Poly(triacetylene) Oligomers: Conformational Analysis by X-Ray Crystallography and Synthesis of a 17.8-nm-Long Monodisperse 24-mer

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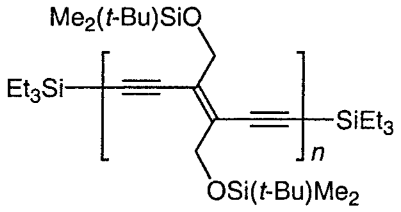
Starting from the octameric poly(triacetylene) (PTA) oligomer **1e** as a large 'macromonomer', the monodisperse tetracosamer (24-mer) **1h** was prepared by a previously introduced statistical deprotection-oligomerization sequence (*Scheme*). It is the longest known molecular rod featuring a fully conjugated, non-aromatic all-carbon backbone. Matrix-assisted laser-desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry was particularly useful in the characterization of oligomer **1h** and clearly demonstrated its monodispersity (*Fig. 1*). In an effort to further clarify the conformational preferences of PTA oligomers, the X-ray crystal structure of the 3.2-nm-long tetramer **1c** was solved (*Figs. 2–4*). In the solid state, the C=C bonds in **1c** all adopt the s-*trans* conformation with respect to the buta-1,3-diynediyl moieties. The π-conjugated system is perfectly planar, with the squared sum of the deviations of the backbone C-atoms from the best plane amounting to 0.077 Å^2. Analysis of the crystal lattice revealed a layered structure, in which the π-conjugated backbone of one oligomer is insulated by the trialkylsilyl groups of adjacent oligomers in neighboring layers.

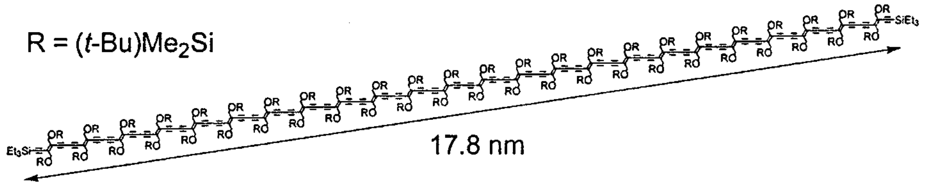
1. Introduction. – Poly(triacetylene)s $[-(C{\equiv}C-CR{=}CR-C{\equiv}C)_n-]$ are a new class of linearly π-conjugated polymers in the progression that starts with polyacetylene $[-(CR{=}CR)_n-]$ and poly(diacetylene) $[-(C{\equiv}C-CR{=}CR)_n-]$, and ultimately leads to carbyne $[-(C{\equiv}C)_n-]$ [1][2]. In recent work, we focused on the preparation and study of monodisperse oligomers as models for the corresponding infinite PTA polymers [3][4]. Thus, we prepared the series **1a–g**, which extends up to a 11.9-nm-long 16-mer and investigated the evolution of the physicochemical properties into the higher oligomeric regime, where saturation of the properties becomes apparent [5]. In good agreement with previous extrapolative studies [6], evaluation of linear and nonlinear optical properties, *Raman* scattering, and electrochemical data supported an onset of saturation at *ca.* $n = 10$ monomeric units, corresponding to 60 C–C bonds. Based on the spectroscopic data, we proposed a preference of the molecular rods for adopting a planar geometry of the π-conjugated backbone, with adjacent C=C bonds adopting an s-*trans* conformation with respect to the bridging buta-1,3-diynediyl linkers. Here, we report the X-ray crystal structure of the 32-Å-long tetrameric rod **1c**, which strongly supports such conformational preference in the solid state (for the X-ray analysis of PTA dimers, see [6]). We also describe the synthesis of the monodisperse tetracosamer (24-mer) **1h**, which is the longest known monodisperse molecular rod featuring a fully conjugated, non-aromatic all-carbon backbone (for other multi-nanometer-long monodisperse oligomers, see [3][4][7][8]).

