5 equiv. (*Entry 6*). Nevertheless, the formation of the undesired, unseparable side-product **23** by homocoupling could never be completely suppressed. The occurrence of **23** at rather low resin loading provides another example of the limited pseudo-dilution effect of polymeric resins in solid-phase syntheses.

2.4. *Optical Spectroscopy.* The electronic absorption and emission spectra of the new oligo(triacetylene)s **15**, **20**, and **23**, and of oligo(phenylene triacetylene)s **7a**–**7d** and **21** in $CHCl_3$ at room temperature are shown in *Table 2* in comparison to the data for the previously prepared oligo(triacetylene)s **14a**–**14d**.

In the UV/VIS spectra, the following trends are observed: the longest-wavelength absorption maxima λ_{max} as well as the end-absorptions λ_{end} expectedly shift to lower energies with increasing oligomer length. Thus, the end-absorptions in the spectra of the oligo(phenylene triacetylene)s shift from 362 nm (monomer **7a**), to 443 nm (dimer **7b**), and to 462 nm (tetramer **7d**). With increasing oligomer length, the spectral fine-structure is lost (for a spectral depiction, see [11]). The bathochromic shifts with increasing conjugation length are less pronounced than in the series of oligo(triace-

Table 2. *UV/VIS and Fluorescence Data of the New Oligo(triacetylene)s* **15**, **20**, *and* **23**, *and of Oligo(phenylene Triacetylene)s* **7a**–**7d** *and* **21** *in Comparison to the Known Oligo(triacetylene)s* **14a**–**14d**. Spectra recorded at room temperature in $CHCl_3$.



14a $n = 1$
14b $n = 2$
14c $n = 3$
14d $n = 4$

Compound	λ_{max}/nm a) [eV] (ε/M^{-1} cm^{-1}) b)	λ_{end}/nm c)	λ_{exc}/nm d) (ε/M^{-1} cm^{-1}) b)	λ_{em}/nm e)	Φ_F f)
20	363 [3.42] (sh, 23800)	405	350 (32000)	388, 410	0.02
15	391 [3.17] (sh, 27300)	441	300 (26600)	425, 448	0.02
23	408 [3.04] (sh, 37100)	451	350 (49300)	439, 464	0.10
7a	337 [3.68] (41100)	362	300 (34200)	364	0.01
7b	360 [3.44] (54200)	443	350 (51000)	414, 439	0.24
7c	381 [3.25] (97800)	457	350 (75700)	436, 459	0.69
7d	384 [3.23] (122000)	462	350 (81100)	444, 475	0.60
21	372 [3.33] (60300)	441	350 (51200)	425, 448	0.19
14a g)	296 [4.18] (sh, 19700)	322	–	–	–
14b g)	376 [3.30] (sh, 24700)	415	356 (25300)	425	0.01
14c g)	407 [3.05] (sh, 36700)	449	356 (31800)	399, 440	0.01
14d g)	439 [2.82] (sh, 56800)	494	–	–	–

a) Experimentally observed longest-wavelength absorption maxima. b) Molar extinction coefficient. c) Experimentally observed wavelength at which the absorption reaches $\varepsilon = 0$ M^{-1} cm^{-1}. d) Excitation wavelength. e) Fluorescence emission band maximum. f) Fluorescence quantum yield: anthracene ($\Phi_F = 0.33$ in hexane) was used as reference compound [25]. g) Data taken from [6b,c].

tylene)s **14a**–**14d**, since the phenyl rings in **7a**–**7d** – with their localized aromatic resonance stabilization – are not as effective in propagating linear π-electron delocalization. Nevertheless, saturation of the optical properties is not yet observed, *i.e.*, the effective conjugation length of oligo(phenylene triacetylene)s involves more than 40 conjugated C-atoms. Substitution of terminal Me_3Si groups by 4-iodoaryl residues results in a bathochromic shift of the longest-wavelength absorption maxima λ_{max} [6e]. This is nicely illustrated by the comparison between the PTA dimers, bis-Me_3Si-end-capped **14b** (376 nm), mono-iodoarylated **15** (391 nm), and bis(iodoarylated) **23** (408 nm).

In sharp contrast to poly(triacetylene) oligomers, the novel oligo(phenylene triacetylene)s are strong emitters in $CHCl_3$ at room temperature. Fluorescence quantum yields Φ_F were measured relative to anthracene in hexane solution ($\Phi_F = 0.33$ [25]; *Table 2*). Whereas PTA dimer **14b** and trimer **14c** are only weakly fluorescent ($\Phi_F = 0.01$), and the tetramer **14d** does not fluoresce at all, the oligo(phenylene triacetylene)s **7b**–**7d** are strong emitters with the highest quantum yield, $\Phi_F = 0.69$, being measured for trimer **7c**. The weaker emitting properties of tetramer **7d** cannot be explained by chromophoric aggregation (as seen for oligo(phenylene ethynylene)s, see [26]) since the *Lambert–Beer* law [27] is observed in the concentration range applied. Rather, radiationless deactivation of the singlet excited state S_1 could become more important with increasing oligomeric length as a result of higher conformational flexibility of the π-conjugated rod. The high fluorescence quantum yields of the oligo(phenylene triacetylene)s **7b** – **7d** are quite remarkable in view of their terminal iodine substituents, which should promote intersystem crossing to the corresponding triplet excited state T_1.

2.5. *Electrochemical Investigations.* The redox characteristics of all new compounds listed in *Table 3* were studied by cyclic (CV) and rotating-disk voltammetry (RDV) in CH_2Cl_2 (+0.1M Bu_4NPF_6) at 20° with a classical three-electrode cell. The working electrode was a glassy-C electrode (3 mm in diameter), and the counter electrode was a Pt wire. An Ag/AgCl electrode was used as reference electrode. All potentials are referred to the ferricinium/ferrocene (Fc^+/Fc) couple used as internal standard.

Table 3. *Redox Characteristics of the New Oligo(phenylene Triacetylene)s* **7a** – **7d** *and* **21**, *and of Oligo(triacetylene)s* **15**, **20**, *and* **23**, *Determined by Cyclic* (CV) *and Rotating-Disk Voltammetry* (RDV) *in* CH_2Cl_2 *at 20°*

Compound	CV [a])		RDV [b])	
	E_{pc} [V] [c])	E_{pa} [V] [c])	$E_{1/2}^{red}$ [V] (slope [mV] [d]))	$E_{1/2}^{ox}$ [V] (slope [mV] [d]))
7a	−2.35	+1.25	−2.34 (80)	[e])
7b	−2.17 −2.32	+1.15	−2.17 (70)	[e])
7c	−2.12 −2.20	+1.15	−2.27 (140)	*ca.* +1.2
7d	–	+1.30	–	[e])
20	−2.24 −2.39	+1.21	[e])	[e])
21	−2.13 −2.29	+1.16 +1.24	[e])	[e])
15	−2.07 −2.32	+1.30	−2.12 (125)	[e])
23	−2.07 −2.30	+1.23	[e])	[e])

[a]) Potentials *vs.* ferricinium/ferrocene (Fc^+/Fc), glassy C-electrode in CH_2Cl_2 + 0.1M Bu_4NPF_6, scan rate ν = 0.1 V s^{-1}. [b]) Potentials *vs.* ferricinium/ferrocene (Fc^+/Fc), rotating disk-electrode in CH_2Cl_2 + 0.1M Bu_4NPF_6. [c]) Peak potential E_{pc} and E_{pa} for irreversible reduction and oxidation, respectively. [d]) Logarithmic analysis of the wave obtained by plotting E *vs.* $\log[(I/I_{lim} - I)]$. [e]) Electrode inhibition.

