Oligo(triacetylene) Derivatives with Pendant Long Alkyl Chains

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Substituted (*E*)-2-(ethynyl)but-2-ene and (*E*)-hex-3-ene-1,5-diyne derivatives **6** and **10**, respectively, were prepared by dicyclohexylcarbodiimide(DCC)-mediated esterification of tris(dodecyloxy)benzoic acid (**4**) with (*E*)-2-[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diol (**3**) and (*E*)-2,3-bis[(trimethylsilyl)ethynyl]but-2-ene-1,4-diol (**8**), respectively, followed by deprotection with Bu_4NF in wet THF (*Schemes 1* and *2*). Oligomerization reactions of diyne derivative **10** were attempted by treatment with the *Hay* catalyst in the presence of monoalkyne **6** as an end-capping reagent. Under these conditions, only compound **7** resulting from the homocoupling of **6** (*Scheme 1*), and polymers of **10** were obtained due to the difference in reactivity of the alkyne groups in **6** and **10**. In contrast, when phenylacetylene was used as the stopper, the oligomerization of **10** afforded a mixture of end-capped oligomers, from which **11**–**13** were isolated by column chromatography (*Scheme 3*). The poly(triacetylenes) (PTA) **16**–**18** were prepared in a similar manner starting from diol **8** and stearic acid (*Schemes 4* and *5*). Whereas the end-capped monomers and dimers **11**, **12**, **16**, and **17** with pendant long alkyl chains do not exhibit any liquid-crystalline behavior, the trimeric derivatives **13** and **18** show mesomorphic properties, thus demonstrating that the poly(triacetylene) backbone can behave as a mesogenic unit.

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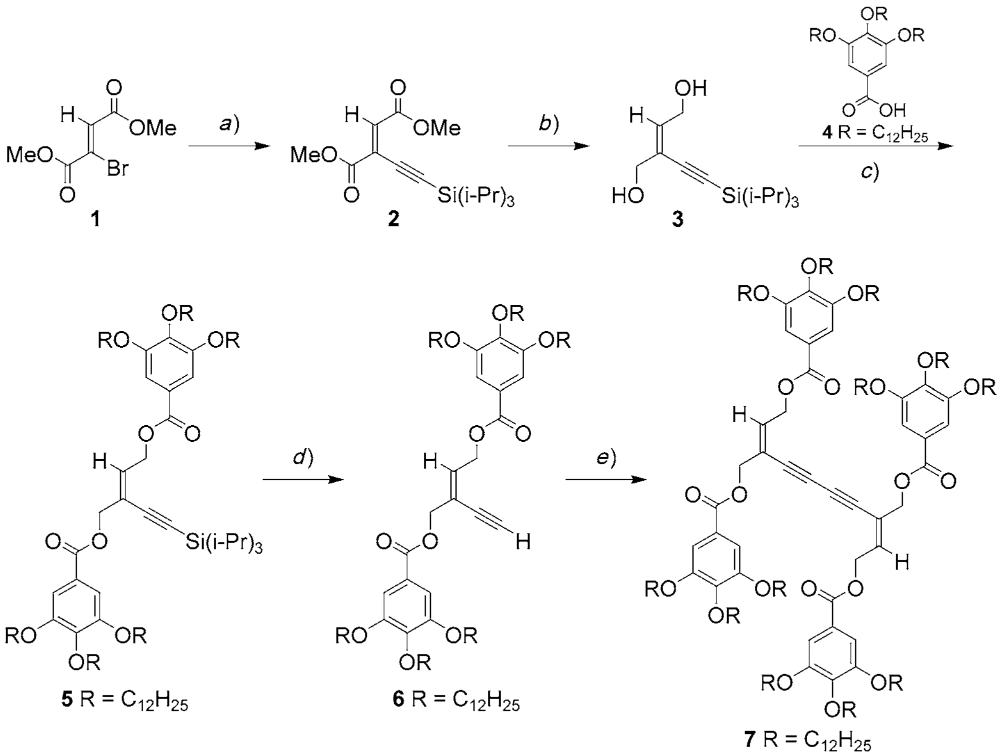
1. Introduction. – In light of their particular electronic properties, oligomers and polymers with extended conjugated C-cores are being intensely investigated with the aim of generating new advanced materials for optoelectronic applications [1]. As far as light-emitting diodes (LEDs) [2] or photovoltaic cells [3][4] are concerned, a challenging task appears to be the understanding of the relationship between the morphology of the thin films and the electroluminescence or charge-transport properties. Indeed, the morphology of the organic films plays a fundamental role in the functional characteristics of the devices [5], and these considerations have led to substantial efforts in structural studies of this kind of compound. In this context, π-conjugated derivatives exhibiting liquid-crystalline properties are of particular interest because they spontaneously form ordered assemblies that can be easily oriented. For conducting oligomers and/or polymers derived from poly(phenylenevinylene) or poly(thiophene), it has been shown that the conjugated backbone is a rigid rod that can act as a mesogenic unit [6]. As part of this research, we have shown that single-stranded conjugated oligomers with a nonaromatic all-C backbone can also be used for the preparation of liquid-crystalline materials [7]. We now report a full account of the synthesis of these poly(triacetylenes) (PTA; for a review, see [8]) [9] substituted with lateral long alkyl chains.