2. Results and Discussion. – 2.1. *Synthesis and Characterization of 24-mer* **1h**. The synthesis of tetracosamer **1h** started from dimer **1b**, which was statistically deprotected



1a–h $n = 1,2,4,6,8,12,16,24$

R = (t-Bu)Me$_2$Si

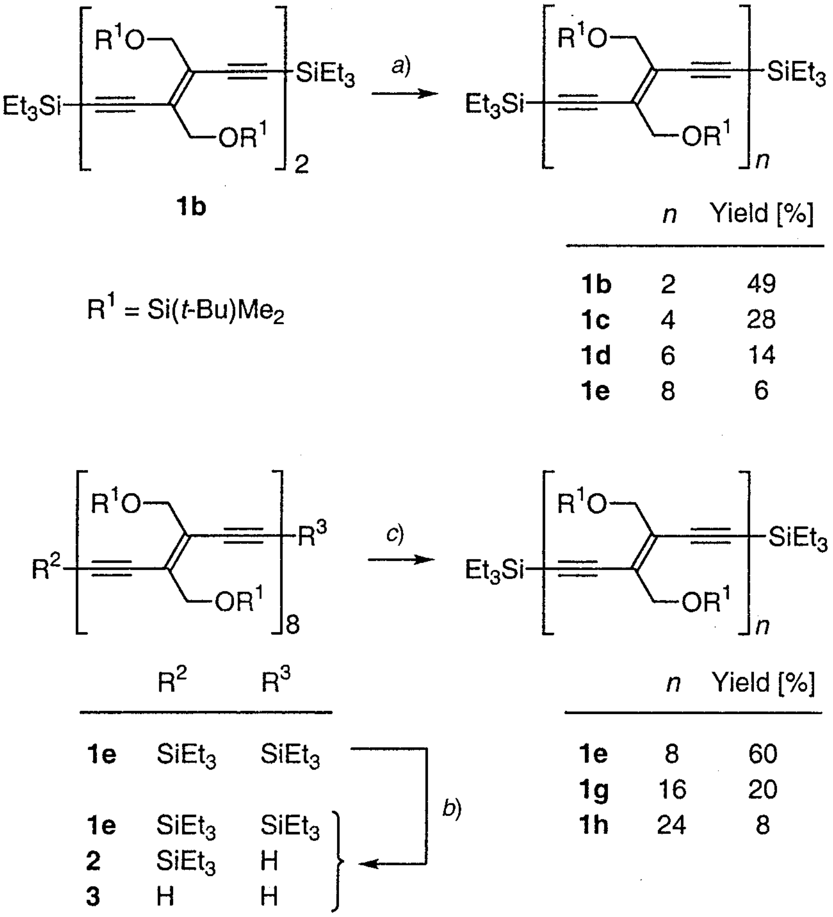


1h

with NaOH in THF/MeOH/H$_2$O to afford a mixture of terminally bis-deprotected and mono-deprotected oligomers, in addition to unchanged starting material (*Scheme*). This mixture was directly oligomerized under *Hay* conditions [9] to yield dimer **1b** (49%), tetramer **1c** (28%), hexamer **1d** (14%), and octamer **1e** (6%), which were purified by gel-permeation chromatography (GPC) as described in [5]. A second cycle of statistical deprotection-oligomerization started from octameric **1e** as 'macromonomer' (*Scheme*). Deprotection provided a mixture of mono-deprotected **2**, bis-deprotected **3**, and starting material, which was directly oligomerized to give octamer **1e** (60%), hexadecamer **1g** (20%), and tetracosamer **1h** (8%). Purification of the three compounds was accomplished first by separating octamer **1e** from the longer-chain derivatives by means of preparative GPC (4 × 180 cm glass column filled with *Bio-Beads S-X1*; eluent: CH$_2$Cl$_2$). Further purification of tetracosamer **1h** was achieved by repetitive preparative high-performance GPC on two *GROM-SDV-Gel 1000* columns (2.2 × 60 cm, connected in series; eluent: THF). Finally, the oligomer was precipitated with MeOH from concentrated CH$_2$Cl$_2$ solution followed by centrifugation. Its purity was revealed by analytical GPC on *Shodex GPC KF-802.5* and *Shodex GPC KF-803L* columns connected in series; the retention times (THF) were 15.16 (**1e**), 13.71 (**1g**), and 12.88 (**1h**) min.