In contrast to the oligo(triacetylene)s **14a** – **14d** [6b,c], the new oligo(phenylene triacetylene)s **7a** – **7d** (as well as the other new chromophores **15**, **20**, **21**, and **23**) displayed only irreversible electron transfers. Strong inhibition of the C-electrode prevented the determination of their oxidation potentials by RDV, whereas the reduction potentials were ascertained. The determination of the reduction potential of tetramer **7d** was impossible by both CV and RDV. Whereas the peak potentials E_{pa} for irreversible first oxidation in both oligomeric series are in the same range (**7a** – **7d**: between 1.15 and 1.30 V; **14a** – **14d**: between 1.23 and 1.29 V [6b]), the anodic shift of the reduction potentials upon increasing the oligomer length is much more pronounced in the oligo(triacetylene)s (the reversible redox potential E_0' changes from −2.68 (**14a**) to −1.80 V (**14d**)) than in the oligo(phenylene triacetylene)s (peak potential E_{pc} changes from −2.35 (**7a**) to −2.12 V (**7c**)). Although comparisons of irreversible peak potentials and reversible reduction potentials need to be taken with caution, the results are in agreement with the UV/VIS data, which indicate that π-electron delocalization in the oligo(triacetylene)s, facilitating electron uptake, is more effective than in the oligo(phenylene triacetylene)s. At present, the reason for the irreversibility of the electron transfers in the new oligomeric series is not clear.

3. Conclusions. – We have described the preparation of the first monodisperse oligo(phenylene triacetylene)s **7a**–**7d** on solid phase by using a *Merrifield* resin with an 1-aryltriazene linker. The key step in the short synthesis involves the Pd^0-catalyzed *Sonogashira* cross-coupling, confirming previous work that this important C,C bond-forming reaction proceeds smoothly on solid supports [9][12d–f][22][23a–c].

The novel oligo(phenylene triacetylene)s **7a**–**7d** display interesting optical properties. Their longest-wavelength absorption maxima λ_{max} expectedly shift bathochromically with increasing π-conjugation length although this shift is not as pronounced as in the series of oligo(triacetylene)s **14a**–**14d**, due to the reduced ability of the phenyl rings to transmit π-electron delocalization along the oligomeric backbone. In sharp contrast to **14b**–**14d**, however, the new oligomers **7b**–**7d** display strong fluorescence with the highest quantum yield, $\Phi_F = 0.69$, measured for trimer **7c**. The preparation of larger oligomers and related polymers will be further pursued with the objective to explore potential electroluminescence applications.

Whereas the *Sonogashira* cross-coupling on solid support proceeded smoothly, optimal conditions for polymer-supported *Cadiot–Chodkiewicz*-type couplings still remain to be found. One problem encountered in the entire study was the formation of undesirable side products (such as **21** and **23**) resulting from site–site interactions. It is clear that the pseudo-dilution effect is quite limited on *Merrifield* beads even at low loadings, presumably due to the substantial conformational flexibility provided by this support, as had already been pointed out in other studies [21][22].

We acknowledge the financial support by the *Swiss National Science Foundation* through the *NCCR 'Nanoscale Science'* and the *ETH Research Council*. We thank Prof. Dr. *M. B. Nielsen* (Odense) for helpful discussions and *Boris Thamberger* for the preparation of starting materials.

Experimental Part

General. Reagents and solvents purchased were reagent grade and used as received. Compounds **4** [6a] and **11** [19] were synthesized according to literature procedures. CH_2Cl_2 was dried over CaH_2, and PhMe and THF over Na/benzophenone ketyl. All reactions, except *Hay* couplings, were carried out in oven-dried glassware under Ar by applying a positive pressure of the protecting gas. For the *Hay* couplings, the following mixture was used as '*Hay* catalyst': CuCl (0.13 g, 1.3 mmol) and N,N,N',N'-*tetramethylethylenediamine* (TMEDA; 0.16 g, 1.4 mmol) in CH_2Cl_2 (4.5 ml). Evaporations and concentrations *in vacuo* were carried out at H_2O-aspirator pressure. TLC: *Macherey-Nagel ALUGRAM SIL G/UV$_{254}$* plates. Column-chromatographic purification refers to flash chromatography (FC) on silica gel *60* (230–400 mesh). Anal. HPLC: *Merck-Hitachi Pump L-7100*, *Merck-Hitachi Autosampler L-7200*, *Merck-Hitachi UV Detector L-7400, Merck-Hitachi Interface L-7000*; all separations were carried out at r.t. on a *Knauer LiChrosorb* 4.0-mm column at a flow rate of 1 ml min^{-1} and a pressure of 35 bar. M.p.: *Büchi Melting Point B-450*; uncorrected. UV/VIS Spectra (λ_{max} [nm] (ε [M^{-1} cm^{-1}])): *Varian Cary-500 UV/VIS/NIR* spectrophotometer, at r.t. Fluorescence spectra (λ_{em} [nm]): *Spex FluoroLog-3.22* spectrophotometer, at r.t. Anthracene in hexane was used as reference compound in quantum-yield determinations [25]. IR Spectra [cm^{-1}]: *Perkin-Elmer 1600 FT-IR*, measured in KBr, $CHCl_3$, CCl_4, or as film. ^1H- and ^{13}C-NMR spectra [ppm]: *Bruker AMX-500*, *Varian Gemini-200* and *-300*, at r.t. in $CDCl_3$ or $(CD_3)_2SO$; solvent peaks ($CDCl_3$: 7.26 ppm for ^1H and 77.0 ppm for ^{13}C; $(CD_3)_2SO$: 2.05 ppm for ^1H and 39.52 ppm for ^{13}C)

as internal references. MS (*m/z* (%)). EI: *VG Tribrid* mass spectrometer at 70-eV ionization energy; MALDI-TOF-MS: *Bruker Reflex-MALDI-TOF* (337-nm N_2-laser system), 2,5-dihydroxybenzoic acid (DHB) as matrix; HR-FT-ICR-MALDI-MS: *Ion Spec Ultima FT-ICR-MS* (337-nm N_2-laser system), DHB and {(2*E*)-3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidene}malononitrile (DCTB) as matrix. Elemental analyses were carried out by the Mikroanalytisches Labor des Laboratoriums für Organische Chemie at ETH Zürich.

Resin Loadings and Yields. In case of an easily detectable element present, the respective resin loadings were determined by elemental analysis. Due to the polydispersity of *Merrifield* resin and the minor-weight fractions of the resin-bound compounds compared to the overall material weight, the data obtained are only approximated values. The following equation was used to determine the resin loadings: $\sigma_x = m_x/M_x$ [mol/g], with σ_x being the resin loading of the element X in mol/g and M_x being the molecular weight of the element X, while m_x corresponds to the weight fraction of X detected by elemental analysis. These resin loadings were compared with the theoretical maximum loading σ_0: $\sigma_0 = N_0/(1 + N_0 \cdot \Delta M)$ [mol/g], with N_0 being the molar amount of the initial functionality per 1 g of resin and ΔM being the change in molecular weight of the resin-bound compound by a reaction. The ratio between the experimentally obtained resin loading σ_x and the theoretical maximum loading σ_0 provides the yield of a reaction on solid support.

Electrochemistry. CH_2Cl_2 purchased was from *Merck*, spectroscopic grade dried over molecular sieves (4 Å), and stored under Ar prior to use. Bu_4NPF_6 was purchased electrochemical grade from *Fluka* and used as received. The electrochemical experiments were carried out at 20° 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 (3 mm in diameter) used either in a motionless mode for CV (0.1 to 10 V s^{-1}) or as rotating-disk electrode for RDV. The counter electrode was a Ag/AgCl electrode, and the pseudo-reference electrode used was a Pt wire. All potentials are referenced to the ferricinium/ferrocene (Fc^+/Fc) couple used as an internal standard. The accessible range of potentials on the glassy C-electrode was +1.4 to −2.4 V *vs.* Fc^+/Fc in CH_2Cl_2. The electrochemical cell was connected to the computerized multipurpose electrochemical device *AUTOLAB* (*Eco Chemie BV*, Utrecht, The Netherlands) by the *GPSE* software running on a personal computer.

General Procedure 1 (*GP 1*) *for Cleavage of Me_3Si-Protecting Groups in Solution.* To Me_3Si-protected alkyne (2 mmol) in MeOH/THF 1:1 (80 ml), 2N NaOH (2.5 ml) was added, and the mixture was stirred for *ca.* 15 min at r.t. (TLC control). After addition of sat. aq. NH_4Cl soln. (120 ml), the two phases were separated, and the aq. phase was extracted with CH_2Cl_2 (3 × 120 ml), dried ($MgSO_4$), and evaporated *in vacuo*. The products were used without further purification.