2. Results and Discussion. – Dimethyl 2-bromofumarate (**1**) [10] was subjected to a Pd-catalyzed cross-coupling reaction [11] with (triisopropylsilyl)acetylene to give compound **2** in 74% yield (*Scheme 1*). Reduction of **2** with diisobutylaluminium

Scheme 1

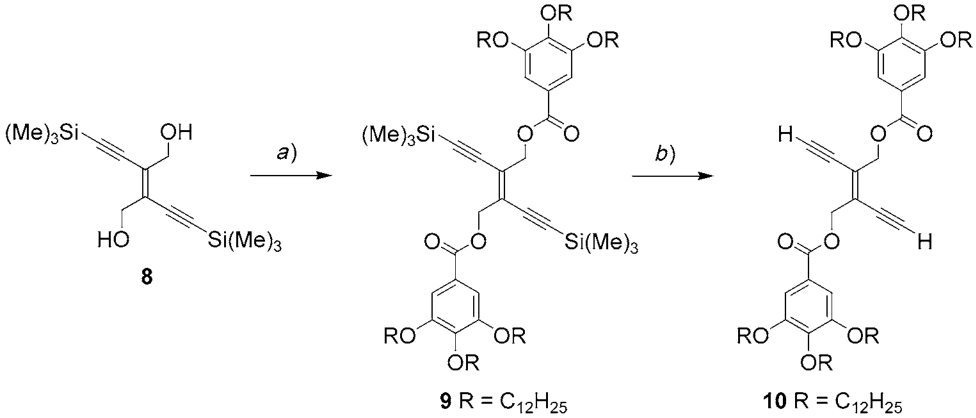


a) (Triisopropylsilyl)acetylene, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t. (74%). *b*) DIBAL-H, CH_2Cl_2, 0–10° (95%). *c*) DCC, *N*,*N*-dimethylpyridin-4-amine (DMAP), CH_2Cl_2, 0° to r.t. (60%). *d*) Bu_4NF, THF, – 78° to r.t. (88%). *e*) CuCl, TMEDA, O_2, CH_2Cl_2, r.t. (83%).

hydride (DIBAL-H) in CH_2Cl_2 gave diol **3** in 95% yield. Dicyclohexylcarbodiimide(DCC)-mediated esterification [12] of acid **4** [13] with diol **3** afforded **5** in 60% yield. The (*E*)-configuration of the alkene fragment in **5** was unambiguously confirmed by 2D-NOESY experiments. Indeed, NOE cross-peaks could be observed between the alkene proton and both allylic CH_2 groups, but none could be detected between the two sets of allylic CH_2 protons. Deprotection of **5** with Bu_4NF in wet THF afforded **6** in 88% yield. Oxidative coupling of terminal alkyne **6** with the *Hay* catalyst [14] (CuCl, *N*,*N*,*N'*,*N'*-tetramethylethane-1,2-diamine (TMEDA)) in CH_2Cl_2 in the presence of dry air gave compound **7** in 83% yield.

For the preparation of the (*E*)-hex-3-ene-1,5-diyne derivative **10** (*Scheme 2*), the key precursor in the synthesis of the oligomers **11**–**13**, diol **8** was prepared in three steps from dimethyl acetylenedicarboxylate as previously reported by *Diederich* and co-workers [15]. Diol **8** was treated with carboxylic acid **4** in CH_2Cl_2 in the presence of DCC and *N*,*N*-dimethylpyridin-4-amine (DMAP) to give diester **9** in 61% yield. Subsequent deprotection of **9** with Bu_4NF in wet THF afforded (*E*)-enediyne monomer **10** in 90% yield.