Tetracosamer **1h** is a highly stable compound, which does not decompose below its melting point above 220°. Its identity was nicely revealed by MALDI-TOF mass spectrometry in the positive-ion and reflector-detection mode, with 3-(indol-3-yl)acrylic acid (IAA) as the matrix (*Fig. 1*). The spectrum displayed as the only major peak the sodium complex of the molecular ion $[M+\mathrm{Na}]^+$ at m/z 8957.6 (calc. for $C_{492}H_{846}O_{48}Si_{50}Na$: 8957.3). The complete absence of signals from shorter or longer oligomers in the spectrum clearly proved the high purity and monodispersity of **1h**. With this oligomer, we reach the polymer-size range that was previously accessible only with polydisperse material. Its length extends well into the saturation regime beyond the effective conjugation length (ECL, around 10 monomeric units [5]), and, correspond-

Scheme. *Synthesis of Tetracosamer* **1h** *by Two Statistical Deprotection-Oligomerization Cycles*



a) 1M NaOH, THF/MeOH 1:1, 20°, 15 min; then CuCl, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), air, CH_2Cl_2, 20°, 4 h. *b*) 1M aq. NaOH, THF/MeOH 6:1, 10 min. *c*) CuCl, TMEDA, air, 1,2-dichlorobenzene, 80°, 2 h.

ingly, the position of the longest-wavelength absorption maximum (λ_{max} 443 nm) in the UV/VIS spectrum ($CHCl_3$) is hardly changed with respect to the corresponding maximum in the spectrum of hexadecamer **1g** (438 nm). Also, as expected from the data for the lower oligomers **1f** and **1g**, the ^{13}C-NMR spectrum (125 MHz, $CDCl_3$) of **1h** displays severe peak overlap in both the regions of the C(sp) and C(sp^2) resonances. Similarly, the resonances of the individual (t-Bu)Me_2SiOCH_2 groups overlap in the ^1H-NMR spectrum (500 MHz, $CDCl_3$). The limited structural information that can be gathered from the NMR data clearly underlines the importance of mass spectrometry for an accurate constitutional assignment.

2.2. *X-Ray Crystal Structure of Tetramer* **1c**. Both spectroscopic (UV/VIS) [5] and computational studies [5b][10] indicated a preference of adjacent olefinic C=C bonds

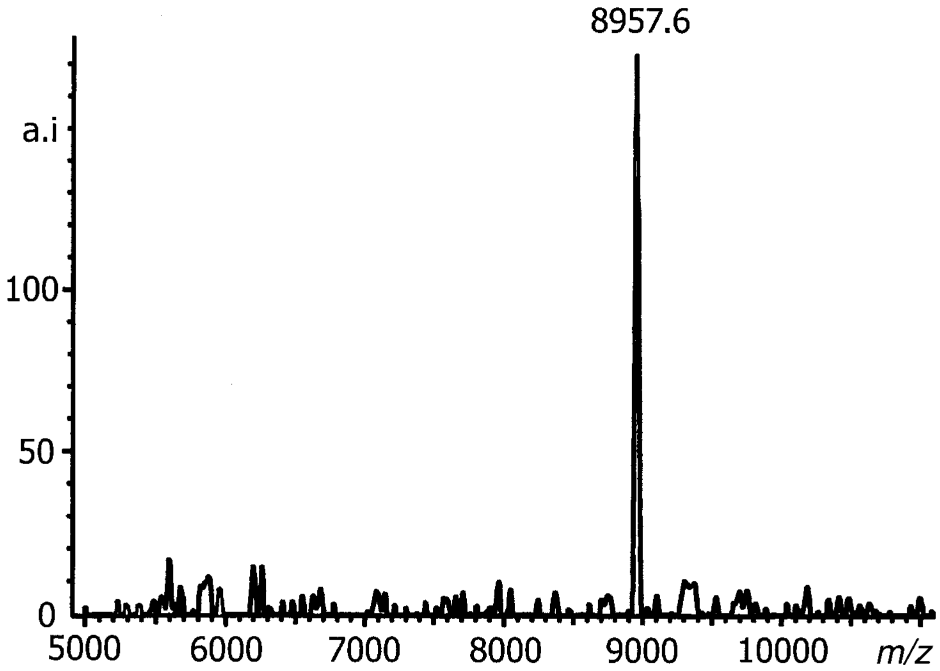


Fig. 1. *MALDI-TOF Mass spectrum of tetracosamer* **1h** *recorded in the positive-ion and reflector-detection mode with IAA as matrix*