General Procedure 2 (*GP 2*) *for* Sonogashira *Cross-Couplings in Soln.* An oven-dried *Schlenk* flask was charged with the linker system **2** or **3** (1.0 equiv.), monomer **4** (1.1 equiv.), $[Pd(PPh_3)_2Cl_2]$ (5 mol-%), and Et_3N (20 ml/1 mmol linker), while Ar was flushed through the flask. After three freeze-pump-thaw cycles, the soln. was frozen once again, and CuI (0.1 equiv.) was added while Ar was flushed through the flask. The flask was evacuated and back-filled with Ar three times. The flask was sealed, and the mixture was allowed to warm up to r.t. After stirring for 20 h, the resulting suspension was taken up in hexane and passed through a plug (SiO_2-*60*; hexane → hexane/CH_2Cl_2 1:1) to remove residual catalyst. After evaporation *in vacuo*, the crude product was purified by FC.

General Procedure 3 (*GP 3*) *for the Cleavage of the Triazene Linker in Soln.* An oven-dried, heavy-walled, and screw-capped sealed tube was charged with the respective linker-alkyne conjugate and MeI (1 ml/0.1 mmol triazene). After three freeze-pump-thaw cycles, the flask was back-filled with Ar, and the soln. was stirred for 6–18 h at 110°–120°. The resulting suspension was taken up in hexane and passed through a plug (SiO_2-*60*; hexane → hexane/CH_2Cl_2 2:1). After evaporation *in vacuo*, the crude product was purified by FC.

General Procedure 4 (*GP 4*) *for Pd^0-Catalyzed* Cadiot–Chodkiewicz *Cross-Couplings in Soln.* An oven-dried *Schlenk* flask was charged with the linker-alkyne conjugate (1.0 equiv.), LiI (0.2 equiv.), 1,2,2,6,6-pentamethylpiperidine (PMP; 2.8 equiv.), $[Pd_2(dba)_3]$ (3 mol-%), and C_6H_6 (3 ml/0.05 mmol alkyne). The mixture was degassed by flushing Ar through the suspension for 10 min. CuI (2 mol-%) and **11** (1.0 equiv.) were added successively, and the mixture was stirred for 7 h at r.t. The resulting suspension was taken up in hexane and passed through a plug (SiO_2-*60*; hexane → hexane/CH_2Cl_2 1:1) to remove residual catalyst. After evaporation *in vacuo*, the crude product was purified by either FC or prep. TLC.

General Procedure 5 (*GP 5*) *for the* Sonogashira *Cross-Coupling of* **4** *to the Solid Support.* To an oven-dried, heavy-walled flask with an Ar inlet, **R2** (1.0 equiv.), **4** (1.5–2.0 equiv.), and Et_3N or THF/Et_2NH 4:1 (2 ml/g resin) were added. This suspension was degassed by three freeze-pump-thaw cycles, and the flask was back-filled with Ar. In a separate dry flask, a catalyst soln. consisting of $[Pd_2(dba)_3]$ (2.5 mM), CuI (4.0 mM), and PPh_3 (20.0 mM) in Et_3N or THF/Et_2NH 4:1 was degassed by three freeze-pump-thaw cycles and stirred at 70° for 2 h under Ar. The supernatant of this soln. (6 ml/g resin) was transferred *via* cannula to the flask containing

R2. This flask was sealed and kept for 24 h at 65° while agitating periodically. The resin was transferred to a fritted filter with CH_2Cl_2, washed with CH_2Cl_2, DMF, a 0.05M soln. of sodium diethyl dithiocarbamate in DMF/$Et(i-Pr)_2N$ 99 : 1, DMF, CH_2Cl_2, and MeOH (30 ml/g resin each), and dried *in vacuo* to constant mass.

General Procedure 6 (*GP 6*) *for Cleavage of Me_3Si Protecting Groups on Solid Support.* A suspension of polymer-bound Me_3Si-protected alkyne in MeOH/THF 1 : 1 (25 ml/g resin) and 2N NaOH (1 ml/g resin) was heated under gentle stirring to 70° for 3 h. The resin was transferred to a fritted filter, washed sequentially with MeOH, H_2O, MeOH, CH_2Cl_2, DMF, CH_2Cl_2, and MeOH (30 ml/g resin each), and dried *in vacuo*.

General Procedure 7 (*GP 7*) *for Oligomeric Extension by* Sonogashira *Cross-Couplings on Solid Support.* To an oven-dried, heavy-walled flask with an Ar inlet, polymer-bound deprotected alkyne (1.0 equiv.), 4-iodoarylated DEE **7a** (2.0 equiv.), and Et_3N or THF/Et_2NH 4 : 1 (2 ml/g resin) were added. This suspension was degassed by three freeze-pump-thaw cycles, and the flask was back-filled with Ar. In a separate dry flask, a catalyst soln. consisting of $[Pd_2(dba)_3]$ (2.5 mM), CuI (4.0 mM), and Ph_3P (20.0 mM) in Et_3N or THF/Et_2NH 4 : 1 was degassed by three freeze-pump-thaw cycles and stirred at 70° for 2 h under Ar. The supernatant of this soln. was transferred *via* cannula to the flask containing the polymer-bound deprotected alkyne (6 ml/g resin). This flask was sealed and kept for 24 h at 65° while agitating periodically. The resin was transferred to a fritted filter with CH_2Cl_2, washed with CH_2Cl_2, DMF, a 0.05M soln. of sodium diethyl dithiocarbamate in DMF/$Et(i-Pr)_2N$ 99 : 1, DMF, CH_2Cl_2, and MeOH (30 ml/g resin each), and dried *in vacuo* to constant mass.

General Procedure 8 (*GP 8*) *for Pd^0-Catalyzed* Cadiot–Chodkiewicz *Cross-Couplings on Solid Support.* An oven-dried, heavy-walled flask with an Ar inlet was charged with resin-bound alkyne (1.0 equiv.), LiI (0.2 equiv.), PMP (2.8 equiv.), and benzene (18 ml/g resin). The suspension was degassed by three freeze-pump-thaw cycles and warmed up to r.t. $[Pd_2(dba)_3]$ (3 mol-%) was added while Ar was flushed through the suspension. Finally, CuI (2 mol-%) and a degassed soln. of **11** (1.5–5 equiv.) were added. The flask was sealed and shaken for 20–24 h at 45°. The suspension was taken up in CH_2Cl_2, transferred to a fritted filter, and washed with CH_2Cl_2 (30 ml/g resin). Excess **11** can be recovered from the first CH_2Cl_2 wash. The resin was washed sequentially with DMF, 0.05M soln. of sodium diethyl dithiocarbamate in DMF/$Et(i-Pr)_2N$ 99 : 1, DMF, CH_2Cl_2, and MeOH (30 ml/g resin each), and dried *in vacuo* to constant mass.

General Procedure 9 (*GP 9*) *for the Cleavage of the Triazene Linkage on Solid Support.* To an oven-dried, heavy-walled flask with an Ar inlet, the respective polymer-supported oligomer and MeI (8 ml/g resin) were added. The suspension was degassed by three freeze-pump-thaw cycles, and the flask was back-filled with Ar and sealed. The suspension was stirred for 24 h at 110–120°. After removal of MeI *in vacuo*, the resin was transferred to a fritted filter with CH_2Cl_2, and the product was extracted from the resin with hot CH_2Cl_2. The resulting soln. was cooled to r.t. and filtered through a plug of SiO_2. After evaporation *in vacuo*, the crude product was purified by FC.

1-(4-Iodophenyl)-3-(2-hydroxyethyl)-3-ethyltriazene (**16**). To a suspension of 2-(ethylamino)ethanol (1.66 ml, 17.0 mmol), K_2CO_3 (9.396 g, 68.0 mmol), and DMF (50 ml) at 0°, 4-iodophenyldiazonium tetrafluoroborate [28] (5.402 g, 17.0 mmol) was added in portions over 1 h. After addition of H_2O (100 ml), the mixture was extracted with CH_2Cl_2 (150 ml). The org. phase was washed with H_2O (1.5 l) and sat. aq. LiCl soln. (500 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give **16** (4.888 g, 92%). Red oil. FT-IR ($CHCl_3$): 3011*m*, 2977*w*, 2878*w*, 1433*s*, 1390*s*, 1338*s*, 1239*m*, 1224*s*, 1158*m*, 1046*m*, 1002*m*, 825*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.24 (*t*, *J* = 7.0, 3 H); 2.00 (*s*, 1 H); 3.70–3.85 (*m*, 6 H); 7.14 (*d*, *J* = 8.4, 2 H); 7.60 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 13.4; 52.5; 60.9; 89.5; 122.2; 137.6; 149.6. FT-ICR-MALDI-MS (DHB, two-layer): 319.0131(3, M^+, $C_{10}H_{14}IN_3O^+$; calc. 319.0182), 318.0095 (31, $[M-H]^+$), 299.9987 (100, $[M-H-H_2O]^+$). Anal. calc. for $C_{10}H_{14}IN_3O$ (319.15): C 37.63, H 4.42, N 13.17; found: C 37.80, H 4.38, N 12.97.