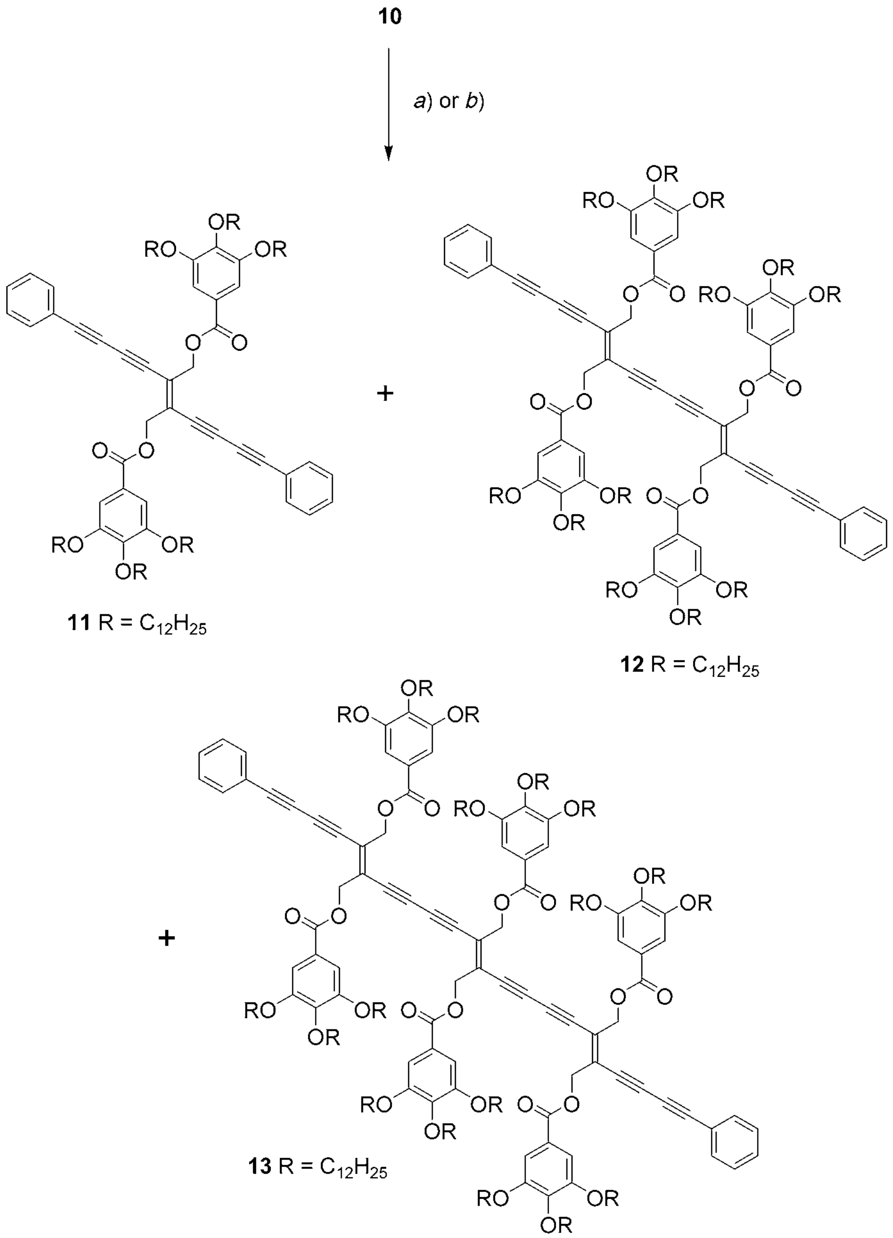
Scheme 2



a) **4**, DCC, DMAP, CH_2Cl_2, 0° to r.t. (61%). *b*) Bu_4NF, THF, – 78° to r.t. (90%).

The oligomerization reactions of monomer **10** were performed in the presence of an end-capping reagent to control the oligomer length [16]. The first end-capping reactions were attempted with mono-alkyne **6** as the stopper. Reaction of **10** with **6** in CH_2Cl_2 in the presence of an excess of the *Hay* catalyst under dry air yielded mainly compound **7** (*Scheme 1*), resulting from the homocoupling of **6**, and polymers from monomer **10**; no end-capped oligomers could be detected in the reaction mixture. The latter result is due to the difference in reactivity of the terminal alkyne functions of **10** and **6** under these conditions. Indeed, TLC monitoring of the reaction established that compound **6** was consumed faster than **10**. Thus, the oligomerization reaction was attempted with another end-capping reagent, namely phenylacetylene. Reaction of **10** and phenylacetylene in CH_2Cl_2 under dry air in the presence of an excess of the *Hay* catalyst furnished a mixture of end-capped oligomers, from which **11**–**13** were isolated by column chromatography (*Scheme 3*). The yield of **11**–**13** was highly dependant of the molar ratio monomer/end-capping reagent. When a large excess of phenylacetylene (10 equiv.) was used, end-capped monomer **11** and end-capped dimer **12** were obtained in 64 and 7% yield, respectively. When **10** and phenylacetylene were used in a 1:1 molar ratio, **11** (15% yield), **12** (19%), and **13** (12%) could be isolated. Higher oligomers were also formed but they could not be isolated as pure compounds. Oligomers **11**–**13** are well soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, or THF, and complete spectroscopic characterization was easily achieved. Both ^1H- and ^{13}C-NMR spectra are in full agreement with the centrosymmetric structures of the end-capped oligomers **11**–**13**. The number of monomer units in each oligomer is confirmed by the aromatic-to-allylic-proton ratio deduced from the integration in the ^1H-NMR spectra. In addition, the number of signals corresponding to the allylic CH_2 in the ^{13}C-NMR spectra of **11**–**13** increases with the number of monomer units. The molecular constitution of the end-capped oligomers **11**–**13** is also confirmed by FAB-MS, which exhibit the expected molecular-ion peaks. In spite of the presence of the bulky 3,4,5-tris(dodecyloxy)benzoyl substituents in **11**–**13**, their absorption spectra are similar to analogous oligo(triacetylene) derivatives [9], showing that there is no

Scheme 3



a) Phenylacetylene (10 equiv.), CuCl, TMEDA, O_2, CH_2Cl_2, r.t. (**11**: 64%; **12**: 7%). *b*) Phenylacetylene (1 equiv.), CuCl, TMEDA, O_2, CH_2Cl_2, r.t. (**11**: 15%; **12**: 19%; **13**: 12%).