in PTA oligomers for adopting the s-*trans* conformation with respect to the buta-1,3-diynediyl moieties. This conformational preference was confirmed for the solid state by X-ray crystallographic analysis of two PTA dimers containing tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne) repeating units [6]. Solid-state structures of PTA oligomers such as **1b**–**h**, with (*E*)-1,2-diethynylethene (DEE, (*E*)-hex-3-ene-1,5-diyne) repeating units, however, were unknown, and only the X-ray crystal structure of monomer **1a** had been solved [11]. Here, we present the X-ray crystal-structure determination of the 3.2-nm-long (distance between terminal Si-atoms) tetramer **1c**.

Extremely thin crystal foils of **1c** of *ca.* 0.001-mm thickness were readily obtained, but the growth of crystals of sufficient thickness suitable for X-ray analysis was a difficult task. This growth behavior indicated the presence of a layered crystal lattice with reduced cohesion between layers. Suitable crystals were eventually obtained by slow evaporation of CH_2Cl_2 from a solution of **1c** in CH_2Cl_2/MeOH/Me_2SO at 20°. Although they were very thin (0.5 × 0.1 × 0.004 mm), a preliminary measurement on a *Picker-Stoe* diffractometer with CuK_α radiation allowed the determination of the unit cell and the recording of some diffraction data. However, the resolution required for a structure determination by direct methods could not be reached. On the other hand, a *Patterson* search trial by means of the program *PATSEE* from the *SHELXTL* package [12] with a molecule modeled by starting from the structure of monomer **1a** [11] was promising. A careful measurement was subsequently started on a *Marresearch* imaging plate detector system equipped with a rotating anode X-ray generator (MoK_α radiation). The model could be successfully refined with this data set. The crystal structure data for **1c** are given in the *Exper. Part*; an ORTEP plot is depicted in *Fig. 2*.

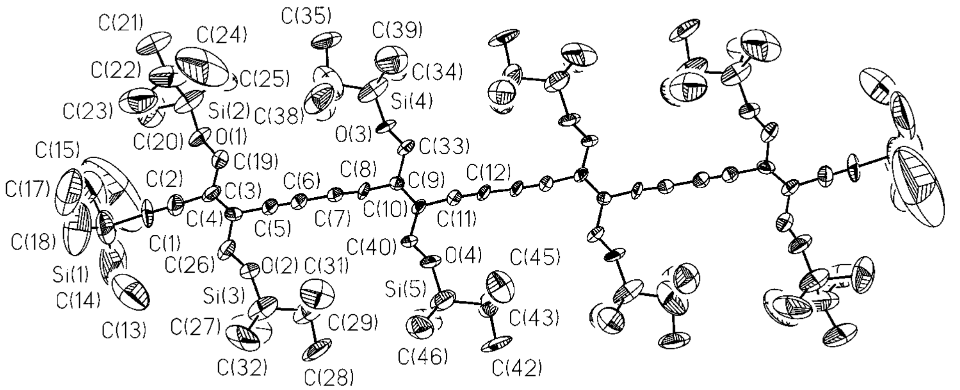


Fig. 2. *X-Ray crystal structure of* **1c**. The ORTEP plot shows ellipsoids at the 25% probability level. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.176(13); C(2)–C(3) 1.50(3); C(3)–C(4) 1.28(2); C(4)–C(5) 1.483(14); C(5)–C(6) 1.187(13); C(6)–(C7) 1.468(14); C(7)–C(8) 1.161(12); C(8)–C(9) 1.367(12); C(9)–C(10) 1.33(2); C(10)–C(11) 1.448(13); C(11)–C(12) 1.204(11); C(12)–C(12′) 1.32(2); Si(1)–C(1)–C(2) 178.2(13); C(1)–C(2)–C(3) 175.3(13); C(2)–C(3)–C(4) 118.5(10); C(2)–C(3)–C(19) 119.3(9); C(3)–C(4)–C(5) 125.0(10); C(26)–C(4)–C(5) 109.5(9); C(4)–C(5)–C(6) 178.3(12); C(5)–C(6)–C(7) 177.2(12); C(6)–C(7)–C(8) 177.0(10); C(7)–C(8)–C(9) 174.6(11); C(8)–C(9)–C(10) 119.2(9); C(8)–C(9)–C(33) 116.7(9); C(9)–C(10)–C(11) 117.5(9); C(40)–C(10)–C(11) 119.5(9); C(10)–C(11)–C(12) 175.0(10); C(11)–C(12)–C(12′) 175.2(14).