1-(4-Iodophenyl)-3-[2-(benzyloxy)ethyl]-3-ethyltriazene (**2**). To a soln. of $PhCH_2Br$ (0.855 g, 5.0 mmol) and **16** (1.595 g, 5.0 mmol) in dry THF (100 ml) at −50°, NaH (0.400 g, 10.0 mmol) was added under Ar. The soln. was warmed to r.t., then heated to reflux for 6 h. After addition of H_2O (100 ml), the mixture was extracted with CH_2Cl_2 (3 × 70 ml). The combined org. phases were dried ($MgSO_4$) and evaporated *in vacuo*. FC (SiO_2-*60*; hexane/CH_2Cl_2 4 : 1) gave **2** (1.625 g, 79%). Yellow oil. FT-IR (film): 3022*m*, 2978*m*, 2931*s*, 2855*s*, 1472*s*, 1427*s*, 1389*s*, 1344*s*, 1239*s*, 1193*m*, 1161*m*, 1093*s*, 1001*m*, 825*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.33 (*t*, *J* = 6.9, 3 H); 3.79 (*t*, *J* = 5.7, 2 H); 3.89 (*q*, *J* = 6.9, 2 H); 3.99 (*t*, *J* = 5.7, 2 H); 4.59 (*s*, 2 H); 7.25 (*d*, *J* = 8.7, 2 H); 7.30–7.45 (*m*, 5 H); 7.68 (*d*, *J* = 8.7, 2 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 14.0; 46.7; 50.0; 67.2; 73.0; 89.2; 122.5; 127.5; 127.6; 128.4; 137.6; 138.0; 150.6. FT-ICR-MALDI-MS (DHB, two-layer): 409.0610 (19, M^+, $C_{17}H_{20}IN_3O^+$; calc. 409.0651), 408.0571 (100, $[M-H]^+$).

*3-[2-(Benzyloxy)ethyl]-1-[4-((*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-6-(trimethylsilyl)hex-3-ene-1,5-diyne-1-yl)phenyl]-3-ethyltriazene* (**5**). The following compounds were reacted according to the *GP 2*: **2** (0.425 g, 1.04 mmol), **4** (0.500 g, 1.15 mmol), $[Pd(PPh_3)_2Cl_2]$ (0.036 g, 0.052 mmol, 5.0 mol-%), CuI (0.020 g, 0.104 mmol), and Et_3N (20 ml). FC (SiO_2-*60*; hexane/CH_2Cl_2 1:1 → hexane/AcOEt 10:1 → hexane/AcOEt 5:1) afforded **5** (0.665 g, 89%). Red oil. FT-IR (film): 2951*s*, 2929*s*, 2856*s*, 2133*w*, 1494*w*, 1462*m*, 1428*m*, 1394*m*, 1344*m*, 1251*s*, 1097*s*, 931*w*, 840*s*. ^1H-NMR (200 MHz, $CDCl_3$): 0.13 (*s*, 12 H); 0.26 (*s*, 9 H); 0.98 (*s*, 18 H); 1.31 (*t*, $J = 7.0$, 3 H); 3.77 (*t*, $J = 5.8$, 2 H); 3.88 (*q*, $J = 7.2$, 2 H); 3.98 (*t*, $J = 5.4$, 2 H); 4.56 (*s*, 2 H); 4.58 (*s*, 2 H); 4.59 (*s*, 2 H); 7.25 – 7.50 (*m*, 9 H). ^{13}C-NMR (50 MHz, $CDCl_3$): – 5.1; – 0.1; 11.4; 18.4; 25.8; 63.9; 64.2; 73.2; 81.4; 86.6; 102.1; 102.2; 106.4; 119.7; 120.5; 127.6; 127.7; 128.4; 128.7; 131.1; 132.1; 138.0; 150.9. FT-ICR-MALDI-MS (DHB, two-layer): 717.4117 (13, M^+, $C_{40}H_{63}N_3O_3Si_3^+$; calc. 717.4177), 608.3524 (100, $[M - BnOH - H]^+$). Anal. calc. for $C_{40}H_{63}N_3O_3Si_3$ (717.22): C 66.89, H 8.84, N 5.85; found: C 66.94, H 8.67, N 5.60.

*3-[2-(Benzyloxy)ethyl]-1-{4-[(*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}hex-3-ene-1,5-diyn-1-yl]phenyl}-3-ethyltriazene* (**9**). The following compounds were reacted according to the *GP 1*: **5** (0.048 g, 0.067 mmol), THF (10 ml), MeOH (10 ml), and 2N NaOH (0.5 ml). Workup provided **9** (0.043 g, 100%). Yellow oil. FT-IR ($CHCl_3$): 3312*m*, 3289*w*, 3054*s*, 2930*m*, 2856*m*, 2188*w*, 1461*w*, 1422*w*, 1394*w*, 1343*w*, 1256*s*, 1096*m*, 841*m*. ^1H-NMR (300 MHz, $CDCl_3$): 0.13 (*s*, 12 H); 0.94 (*s*, 18 H); 1.29 (*t*, $J = 7.2$, 3 H); 3.54 (*s*, 1 H); 3.75 (*t*, $J = 5.7$, 2 H); 3.86 (*q*, $J = 7.2$, 2 H); 3.96 (*t*, $J = 5.4$, 2 H); 4.54 (*s*, 2 H); 4.55 (*s*, 2 H); 4.56 (*s*, 2 H); 7.25 – 7.45 (*m*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): – 5.3; 18.3; 25.7; 63.9; 64.0; 73.2; 81.1; 86.2; 88.3, 102.1; 115.0; 119.5; 120.5; 127.5; 127.6; 127.8; 128.4; 132.1; 132.4; 139.3; 151.1. FT-ICR-MALDI-MS (DHB, two-layer): 646.3754 (2, M^+, $C_{37}H_{55}N_3O_3Si_2^+$, calc. 646.0300), 536.3134 (100, $[M - BnOH - 2\,H]^+$).

*3-[2-(Benzyloxy)ethyl]-3-ethyl-1-{4-[(*E,E*)-3,4,9,10-tetrakis{[(*tert*-butyl)dimethylsilyloxy]methyl}-12-(trimethylsilyl)dodeca- 3,9-diene-1,5,7,11-tetrayn-1-yl]phenyl}triazene* (**12**). The following compounds were reacted according to *GP 4*: **9** (0.036 g, 0.050 mmol), **11** (0.025 g, 0.050 mmol), $[Pd_2(dba)_3]$ (0.0012 g, 0.0014 mmol, 2.8 mol-%), CuI (0.00025 g, 0.0012 mmol), PMP (0.023 ml, 0.126 mmol), LiI (0.0012 g, 0.009 mmol), and benzene (3 ml). Prep. TLC (SiO_2; hexane/CH_2Cl_2 1:1) afforded **12** (0.030 g, 56%). Red-brown oil. FT-IR ($CHCl_3$): 2956*s*, 2856*s*, 2367*w*, 2133*w*, 1472*m*, 1433*m*, 1389*m*, 1344*m*, 1252*m*, 1100*s*, 839*s*. ^1H-NMR (300 MHz, $CDCl_3$): 0.11 (*s*, 12 H); 0.13 (*s*, 12 H); 0.21 (*s*, 9 H); 0.93 (*s*, 36 H); 1.28 (*t*, $J = 7.2$, 3 H); 3.75 (*t*, $J = 5.7$, 2 H); 3.86 (*q*, $J = 7.2$, 2 H); 3.96 (*t*, $J = 5.4$, 2 H); 4.44, (*s*, 2 H); 4.49 (*s*, 2 H); 4.54 (*s*, 2 H); 4.55 (*s*, 2 H); 4.58 (*s*, 2 H); 7.25 – 7.45 (*m*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): – 5.3; – 0.3; 10.8; 18.3; 25.8; 63.9; 64.2; 68.1; 73.2; 81.9; 82.6; 85.1; 85.7; 86.9; 101.6; 104.2, 109.2; 119.4; 120.6; 127.6; 127.7; 128.5; 128.9; 129.7; 132.3; 133.1; 133.9; 138.1; 151.3. FT-ICR-MALDI-MS (DHB, two-layer): 1102.6140 (39, $[M + Na]^+$, $C_{60}H_{97}N_3NaO_5Si_5{}^+$; calc. 1102.6172), 1079.6144 (41, M^+; $C_{60}H_{97}N_3O_5Si_5{}^+$; calc. 1079.6275), 897.4910 (100, $[M - BnOH - 2\,H]^+$).