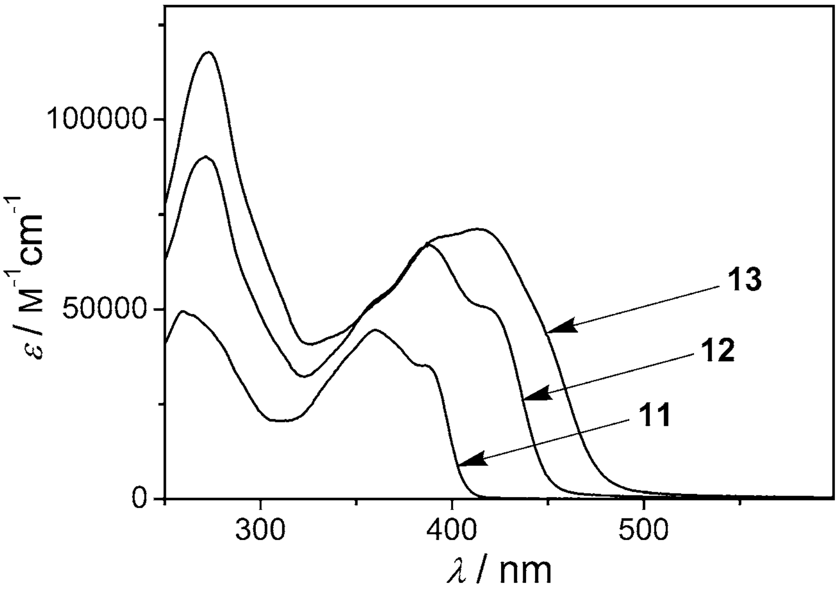


Figure. *Absorption spectra of* **11**–**13** *recorded in* CH_2Cl_2

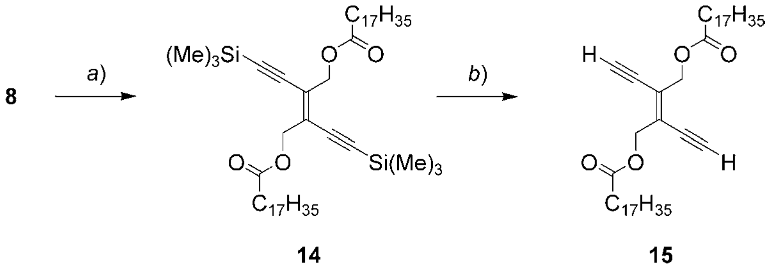
significant distortion from planarity for steric reasons. Indeed, end-capped dimer **12** shows end absorption at *ca.* 450 nm and end-capped trimer **13** at *ca.* 500 nm in good agreement with previously reported data (*Fig.*) [9]. In addition to the centrosymmetric structures deduced from the ^{1}H- and ^{13}C-NMR spectra, the latter observation also supports an all-*trans* configuration for **11**–**13**.

Whereas the end-capped monomer **11** and dimer **12** do not exhibit any liquid-crystalline behavior, mesomorphic properties were observed for trimer **13**. As already reported in the preliminary communication [7], these have been deduced from optical and X-ray diffraction investigations. Polarized optical microscopy (POM) revealed a fluid birefringent phase at room temperature for **13**, and the clearing temperature was determined to be 40°. However, the birefringent optical texture observed on cooling the sample from the isotropic phase was noncharacteristic.

The oligomers **16**–**18** were prepared in a similar manner starting from diol **8** (*Schemes 4* and *5*). DCC-Mediated esterification of **8** with stearic acid to diester **14** and subsequent deprotection with Bu_4NF provided the desired (*E*)-enediyne monomer **15**. Compound **15** is relatively unstable in the neat state at room temperature and decomposes slowly to a black solid. In contrast, monomer **10** is an air-stable compound that can be stored at room temperature for prolonged periods of time. As previously shown by X-ray crystal-structure analysis of some related compounds [17], the presence of bulky substituents in **10** isolates the sensitive (*E*)-enediyne units and prevents intermolecular reactions that would lead to decomposition.