In the crystal of **1c**, all C=C bonds adopt the s-*trans* conformation with respect to the buta-1,3-diynediyl fragments. The distance between terminal Si-atoms in **1c** is 3.2 nm, which is in good agreement with a length of 3.15 nm predicted by force-field calculations [11]. The π-conjugated backbone is nearly perfectly planar (*Fig3*). We calculated the best plane through all of its C-atoms according to the formulae given in [13] and found that the squared sum of the deviations of all backbone C-atoms from the best plane through the backbone is only 0.077 Å^2. With 0.129 Å, the atoms C(1) and C(1′) show the highest deviation from planarity. Thus, the solid-state structure nicely confirms conformational predictions from optical spectroscopy and calculations.

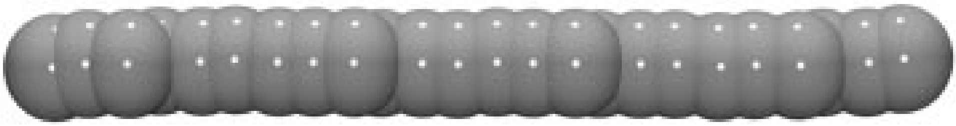


Fig. 3. *Space-filling representation of the π-conjugated backbone of* **1c** *in the solid state, clearly showing its planarity.* Lateral (t-Bu)Me_2SiOCH_2 and terminal Et_3Si groups are omitted for clarity.

The crystal lattice of **1c** is displayed in *Fig. 4*. As expected from the mechanical properties of the crystals, the oligomers form a layered structure featuring only weak contacts between layers. The planes of neighboring layers are separated by 4.0 Å. Neighboring oligomers in the same or different layers are insulated from one another by the lateral and terminal trialkylsilyl groups. Thus, the π-conjugated all-carbon backbone of one rod is sandwiched between the Si(t-Bu)Me_2 groups of two rods in neighboring layers, leading to a separation of the C-backbones of nearest-neighbor rods in adjacent layers of 6.63 Å.

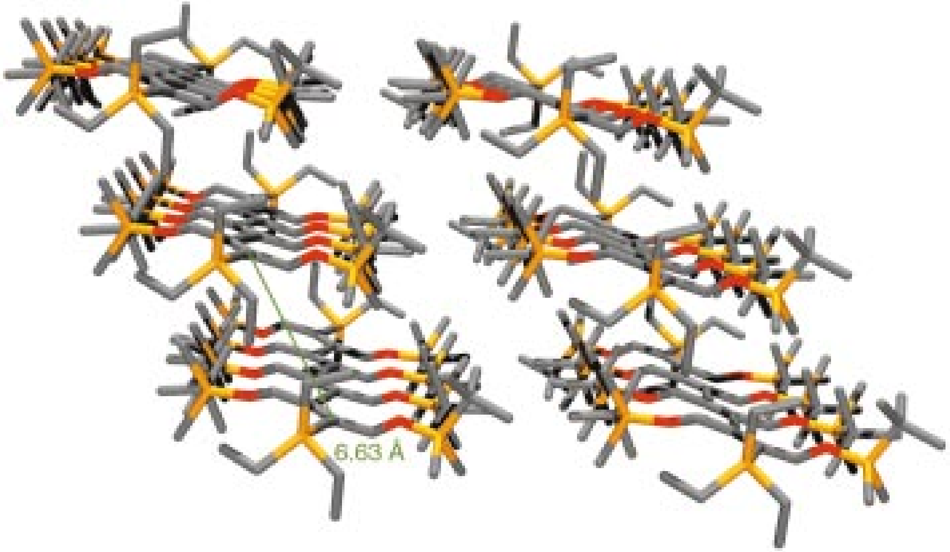


Fig. 4. *View of the crystal lattice of* **1c**. Grey: C-Atoms, red: O-atoms, orange: Si-atoms.