3-Benzyl-1-(4-iodophenyl)-3-propyltriazene (**3**). To a suspension of $PhCH_2NH(Pr)$ [29] (2.237 g, 15.0 mmol), K_2CO_3 (8.291 g, 60.0 mmol), and DMF (100 ml) at 0°, 4-iodophenyldiazonium tetrafluoroborate [28] (4.639 g, 14.6 mmol) was added in portions over 1 h. After addition of H_2O (200 ml), the mixture was extracted with CH_2Cl_2 (200 ml). The org. phase was washed with H_2O (2 l) and sat. aq. LiCl soln. (500 ml), dried ($MgSO_4$), and evaporated *in vacuo*. FC (SiO_2-*60*; hexane/CH_2Cl_2 2:1) afforded **3** (4.595 g, 81%). Red oil. FT-IR (film): 3028*m*, 2965*s*, 2873*m*, 2367*w*, 1894*w*, 1677*w*, 1600*w*, 1495*m*, 1478*s*, 1450*s*, 1388*s*, 1344*s*, 1172*s*, 1150*s*, 1094*s*. ^1H-NMR (200 MHz, $CDCl_3$): 1.04 (*t*, $J = 7.6$, 3 H); 1.80 ('*q*', $J = 7.6$, 2 H); 3.77 (*t*, $J = 7.6$, 2 H); 5.07 (*s*, 2 H); 7.41 (*m*, 5 H); 7.78 (br. *s*, 2 H); 7.81 (br. *s*, 2 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 11.3; 21.6; 49.3; 55.7; 89.4; 122.5; 127.3; 127.8, 128.4; 136.5; 137.6; 150.3. FT-ICR-MALDI-MS (DHB, two-layer): 379.0447 (17, M^+, $C_{16}H_{18}IN_3^+$; calc. 379.0545), 378.0414 (100, $[M - H]^+$), 364.2017 (11, $[M - Me]^+$), 252.1477 (3, $[M - I]^+$). Anal. calc. for $C_{16}H_{18}IN_3$ (379.08): C 50.67, H 4.78, N 11.08; found: C 50.85, H 4.90, N 10.92.

*3-Benzyl-1-[4-((*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-6-(trimethylsilyl)hex-3-ene-1,5-diyn-1-yl)phenyl]-3-propyltriazene* (**6**). The following compounds were reacted according to *GP 2*: **3** (0.394 g, 1.04 mmol), **4** (0.500 g, 1.15 mmol), $[Pd(PPh_3)_2Cl_2]$ (0.036 g, 0.052 mmol, 5.0 mol-%), CuI (0.020 g, 0.104 mmol), and Et_3N (6 ml). FC (SiO_2-*60*; hexane/CH_2Cl_2 2:1) afforded **6** (0.658 g, 90%). Red oil. FT-IR (film): 2963*s*, 2918*s*, 2823*s*, 2133*m*, 1494*m*, 1448*m*, 1400*m*, 1361*m*, 1251*m*, 1097*m*, 931*w*, 839*s*. ^1H-NMR (200 MHz, $CDCl_3$): 0.16 (*s*, 12 H); 0.26 (*s*, 9 H); 0.94 (*t*, $J = 6.6$, 3 H); 0.97 (*s*, 18 H); 1.69 ('*q*', $J = 6.6$, 2 H); 3.68 (*t*, $J = 6.6$, 2 H); 4.58 (br. *s*, 4 H); 4.99 (*s*, 2 H); 7.33 (*m*, 5 H); 7.47 (*m*, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): – 5.1; – 0.1; 11.4; 18.4; 25.8; 63.8; 64.1; 86.6; 102.0; 102.1; 106.4; 119.7; 120.5; 127.4; 127.9; 128.5; 131.0; 132.1; 136.8; 150.7. MALDI-TOF-MS (DCTB): 688.4 ($[M + H]^+$), 631.3 ($[M - t\text{-Bu}]^+$). Anal. calc. for $C_{39}H_{61}N_3O_2Si_3$ (688.19): C 68.07, H 8.93, N 6.11; found: C 68.67, H 8.46, N 6.04.

*(*E*)-3,4-Bis{[(*tert*-butyl)dimethylsilyl)oxy]methyl}-1-(4-iodophenyl)-6-(trimethylsilyl)hex-3-ene-1,5-diyne* (**7a**). The following compounds were reacted according to *GP 3*: **6** (0.097 g, 0.146 mmol) and MeI (1.5 ml). FC (SiO_2-*60*; hexane/CH_2Cl_2 2:1) afforded **7a** (0.062 g, 66%). Colorless solid. M.p. 51°. UV/VIS ($CHCl_3$): 253 (14100), 317 (47800), 337 (41100). FT-IR ($CHCl_3$): 3013*m*, 2957*m*, 2924*m*, 2857*m*, 2135*w*, 1599*w*, 1499*w*, 1489*w*, 1388*w*, 1252*m*, 1222*s*. ^1H-NMR (300 MHz, $CDCl_3$): 0.11 (*s*, 12 H); 0.22 (*s*, 9 H); 0.93 (*s*, 18 H); 4.49 (*s*, 2 H); 4.54 (*s*, 2 H); 7.15 (*d*, $J = 8.4$, 2 H); 7.72 (*d*, $J = 8.4$, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): – 5.3; – 0.3; 18.2; 25.8; 63.9;

64.0; 88.0; 94.5; 100.1; 101.8; 107.2; 122.8; 129.9; 130.5; 132.9; 137.6. FT-ICR-MALDI-MS (DHB, two-layer): 661.1825 (24, $[M+\mathrm{Na}]^+$; $C_{29}H_{47}INaO_2Si_3^+$; calc. 661.1826), 638.1867 (46, M^+, $C_{29}H_{47}IO_2Si_3^+$; calc. 638.1928), 637.1841 (100, $[M-\mathrm{H}]^+$), 581.1235 (29, $[M-t\text{-Bu}]^+$). Anal. calc. for $C_{29}H_{47}IO_2Si_3$ (638.85): C 54.52, H 7.42; found: C 55.07, H 7.80.

*(*E*)-2-(Phenylethynyl)-3-[(trimethylsilyl)ethynyl]but-2-ene-1,4-diol* (**8**). To a soln. of **6** (0.10 g, 0.15 mmol) in CH_2Cl_2 (40 ml) at r.t., $HSiCl_3$ (15 µl, 0.15 mmol) was added. After stirring for 15 min, SiO_2 (0.15 g) was added, and the resulting suspension was filtered. The filtrate was evaporated *in vacuo*, and FC (SiO_2-*60*; hexane/AcOEt 5:2) afforded **8** (0.022 g, 52%). Yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.24 (*s*, 9 H); 1.85–1.95 (2 H); 4.47 (*s*, 2 H); 4.49 (*s*, 2 H); 7.3–7.5 (*m*, 5 H). EI-MS: 284.1 (M^+).