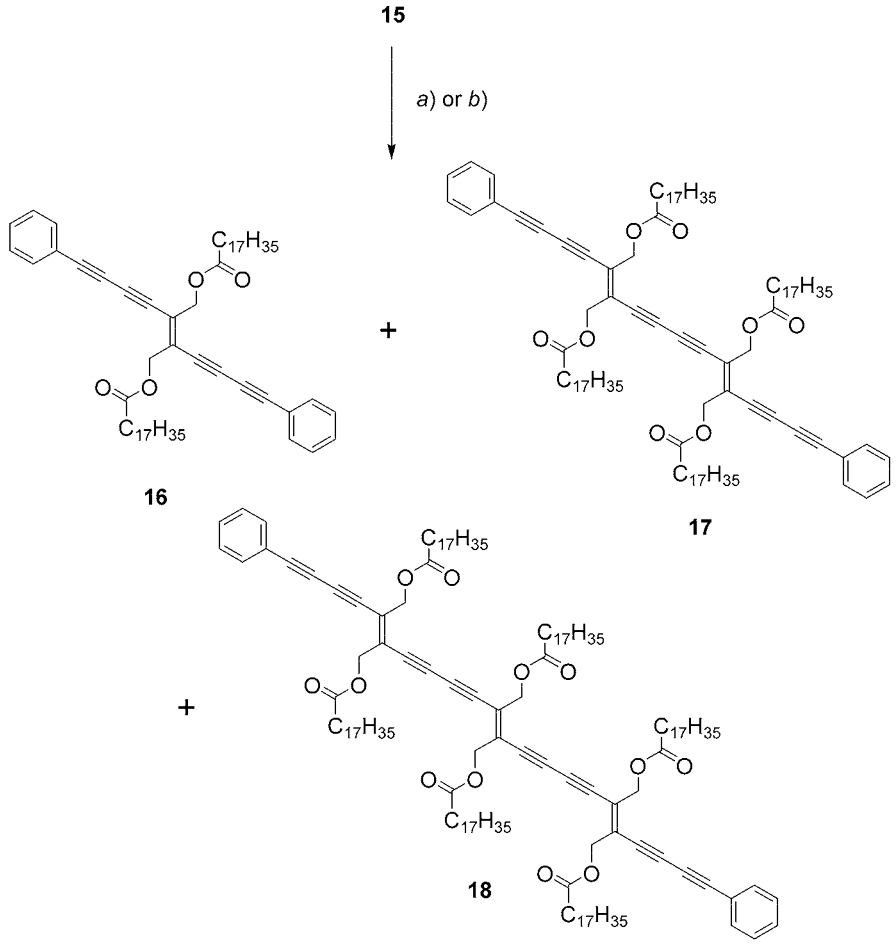
Treatment of **15** with an excess of phenylacetylene (10 equiv.) in CH_2Cl_2 under *Hay* coupling conditions afforded **16** and **17** (25 and 5% yield, resp.). Starting from phenylacetylene and **15** in a 1:1 molar ratio, **16** (9% yield), **17** (5%), and **18** (2%) could

Scheme 4



a) Stearic acid, DCC, DMAP, CH_2Cl_2, 0° to r.t. (84%). *b*) Bu_4NF, THF, $-78°$ to r.t. (61%).

Scheme 5



a) Phenylacetylene (10 equiv.), CuCl, TMEDA, O_2, CH_2Cl_2, r.t. (**16**: 25%; **17**: 5%). *b*) Phenylacetylene (1 equiv.), CuCl, TMEDA, O_2, CH_2Cl_2, r.t. (**16**: 9%; **17**: 5%; **18**: 2%).

be isolated. Whereas the yields for the preparation of **11**–**13** are similar to those reported for related reactions [9], the yields of **16**–**18** are limited by the instability of monomer **15**. In spite of the low solubility of **16**–**18** in common organic solvents, complete spectroscopic characterization could be achieved. The UV/VIS spectra of **16**–**18** are similar of those of the corresponding oligomers **11**–**13** and are in good agreement with an all-*trans* configuration for **16**–**18**.

As observed for the end-capped oligomers **11**–**13** with the 3,4,5-tris(dodecyloxy)phenyl pendant groups, only the trimeric derivative **18** showed liquid-crystalline properties. POM Observation of **18** revealed a fluid birefringent phase between 80 and 115°, but the optical texture observed on cooling the sample from the isotropic phase was noncharacteristic [7].

3. Conclusions. – We established that the end-capping oligomerization of (*E*)-hex-3-ene-1,5-diyne monomers substituted with pendant long alkyl chains is an efficient strategy for the preparation of PTAs when the end-capping reagent is well chosen. Indeed, by using mono-alkyne **6** as the stopper for the oligomerization of monomer **10**, only compound **7**, resulting from the homocoupling of **6**, and polymers of **10** were obtained due to the difference in reactivity of the alkyne groups in **6** and **10**. In contrast, the use of phenylacetylene as the stopper allowed us to prepare the end-capped oligomers **11**–**13** and **16**–**18** from monomers **10** and **15**, respectively. In the design of these derivatives, the pendant long alkyl chains were introduced to determine if the PTA backbone is capable of behaving as a mesogenic unit. Whereas the end-capped mono- and dimers **11**, **12**, **16**, and **17** do not exhibit any liquid-crystalline behavior, the corresponding trimers **13** and **18** show mesomorphic properties, thus revealing that the PTA backbone can effectively act a mesogenic core.