3. Conclusions. – With the tetracosameric PTA rod **1h**, a molecular wire with a linear π-conjugated, all-carbon backbone of unprecedented length was obtained and fully characterized. This extension of monodisperse molecular chemical systems into the multinanometer size regime was possible due to the exceptional versatility of oxidative acetylenic coupling methodology [10] and the recent impressive advances in GPC separation and mass-spectrometric characterization techniques. With its 17.8-nm length, oligomer **1h** has the potential for use as a molecular wire and for bridging photolithographic gaps in future molecular electronic circuitry. The X-ray crystal structure of the 3.2-nm-long tetrameric PTA rod **1c** showed a planar π-conjugated backbone with all C=C bonds adopting the s-*trans* conformation with respect to the buta-1,3-diynediyl moieties, thereby confirming earlier predictions based on theoretical calculations and UV/VIS data. We assume that this conformation is also the preferred one in other PTA rods.

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Experimental Part

General. Reagents and solvents were reagent grade and used without further purification. Compound **1e** was prepared according to the procedure described in [5]. CH_2Cl_2 was distilled over CaH_2 under N_2. Prep. gravity GPC: *BIO-RAD Beads S-X1* (pore size 200–400 μm) as stationary phase at ambient pressure and temp.; eluent: CH_2Cl_2; 10–20 drops min^{-1}; fractions of 5–10 ml. Prep. high-performance GPC: *Merck-Hitachi HPLC Pump L-7100* and *UV-Detector L-7400* with two *NovoGrom GROM-SDV-Gel 1000* columns (2.2 × 60 cm) from *GROM Analytik und HPLC* connected in series. Anal. GPC: same pump and detector as above, *Merck-Hitachi RI Detector L-7490* and *Chromointegrator D-2500* with two *Shodex PGC KF-802.5* and *Shodex GPC KF-803L* columns connected in series; flow rate 1 ml min^{-1}; oven temp.: 40°; detection at 400 nm. M.p.: *Büchi B-540*; uncorrected. UV/VIS Spectra (λ [nm]: ε [M^{-1} cm^{-1}]): *Varian Cary-5*, at 293 K. IR Spectra [cm^{-1}]: *Perkin-Elmer 1600-FTIR*. ^{1}H- and ^{13}C-NMR spectra: *Bruker AMX-500, Varian Gemini-200* and *300* at 293 K in $CDCl_3$; solvent peaks (7.24 ppm for ^{1}H and 77.0 ppm for ^{13}C) as internal reference. MALDI-TOF MS (*m/z* (%)): *Bruker Reflex-MALDI-TOF* (337-nm N_2-laser system, 3-(indol-3-yl)acrylic acid (IAA) as matrix).

X-Ray Crystal Structure of **1c**. Crystals were grown at 20° from a soln. of **1c** in CH_2Cl_2/MeOH/Me_2SO in a 25-ml flask. The flask was covered with a plastic cap containing a small hole (introduced with a syringe) to allow slow evaporation of CH_2Cl_2. Crystal data at 293 K for $C_{92}H_{166}O_8Si_{10}$ (M_r 1681.15): triclinic, space group $P\bar{1}$ (No. 2), $D_c = 0.984$ g cm^{-3}, $Z = 1$, $a = 6.63(9)$, $b = 13.17(9)$, $c = 32.73(9)$ Å, $\alpha = 86.17(9)°$, $\beta = 89.59(9)°$, $\gamma = 84.28(10)°$, $V = 2836(42)$ Å^3. *Marresearch* imaging plate detector system, MoK_α radiation, $\lambda = 0.71073$ Å. The structure was solved as described in the text and refined with 499 parameters and 45 restraints (bond lengths and angles of lateral and terminal trialkylsilyl groups were restrained) by full-matrix least-squares analysis based on F^2 with experimental weights; all heavy atoms were refined anisotropically, H-atoms fixed isotropically with positions calculated from stereochemical considerations. Final $R(F) = 0.111$ for 1031 observed reflections with $I > 2\sigma(I)$ and $wR(F^2) = 0.393$ for all 3355 data. *Cambridge Crystallographic Data Centre* Deposition No. CCDC-152535. 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).