*3-Benzyl-1-[4-((*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}hex-3-ene-1,5-diyn-1-yl)phenyl]-3-propyltriazene* (**10**). The following compounds were reacted according to *GP 1*: **6** (0.10 g, 0.146 mmol), THF (10 ml), MeOH (10 ml), and 2N NaOH (1 ml). After workup, **10** (0.087 g, 97%) was obtained as a red-brown oil. FT-IR ($CHCl_3$): 3300*m*, 2928*s*, 2845*s*, 2189*w*, 1600*w*, 1494*m*, 1448*s*, 1400*s*, 1355*s*, 1250*s*, 1094*s*, 839*s*, 778*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.15 (*s*, 12 H); 0.89 (*t*, $J=7.0$, 3 H); 0.96 (*s*, 18 H); 1.69 ('*q*', $J=7.0$, 2 H); 3.56 (*s*, 1 H); 3.68 (*t*, $J=7.0$, 2 H); 4.58 (br. *s*, 4 H); 4.99 (*s*, 2 H); 7.30 (*m*, 5 H); 7.45 (*m*, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): –5.0; 11.4; 18.4; 25.9; 64.0; 64.1; 80.9; 86.3; 88.3; 102.0; 119.7; 120.6; 127.6; 128.0; 128.6; 131.9; 132.2; 150.9. FT-ICR-MALDI-MS (DHB, two-layer): 614.3619 (39, $[M-\mathrm{H}]^+$, $C_{36}H_{52}N_3O_2Si_2^+$; calc. 614.3598), 569.2479 (7, $[M-\mathrm{H}-3\,\mathrm{Me}]^+$); 481.2674 (100, $[M-3\,\mathrm{H}-\mathrm{OSi}(t\text{-Bu})\mathrm{Me}_2]^+$).

*3-Benzyl-3-propyl-1-[4-((*E,E*)-3,4,9,10-tetrakis{[(*tert*-butyl)dimethylsilyloxy]methyl}-12-(trimethylsilyl)-dodeca-3,9-diene-1,5,7,11-tetrayn-1-yl)phenyl]triazene* (**13**). The following compounds were reacted according to *GP 4*: **10** (0.034 g, 0.055 mmol), **11** (0.028 g, 0.055 mmol), $[Pd_2(dba)_3]$ (0.0014 g, 0.0017 mmol, 3.1 mol-%), CuI (0.00025 g, 0.0012 mmol), PMP (0.023 ml, 0.126 mmol), LiI (0.0012 g, 0.009 mmol), and C_6H_6 (3 ml). Prep. TLC (SiO_2; hexane/CH_2Cl_2 1:1) afforded **13** (0.020 g, 43%) and **14b** (4 mg, 17%) [6b]. Red-brown, viscous oil. FT-IR ($CHCl_3$): 3677*w*, 3611*w*, 3011*s*, 2389*m*, 2134*w*, 1517*m*, 1416*m*, 1228*s*, 1200*s*, 1044*m*, 794*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.11 (*s*, 12 H); 0.12 (*s*, 12 H); 0.21 (*s*, 9 H); 0.92 (*s*, Me); 0.93 (*s*, 36 H); 1.67 ('*q*', $J=7.0$, 2 H); 3.66 (*t*, $J=7.0$, 2 H); 4.43 (br. *s*, 2 H); 4.49 (br. *s*, 2 H); 4.53 (br. *s*, 2 H); 4.58 (br. *s*, 2 H); 4.98 (*s*, 2 H); 7.20–7.40 (*m*, 5 H); 7.43 (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): –5.1; –0.2; 11.4; 18.4; 25.9; 63.9; 64.1; 64.2; 81.9; 82.6; 85.1; 85.7; 86.9; 88.3; 101.6; 104.2; 119.5; 120.7; 127.7; 128.0; 128.6; 129.7; 130.9; 132.2; 132.3; 133.1; 133.8; 151.1. FT-ICR-MALDI-MS (DHB, two-layer): 1072.6055 ($[M+\mathrm{Na}]^+$, $C_{59}H_{95}N_3NaO_4Si_5^+$; calc. 1072.6068). Anal. calc. for $C_{59}H_{95}N_3O_4Si_5$ (1050.85): C 67.44, H 9.11, N 4.00; found: C 67.48, H 9.13, N 3.73.

*(*E,E*)-1-(4-Iodophenyl)-3,4,9,10-tetrakis{[(*tert*-butyl)dimethylsilyloxy]methyl}-12-(trimethylsilyl)dodeca-3,9-diene-1,5,7,11-tetrayne* (**15**). The following compounds were reacted according to *GP 3*: **13** (0.010 g, 0.0097 mmol) and MeI (1 ml). FC (SiO_2-*60*; hexane/CH_2Cl_2 1:1) afforded **15** (0.006 g, 21%). Yellow solid. Mp 62°. UV/VIS ($CHCl_3$): 260 (30500), 287 (29000), 303 (33100), 324 (33300), 367 (46700), 391 (sh, 33200). FT-IR ($CHCl_3$): 2955*s*, 2929*s*, 2911*m*, 2856*s*, 2381*w*, 2133*w*, 1475*m*, 1389*w*, 1361*w*, 1252*s*, 1104*s*, 838*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.08–0.12 (br. *s*, 24 H); 0.21 (*s*, 9 H); 0.92 (*s*, 36 H); 4.43 (br. *s*, 2 H); 4.48 (br. *s*, 2 H); 4.51 (br. *s*, 2 H); 4.53 (br. *s*, 2 H); 7.16 (*d*, $J=8.4$, 2 H); 7.69 (*d*, $J=8.4$, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): –5.1; –0.2; 18.4; 25.9; 63.9; 64.1; 82.3; 82.6; 85.6; 85.7; 88.3; 94.8; 101.7; 102.0; 102.2; 122.5; 128.9; 129.0; 129.7; 133.0; 133.3; 133.5; 137.8. FT-ICR-MALDI-MS (DHB, two-layer): 1023.3815 (100, $[M+\mathrm{Na}]^+$, $C_{49}H_{81}INaO_4Si_5^+$; calc. 1023.3924), 897.4863 (13, $[M-\mathrm{OSi}(t\text{-Bu})\mathrm{Me}_2]^+$). Anal. calc. for $C_{49}H_{81}IO_4Si_5$ (1001.51): C 58.77, H 8.15; found: C 59.13, H 7.75.

Resin-Bound 3-Ethyl-3-(2-hydroxyethyl)-1-(4-iodophenyl)triazene (**R2**). A *Schlenk* flask was charged with *Merrifield* resin (1.684 g, 1.57 mmol Cl) and three times evacuated and back-filled with Ar. A soln. of **16** (2.50 g, 7.80 mmol) in dry THF (20 ml) was transferred *via* cannula onto the *Merrifield* resin under Ar. The mixture was cooled to –78°, and NaH (0.186 g, 4.65 mmol) was added in portions under a Ar blanket. After complete addition, the mixture was warmed first to r.t., then heated to 45°. After 5 d, the mixture was cooled, and MeOH/H_2O 1:1 (10 ml) was added. The polymer was isolated by filtration, washed with CH_2Cl_2, H_2O, MeOH, AcOEt, hexane, CH_2Cl_2, and MeOH (3 × 100 ml of each), and dried *in vacuo* to a constant mass of 1.79 g. An elemental analysis revealed an iodide loading of 0.57 mmol/g (79%). FT-IR (CCl_4): 3062*s*, 3029*s*, 2928*s*, 2852*s*, 1942*w*, 1871*w*, 1803*w*, 1602*s*, 1493*s*, 1454*s*, 1369*m*, 1344*m*, 1327*m*, 1179*m*, 1091*m*, 1028*m*, 906*w*. Gel-phase ^{13}C-NMR (75 MHz, $CDCl_3$): 14.4; 22.8; 31.7; 40.5; 42.0; 42.7; 44.0; 45.5; 46.0; 73.2; 89.3; 122.5, 127.9; 137.7; 145.3; 150.5.

*Resin-Bound 1-[4-((*E*)-3,4-Bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-6-(trimethylsilyl)hex-3-ene-1,5-diyn-1-yl)phenyl]-3-ethyl-3-(2-hydroxyethyl)triazene* (**17**). The following compounds were reacted according to *GP 5*: **R2** (0.500 g, 0.29 mmol), **4** (0.308 g, 0.60 mmol), $[Pd_2(dba)_3]$ (0.011 g, 0.012 mmol, 4.1 mol-%), CuI (0.0036 g, 0.019 mmol), PPh_3 (0.025 g, 0.095 mmol), and Et_3N (6 ml). After workup, the polymer was dried *in* *vacuo* to a constant mass of 0.516 g (91%). FT-IR (CCl_4): 3067*w*, 3022*m*, 2927*s*, 2855*m*, 2367*w*, 2133*w*, 1452*s*, 1390*m*, 1344*m*, 1092*m*, 1033*w*, 928*w*.