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Experimental Part

General. Reagents and solvents were purchased as reagent grade and used without further purification. Compounds **1** [10], **4** [13] and **8** [16] were prepared according to literature procedures. All reactions were performed in standard glassware under Ar. Evaporation and concentration were done at water-aspirator pressure and drying *in vacuo* at 10^{-2} Torr. Column chromatography (CC): silica gel *60* (230–400 mesh, 0.040–0.063 mm) from *E. Merck*. TLC: glass sheets coated with silica gel *60 F_{254}* from *E. Merck*, visualization by UV light. M.p.s: electrothermal digital melting-point apparatus; uncorrected. UV/VIS Spectra (λ_{max} in nm (ε)): *Hitachi U-3000* spectrophotometer. IR Spectra (cm^{-1}): *ATI-Mattson Genesis FTIR* instrument. NMR Spectra (δ in ppm, *J* in Hz): *Bruker AC-200*; solvent peaks as reference. FAB-MS (*m/z* (% rel. intensity)): *ZA-HF* instrument; 4-nitrobenzyl alcohol as matrix.

*Dimethyl (2*E*)-2-[(Triisopropylsilyl)ethynyl]but-2-enedioate* (**2**). To a degassed soln. of **1** (4.0 g, 17.94 mmol) in Et_3N (100 ml) were added (triisopropylsilyl)acetylene (4.4 ml, 19.73 mmol), $[PdCl_2(PPh_3)_2]$ (379 mg, 0.54 mmol, 3 mol-%), and CuI (171 mg, 0.90 mmol, 5 mol-%). The mixture was stirred at r.t. under positive Ar pressure for 36 h. Evaporation gave a black oil that was diluted with Et_2O (150 ml) and washed with sat. aq. NaCl soln. (2 × 150 ml). The combined aq. phase was extracted with Et_2O and the combined org. phase dried ($MgSO_4$) and evaporated. CC (SiO_2, hexane/CH_2Cl_2 2:1) yielded **2** (4.31 g, 74%). Pale yellow oil. IR (CH_2Cl_2): 2147 ($C\equiv C$), 1730 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.14 (*s*, 21 H); 3.81 (*s*, 3 H); 3.85 (*s*, 3 H); 7.09 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 11.15; 18.41; 51.88; 53.03; 99.25; 107.36; 126.09; 133.72; 163.85; 164.40. Anal. calc. for $C_{17}H_{28}SiO_4$: C 62.93, H 8.70; found: C 62.75, H 8.98.

*(2*E*)-2-[(Triisopropylsilyl)ethynyl]but-2-ene-1,4-diol* (**3**). To a soln. of **2** (3.40 g, 10.48 mmol) in CH_2Cl_2 (200 ml) at 0°, 1.0M DIBAL-H in hexane (53 ml, 53 mmol) was added dropwise over 30 min. The mixture was allowed to warm slowly to 10° (30 min) and was stirred at 10° for 2 h. MeOH was carefully added until no further gas evolution was observed. Then sat. aq. NH_4Cl soln. was added until the mixture became thick and a white solid started to form. Additional CH_2Cl_2 was added, and the resulting mixture was filtered. The solid was washed with CH_2Cl_2, and the combined fractions were dried ($MgSO_4$) and evaporated: **3** (2.66 g, 95%), which was used without further purification. Pale yellow oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.09 (*s*, 21 H); 1.67 (*t*, $J = 6$, 1 H); 1.76 (*t*, $J = 6$, 1 H); 4.16 (*d*, $J = 6$, 2 H); 4.45 (*m*, 2 H); 6.18 (*t*, $J = 6$, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 11.09; 18.54; 60.98; 64.55; 98.19; 101.83; 124.88; 135.17.

*(2*E*)-2-[(Triisopropylsilyl)ethynyl]but-2-ene-1,4-diyl Bis[3,4,5-tris(dodecyloxy)benzoate]* (**5**). DCC (2.80 g, 13.56 mmol) and DMAP (158 mg, 1.29 mmol) were added to a stirred soln. of **4** (8.72 g, 12.92 mmol) and **3** (1.73 g, 6.46 mmol) in CH_2Cl_2 (150 ml) at 0°, and, after warming slowly to r.t. (over 1 h), the mixture was stirred for 72 h, then filtered, and evaporated. CC (SiO_2, hexane/CH_2Cl_2 5:4) yielded **5** (6.11 g, 60%). Colorless crystals. M.p. 26°. IR (CH_2Cl_2): 2146 (C≡C), 1713 (C=O). ^{1}H-NMR (CD_2Cl_2, 200 MHz): 0.87 (*t*, $J = 6$, 18 H); 1.08 (*s*, 21 H); 1.27 (*m*, 108 H); 1.76 (*m*, 12 H); 3.99 (*m*, 12 H); 4.86 (*s*, 2 H); 5.08 (*d*, $J = 6.5$, 2 H); 6.29 (*t*, $J = 6.5$, 1 H); 7.27 (*s*, 2 H); 7.32 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 11.12; 14.09; 18.56; 22.68; 26.09; 29.37; 29.64; 29.69; 31.92; 62.99; 66.03; 69.16 (2 C); 76.46 (2 C); 99.75; 100.92; 108.10; 108.19; 122.71; 124.27; 124.40; 133.88; 142.53; 142.59; 152.81 (2 C); 165.77; 166.14. Anal. calc. for $C_{101}H_{180}SiO_{10}$: C 76.65, H 11.46; found: C 76.68, H 11.53.