*(all-*E*)-3,4,9,10,15,16,21,22,27,28,33,34,39,40,45,46,51,52,57,58,63,64,69,70,75,76,81,82,87,88,93,94,99,100,105,106,111,112,117,118,123,124,129,130,135,136,141,142-Octatetracontakis{[(*tert*-butyl)dimethylsilyloxy]methyl}-1,144-bis(triethylsilyl)tetratetracontahecta-3,9,15,21,27,33,39,45,51,57,63,69,75,81,87,93,99,105,111,117,123,129,135,141-tetracosaene-1,5,7,11,13,17,19,23,25,29,31,35,37,41,43,47,49,53,55,59,61,65,67,71,73,77,79,83,85,89,91,95,97,101,103,107,109,113,115,119,121,125,127,131,133,137,139,143-octatetracontayne* (**1h**). 1M NaOH (0.075 ml) was added at 20° to **1e** (0.158 g, 0.050 mmol) in THF/MeOH 6 : 1 (42 ml), and the mixture was stirred in the dark. After 10 min, sat. aq. NH_4Cl soln. (50 ml) was added, and the mixture was extracted with CH_2Cl_2 (2 × 50 ml). The combined org. layers were dried ($MgSO_4$) and evaporated at water-aspirator pressure. A catalyst soln. was prepared by adding TMEDA (0.027 ml, 0.176 mmol) to a suspension of CuCl (5.0 mg, 0.050 mmol) in 1,2-dichlorobenzene (19 ml, over 4-Å molecular sieves). This green catalyst soln. was transferred to the product obtained by deprotection of **1e** in 1,2-dichlorobenzene (10 ml), and the mixture was stirred under air for 2 h at 80° and for 12 h at 20°. Sat. aq. NH_4Cl soln. (50 ml) was added, and the mixture was extracted with CH_2Cl_2 (4 × 50 ml). The combined org. layers were dried ($MgSO_4$) and evaporated at water-aspirator pressure. Prep. gravity GPC (4 × 180 cm glass column filled with *Bio-Beads S-X1*; CH_2Cl_2), followed by high-performance GPC (two *GROM-SDV-Gel 1000* columns (2.2 × 60 cm connected in series; THF, 6–7 runs) and precipitation with MeOH from concentrated CH_2Cl_2 soln., gave **1h** (11 mg, 8%). The GPC separations also afforded **1e** (92 mg, 60%) and **1g** (30 mg, 20%). The spectral properties of **1e** and **1g** were identical to those reported in [5].

Data of **1h**: M.p. > 220°. UV/VIS ($CHCl_3$): 284 (103200), 300 (96600), 320 (91300), 443 (285100). IR ($CHCl_3$): 2956*s*, 2930*s*, 2889*m*, 2857*s*, 2189*w*, 2133*w*, 1728*w*, 1600*w*, 1472*m*, 1456*m*, 1389*w*, 1362*w*, 1257*s*, 1109*s*, 1006*s*, 939*w*, 838*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.088, 0.096, 0.104 (3*s*, 288 H); 0.64 (*q*, $J = 7.9$, 12 H); 0.910, 0.916 (2*s*, 432 H); 1.01 (*t*, $J = 7.9$, 18 H): 4.42, 4.46, 4.50 (3*s*, 96 H). ^{13}C-NMR (125 MHz, $CDCl_3$ + *ca.* 20 mM [Cr(acac)$_3$]): −5.31 (overlap); 4.15; 7.32; 18.20 (overlap); 25.72 (overlap); 63.70 (overlap); 80.97; 83.09–83.96 (overlap); 85.05; 85.17; 87.21 (overlap); 102.52; 107.25 (overlap); 108.0 (overlap); 108.99; 129.63 (overlap); 132.25 (overlap). MALDI-TOF-MS (IAA): 8957.6 (100, $[M + Na]^+$; calc. for $C_{492}H_{846}O_{48}Si_{50}Na$: 8957.3).

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