*Resin-Bound 1-[4-((*E*)-3,4-Bis{[(*tert*-butyl)dimethylsilyloxy]methyl}hex-3-ene-1,5-diyn-1-yl)-phenyl]-3-ethyl-3-(2-hydroxyethyl)triazene* (**18**). The following compounds were reacted according to *GP 6*: **17** (0.300 g, 0.13 mmol immobilized DEE), THF (5 ml), MeOH (5 ml), and 2N NaOH (1 ml). After workup, the polymer was dried *in vacuo* to a constant mass of 0.230 g (quant.). FT-IR (CCl_4): 3311*m*, 3022*w*, 2955*m*, 2927*m*, 2855*m*, 1448*s*, 1428*m*, 1389*m*, 1344*m*, 1173*w*.

(E*)-3,4-Bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-1,6-bis(4-iodophenyl)hex-3-ene-1,5-diyne* (**20**) *and 1,4-Bis((*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-6-(4-iodophenyl)hex-3-ene-1,5-diyn-1-yl)benzene* (**21**). The following compounds were reacted according to the modified *GP 7* (using **19** instead of **7a** as chain-extending building block): immobilized DEE monomer **18** (1.10 g, 0.20 mmol) and **19** (0.332 g, 1.0 mmol). After workup, the resin-bound products were cleaved according to *GP 9*: immobilized, phenyl-substituted DEE (1.0 g, 0.16 mmol) and MeI (10 ml). FC (SiO_2-*60*; hexane/CH_2Cl_2 2:1) afforded **20** (0.023 g, 19%) and **21** (0.052 g, 27%).

Data of **20**: Yellow solid. M.p. 154°–155°. UV/VIS ($CHCl_3$): 279 (18200), 316 (27200), 340 (37200), 363 (23800). FT-IR ($CHCl_3$): 2958*s*, 2872*m*, 1705*w*, 1647*w*, 1432*s*, 1391*m*, 1362*m*, 1314*m*, 1248*m*, 1232*s*, 1215*m*, 1158*s*, 1120*m*, 1026*w*, 861*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.13 (*s*, 12 H); 0.93 (*s*, 18 H); 4.58 (*s*, 4 H); 7.17 (*d*, $J = 8.7$, 4 H); 7.68 (*d*, $J = 8.7$, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): –5.2; 18.3; 25.8; 64.0; 88.2; 94.5; 100.2; 122.8; 129.8; 132.9; 137.7. FT-ICR-MALDI-MS (DHB, two-layer): 791.0708 ($[M+\mathrm{Na}]^+$, $C_{32}H_{42}I_2NaO_2Si_2^+$; calc. 791.0711), 768.0758 (M^+, $C_{32}H_{42}I_2O_2Si_2^+$; calc. 768.0813), 753.0613 ($[M-\mathrm{Me}]^+$), 711.0112 ($[M-t\text{-Bu}]^+$). Anal. calc. for $C_{32}H_{42}I_2O_2Si_2$ (768.66): C 50.00, H 5.51; found: C 50.11, H 5.51.

Data of **21**: Yellow solid. M.p. 224°–226°. UV/VIS ($CHCl_3$): 257 (24400), 289 (22500), 336 (44500), 372 (60300). FT-IR ($CHCl_3$): 3008*s*, 2975*m*, 2924*w*, 2896*w*, 2857*w*, 2431*w*, 2397*m*, 1698*w*, 1652*w*, 1600*m*, 1516*w*, 1508*w*, 1471*w*, 1443*w*, 1415*w*, 1244*m*, 1046*m*, 928*m*, 872*m*, 836*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.15 (*s*, 24 H); 0.94 (*s*, 36 H); 4.61 (*s*, 8 H); 7.18 (*d*, $J = 8.4$, 4 H); 7.42 (*s*, 4 H); 7.69 (*d*, $J = 8.4$, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): –5.2; 18.3; 25.8; 64.0; 64.1; 88.3; 89.0; 94.5; 100.2; 100.9; 122.8; 123.4; 129.8; 129.9; 131.5; 132.9; 137.7. FT-ICR-MALDI-MS (DHB, two-layer): 1229.3074 (29, $[M+\mathrm{Na}]^+$, $C_{58}H_{80}I_2NaO_4Si_4^+$; calc. 1229.31201), 1206.3191 (83, M^+; $C_{58}H_{80}I_2O_4Si_4^+$; calc. 1206.3223), 1205.3175 (100, $[M-\mathrm{H}]^+$, $C_{58}H_{79}I_2O_4Si_4^+$; calc. 1205.3145).

General Procedures for the Synthesis of the Oligo(phenylene Triacetylene)s **7b**–**7d**. a) *Unidirectional, Stepwise Oligomer Growth*. The attachment of **4** to *Merrifield* resin **R2** was followed by sequential repetition of *GP 6* and *GP 7*, until the desired oligomer was synthesized. Finally, this oligomer was cleaved from the solid support according to *GP 9* and purified by FC.

b) *Unidirectional, Iterative Divergent/Convergent Oligomer Growth*. After attachment of **4** to *Merrifield* resin **R2**, one sequence of *GP 6*, *GP 7*, and *GP 9* led to dimer **7b**, which was purified by FC. This compound was then subjected to another sequence of *GP6*, *GP7*, and *GP9* to give, after FC, tetramer **7d**.

*1-((*E*)-3,4-Bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-6-(4-iodophenyl)hex-3-ene-1,5-dyine-1-yl)-4-((*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-6-(trimethylsilyl)hex-3-ene-1,5-diyn-1-yl)benzene* (**7b**). The following compounds were reacted according to *GP 9*: immobilized DEE dimer (0.800 g, 0.12 mmol) and MeI (10 ml). FC (SiO_2-*60*; hexane/CH_2Cl_2 2:1) afforded **7b** (0.106 g, 82%). Yellow solid. M.p. 179°–180°. UV/VIS ($CHCl_3$): 273 (18900), 321 (37000), 360 (54200). FT-IR (CCl_4): 2952*m*, 2928*m*, 2925*w*, 2857*m*, 2129*w*, 1504*w*, 1481*w*, 1471*w*, 1465*w*, 1387*w*, 1359*w*, 1251*m*, 1101*m*, 1006*w*, 928*w*, 838*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.12 (*s*, 12 H); 0.14 (*s*, 12 H); 0.22 (*s*, 9 H); 0.93 (*s*, 36 H); 4.51 (*s*, 2 H); 4.54 (*s*, 2 H); 4.59 (*s*, 2 H); 4.61 (*s*, 2 H); 7.16 (*d*, $J = 8.4$, 2 H); 7.40 (*s*, 4 H); 7.68 (*d*, $J = 8.4$, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): –4.9; 0.0; 18.5; 26.2; 63.9; 64.1; 64.2; 88.2; 88.7; 88.8; 94.5; 100.1; 100.7; 100.8; 101.8; 107.1; 122.6; 123.1; 123.2; 129.6; 129.7; 130.3; 131.2; 132.7, 137.5. FT-ICR-MALDI-MS (DHB, two-layer): 1099.4236 (100, $[M+\mathrm{Na}]^+$; $C_{55}H_{85}INaO_4Si_5^+$; calc. 1099.4237), 1076.4361 (17, M^+; $C_{55}H_{85}IO_4Si_5^+$; calc. 1076.4339), 1019.3694 (32, $[M-t\text{-Bu}]^+$). Anal. calc. for $C_{55}H_{85}IO_4Si_5$ (1077.61): C 61.30, H 7.95; found: C 61.51, H 7.93.