*(2*E*)-2-Ethynylbut-2-ene-1,4-diyl Bis[3,4,5-tris(dodecyloxy)benzoate]* (**6**). At −78°, 1M of Bu_4NF in THF (2.6 ml, 2.60 mmol) was added to a stirred soln. of **5** (3.40 g, 2.15 mmol) in wet THF (200 ml). After warming slowly to r.t. (2 h), sat. aq. NH_4Cl soln. (100 ml) was added and the mixture extracted with CH_2Cl_2. The org. layer was washed with H_2O, dried ($MgSO_4$) and evaporated. CC (SiO_2, CH_2Cl_2/hexane 5:4) yielded **6** (2.71 g, 88%). Colorless solid. M.p. 63°. IR ($CHCl_3$): 3304 (≡C−H), 2145 (C≡C), 1714 (C=O). ^{1}H-NMR (CD_2Cl_2, 200 MHz): 0.88 (*m*, 18 H); 1.27 (*m*, 108 H); 1.74 (*m*, 12 H); 3.38 (*s*, 1 H); 4.00 (*m*, 12 H); 4.85 (*s*, 2 H); 5.07 (*d*, $J = 6.5$, 2 H); 6.35 (*t*, $J = 6.5$, 1 H); 7.25 (*s*, 2 H); 7.28 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.08; 22.68; 26.09; 29.36; 29.64; 29.69; 31.91; 62.77; 65.73; 69.18; 73.48; 78.15; 85.01; 108.13; 108.21; 121.43; 124.14; 124.27; 134.95; 142.59; 142.72; 152.84; 165.73; 166.14. Anal. calc. for $C_{92}H_{160}O_{10}$: C 77.48, H 11.31; found: C 77.61, H 11.38.

*(1*E*,7*E*)-Tetrakis{{[3,4,5-tris(dodecyloxy)benzoyl]oxy}methyl}octa-1,7-diene-3,5-diyne* (=*(2*E*,8*E*)-3,8-Bis{{[3,4,5-tris(dodecyloxy)benzoyl]oxy}methyl}deca-2,8-diene-4,6-diyne-1,10-diyl Bis[3,4,5-tris(dodecyloxy)-benzoate]*; **7**). CuCl (50 mg, 0.51 mmol) and TMEDA (0.5 ml, 3.30 mmol) were added to a soln. of **6** (200 mg, 0.14 mmol) in CH_2Cl_2 (70 ml). The mixture was vigorously stirred overnight in the presence of dry air, then filtered over a short plug (SiO_2, CH_2Cl_2), and evaporated. CC (SiO_2, CH_2Cl_2/hexane 3:1) yielded **7** (166 mg, 83%). Colorless crystals. M.p. 55°. IR ($CHCl_3$): 2156 (C≡C), 1714 (C=O). ^{1}H-NMR (CD_2Cl_2, 200 MHz): 0.87 (*m*, 36 H); 1.26 (*m*, 216 H); 1.76 (*m*, 24 H); 3.98 (*m*, 24 H); 4.85 (*s*, 4 H); 5.07 (*d*, $J = 6$, 4 H); 6.45 (*t*, $J = 6$, 2 H); 7.24 (*s*, 4 H); 7.27 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.32; 23.13; 26.52; 26.57; 29.83; 29.88; 30.03; 30.12; 30.17; 30.79; 32.38; 63.20; 65.58; 69.58; 73.84; 78.34; 80.42; 108.26; 108.30; 121.24; 124.53; 124.69; 138.08; 142.91; 143.06; 153.35; 165.83; 166.24. Anal. calc. for $C_{184}H_{318}O_{20}$: C 77.53, H 11.24; found: C 77.65, H 11.26.

*(2*E*)-2,3-Bis[(trimethylsilyl)ethynyl]but-2-ene-1,4-diyl Bis[3,4,5-tris(dodecyloxy)benzoate]* (**9**). As described for **5**, with DCC (2.993 g, 14.51 mmol), DMAP (161 mg, 1.32 mmol), **4** (9.79 g, 14.51 mmol), **8** (1.85 g, 6.59 mmol), and CH_2Cl_2 (150 ml) (stirring for 41 h). CC (SiO_2, hexane/CH_2Cl_2 5:2) yielded **9** (6.41 g, 61%). Colorless crystals. M.p. 50°. IR (CH_2Cl_2): 2149 (C≡C), 1714 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.08 (*s*, 18 H); 0.89 (*m*, 18 H); 1.27 (*m*, 108 H); 1.78 (*m*, 12 H); 4.02 (*m*, 12 H); 5.14 (*s*, 4 H); 7.32 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): −0.43; 14.09; 22.68; 26.08; 29.37; 29.64; 29.70; 30.31; 31.93; 64.03; 69.18; 73.46; 99.35; 108.28; 109.68; 124.49; 127.56; 142.55; 152.80; 165.92. Anal. calc. for $C_{100}H_{176}Si_2O_{10}$: C 75.32, H 11.12; found: C 75.17, H 11.19.