(E*)-3,4-Bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-1-[4-((*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-6-(4-iodophenyl)hex-3-ene-1,5-diyn-1-yl)phenyl]-6-[4-((*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-6-(trimethylsilyl)hex-3-ene-1,5-diyn-1-yl)phenyl]hex-3-ene-1,5-diyne* (**7c**). The following compounds were reacted according to *GP 9*: immobilized DEE trimer (1.300 g, 0.17 mmol) and MeI (13 ml). FC (SiO_2-*60*; hexane/CH_2Cl_2 2:1) afforded **7c** (0.144 g, 56%). Yellow solid. M.p. 230°–231°. UV/VIS ($CHCl_3$): 283 (25400), 309 (sh, 36200), 381 (97800). FT-IR (CCl_4): 3005*s*, 2973*m*, 2927*w*, 2890*w*, 2853*w*, 2433*w*, 2396*m*, 1600*m*, 1510*w*, 1443*w*, 1253*m*, 1138*w*, 1043*m*, 931*m*, 836*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.11 (*s*, 12 H); 0.13 (*s*, 24 H); 0.21 (*s*, 9 H); 0.92 (*s*, 54 H); 4.50 (*s*, 2 H); 4.53 (*s*, 2 H); 4.59 (br. *s*, 8 H); 7.15 (*d*, $J = 8.1$, 2 H); 7.39 (*m*, 4 H), 7.40 (*m*, 4 H); 7.67 (*d*, $J = 8.1$, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): –5.0; –0.2; 18.6; 25.9; 63.9; 64.1; 88.3; 88.7; 88.8; 94.5; 100.2; 100.8;

100.9; 101.0; 101.8 107.2; 122.6; 123.2; 123.3; 128.7; 129.8; 130.5; 130.9; 131.4; 132.4; 132.8, 137.6. FT-ICR-MALDI-MS (DHB, two-layer): 1537.6630 ($[M+Na]^+$, $C_{81}H_{123}INaO_6Si_7^+$; calc. 1537.6647), 1514.6686 (M^+, $C_{81}H_{123}IO_6Si_7^+$; calc. 1514.6749), 1457.6062 (6, $[M-t\text{-Bu}]^+$). Anal. calc. for $C_{81}H_{123}IO_6Si_7$ (1516.37): C 64.16, H 8.18; found: C 64.31, H 7.99.

*1-{(*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-6-[4-((*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-6-(4-iodophenyl)hex-3-ene-1,5-diyn-1-yl)phenyl]hex-3-ene-1,5-diyn-1-yl}-4-((*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyl-oxy]methyl}-6-[4-((*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-6-(trimethylsilyl)hex-3-ene-1,5-diyn-1-yl)phenyl]hex-3-ene-1,5-diyn-1-yl)benzene* (**7d**). The following compounds were reacted according to *GP 9*: immobilized DEE tetramer (0.830 g, 0.099 mmol) and MeI (10 ml). FC (SiO_2-*60*; hexane/CH_2Cl_2 2:1 → 0:1) afforded **7d** (0.070 g, 36%). Yellow solid. M.p. > 240° (dec.). UV/VIS ($CHCl_3$): 384 (122000). FT-IR (CCl_4): 3009*s*, 2973*m*, 2928*w*, 2854*w*, 2431*w*, 2394*m*, 1600*m*, 1517*w*, 1445*w*, 1332*w*, 1253*m*, 1140*w*, 1045*m*, 1029*w*, 965w, 929*m*, 875*w*, 836*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.12 – 0.16 (48 H); 0.21 (*s*, 9 H); 0.92 – 0.95 (*m*, 72 H); 4.51 (*s*, 2 H); 4.54 (*s*, 2 H); 4.59 – 4.63 (*m*, 12 H); 7.17 (*d*, *J* = 8.4, 2 H); 7.40 – 7.42 (*m*, 12 H); 7.68 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): – 5.1; – 0.2; 18.3; 25.9; 63.7; 63.9; 88.0; 88.5; 88.7; 88.8; 94.2; 100.0; 100.5; 100.6; 100.7; 101.6; 106.9; 122.4; 123.0; 123.3; 128.5; 129.5; 130.1; 130.5; 131.1; 132.1; 132.5, 137.3. FT-ICR-MALDI-MS (DCTB): 1976.9069 (100, $[M+H+Na]^+$, $C_{107}H_{162}INaO_8Si_9^+$; calc. 1976.9316), 1895.8357 (37, $[M-t\text{-Bu}]^+$). Anal. calc. for $C_{107}H_{161}IO_8Si_9$ (1955.12): C 65.73, H 8.30; found: C 65.77, H 8.29.

*(*E*)-3,4-Bis{[(*tert*-butyl)dimethylsilyloxy]methyl}-1-(4-iodophenyl)hex-3-ene-1,5-diyne* (**22**). The following compounds were reacted according to *GP 1*: **7a** (0.120 g, 0.188 mmol), THF (40 ml), MeOH (40 ml), and 2N NaOH (1 ml). Workup afforded **22** (0.091 g, 85%). Colorless solid. M.p. 119° – 120°. FT-IR (CCl_4): 3308*w*, 2955*s*, 2929*s*, 2856*m*, 1712*m*, 1583*w*, 1471*m*, 1389*w*, 1253*s*, 1057*m*, 1005*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.11 (12 H); 0.92 (18 H); 3.56 (*s*, 1 H); 4.52 (*s*, 2 H); 4.53 (*s*, 2 H); 7.16 (*d*, *J* = 8.4, 2 H); 7.67 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): – 5.0; 18.4; 25.9; 63.8; 64.0; 80.5; 87.6; 90.0; 94.6; 100.0; 122.5; 131.3; 132.4; 133.5; 137.3. FT-ICR-MALDI-MS (DHB, two-layer): 589.1421 (100, $[M+Na]^+$, $C_{26}H_{39}INaO_2Si_2^+$; calc. 589.1431). Anal. calc. for $C_{26}H_{39}IO_2Si_2$ (566.67): C 55.11, H 6.94; found: C 55.28, H 6.78.

*(*E,E*)-3,4,9,10-Tetrakis{[(*tert*-butyl)dimethylsilyloxy]methyl}-1,12-bis(4-iodophenyl)-dodeca-3,9-dien-1,5,7,11-tetrayne* (**23**). To **22** (0.091 g, 0.16 mmol) in CH_2Cl_2 (40 ml), *Hay* catalyst soln. (0.6 ml) was added. The soln. was stirred 18 h at r.t. and then passed through a plug (SiO_2-*60*; CH_2Cl_2). Evaporation *in vacuo* and FC (SiO_2-*60*; hexane/CH_2Cl_2 2:1 → CH_2Cl_2) afforded **23** (0.035 g, 19%). Yellow solid. M.p. 166° – 168°. UV/VIS ($CHCl_3$): 256 (26900), 366 (57100), 379 (sh, 55800), 408 (sh, 37100). FT-IR (CCl_4): 2952*s*, 2925*s*, 2885*m*, 2857*s*, 2358*m*, 1482*m*, 1471*m*, 1459*w*, 1359*w*, 1256*m*, 1099*m*, 1024*w*, 1008*m*, 906*s*, 836*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.12 (*s*, 24 H); 0.93 (*s*, 36 H); 4.52 (*s*, 4 H); 4.54 (*s*, 4 H); 7.16 (*d*, *J* = 8.4, 4 H); 7.68 (*d*, *J* = 8.4, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): – 4.9; 18.5; 25.9; 63.9; 64.0; 82.4; 85.9; 88.0; 94.7; 102.0; 122.3; 128.7; 132.7; 133.1, 137.5. FT-ICR-MALDI-MS (DCTB): 1153.2789 (100, $[M+Na]^+$, $C_{52}H_{76}INaO_4Si_4^+$; calc. 1153.2808), 1130.2777 (18, M^+, $C_{52}H_{76}IO_4Si_4I^+$; calc. 1130.2910), 1073.2084 (17, $[M-t\text{-Bu}]^+$). Anal. calc. for $C_{52}H_{76}I_2O_4Si_4$ (1131.32): C 55.21, H 6.77; found: C 55.04, H 6.84.

Cadiot – Chodkiewicz *Coupling on Solid Phase*. The following compounds were reacted according to *GP 8*: immobilized DEE monomer **18** (0.500 g, 0.085 mmol), **11** (0.219 g, 0.43 mmol), LiI (0.002 g, 0.017 mmol), PMP (0.04 ml, 0.238 mmol), $[Pd_2(dba)_3]$ (0.0022 g, 0.0026 mmol, 3 mol-%), and benzene (9 ml). After workup, the resin-bound products were cleaved according to *GP 9*: immobilized DEE derivatives (0.48 g) and MeI (5 ml). FC (SiO_2-*60*; hexane/CH_2Cl_2 2:1) afforded **22** (0.001 g, 2%) and an inseparable mixture of **15** and **23**. Further investigation of this mixture by calibrated, anal. HPLC (hexane/CH_2Cl_2 2:1) provided **15** (37%) and **23** (10%).

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Received October 7, 2003