*(2*E*)-2,3-Diethynylbut-2-ene-1,4-diyl Bis[3,4,5-tris(dodecyloxy)benzoate]* (**10**). As described for **6**, with 1M Bu_4NF in THF (7.1 ml, 7.10 mmol), **9** (5.41 g, 3.39 mmol), wet THF (200 ml), and sat. aq. NH_4Cl soln. (100 ml). Extraction with hexane and CC (SiO_2, hexane/CH_2Cl_2 1:1) yielded **10** (4.42 g, 90%). Colorless solid. M.p. 61°. IR ($CHCl_3$): 3301 (≡C−H), 2116 (C≡C), 1713 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*m*, 18 H); 1.27 (*m*, 108 H); 1.78 (*m*, 12 H); 3.64 (*s*, 2 H); 4.02 (*t*, $J = 6.5$, 8 H); 4.03 (*t*, $J = 6.5$, 4 H); 5.17 (*s*, 4 H); 7.31 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.09; 22.68; 28.09; 29.29; 29.38; 29.64; 29.70; 30.32; 31.92; 64.01; 69.15; 73.49; 78.47; 108.21; 124.14; 128.07; 142.63; 152.81; 165.92. FAB-MS: 1449 (5, M^+), 1281 (1, $[M - C_{12}H_{25}]^+$), 775 (25,

$[M-(C_{12}H_{25}O)_3C_6H_2CO_2]^+$), 674 (8, $[(C_{12}H_{25}O)_3C_6H_2CO_2]^+$), 657.5 (100, $[(C_{12}H_{25}O)_3C_6H_2CO]^+$). Anal. calc. for $C_{94}H_{160}O_{10}$: C 77.85, H 11.12; found: C 78.01, H 11.27.

*(5*E*)-1,10-Diphenyl-5,6-bis{{[3,4,5-tris(dodecyloxy)benzoyl]oxy}methyl}dec-5-ene-1,3,7,9-tetrayne (=(2*E*)-2,3-Bis(4-phenylbut-1,3-diynyl)but-2-ene-1,4-diyl Bis[3,4,5-tris(dodecyloxy)benzoate];* **11**) and *(5*E*,11*E*)-1,16-Diphenyl-5,6,11,12-tetrakis{{[3,4,5-tris(dodecyloxy)benzoyl]oxy}methyl}hexadeca-5,11-diene-1,3,7,9,13,15-hexayne (=(2*E*,8*E*)-2,9-Bis(4-phenylbut-1,3-diynyl)-3,8-bis{{[3,4,5-tris(dodecyloxy)benzoyl]oxy}methyl}deca-2,8-diene-4,6-diyne-1,10-diyl Bis[3,4,5-tris(dodecyloxy)benzoate];* **12**). CuCl (100 mg, 1.01 mmol) and TMEDA (1 ml, 6.60 mmol) were added to phenylacetylene (176 mg, 1.72 mmol) and **10** (250 mg, 0.172 mmol) in CH_2Cl_2 (70 ml). The mixture was vigorously stirred for 10 h in the presence of dry air, then filtered over a short plug (SiO_2, CH_2Cl_2), and evaporated. CC (SiO_2) eluting with hexane/CH_2Cl_2 4:1 gave 1,4-diphenylbuta-1,3-diyne, with hexane/CH_2Cl_2 2:1 **11** (183 mg, 64%), and with hexane/CH_2Cl_2 4:3 **12** (19 mg, 7%).

Data of **11**: Pale yellow crystals. M.p. 69–70°. UV/VIS (CH_2Cl_2): 243 (sh, 34140), 259 (49450), 360 (44560), 387 (sh, 35080). IR (CH_2Cl_2): 2211 (C≡C), 1718 (C=O). ^1H-NMR ($CDCl_3$, 200 MHz): 0.89 (*m*, 18 H); 1.26 (*m*, 108 H); 1.76 (*m*, 12 H); 4.02 (*t*, $J=6.5$, 4 H); 4.04 (*t*, $J=6.5$, 8 H); 5.21 (*s*, 4 H); 7.35 (*s*, 4 H); 7.37 (*m*, 6 H); 7.48 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.09; 22.68; 26.11; 29.20; 29.38; 29.64; 30.34; 31.93; 64.16; 69.11; 73.44; 76.55; 87.47; 88.68; 108.11; 121.11; 124.14; 128.48; 129.16; 129.76; 132.48; 142.55; 152.84; 165.89. FAB-MS: 1650 (7, $[M+H]^+$), 976 (24, $[M-(C_{12}H_{25}O)_3C_6H_2CO_2]^+$), 657.5 (100, $[(C_{12}H_{25}O)_3C_6H_2CO]^+$). Anal. calc. for $C_{110}H_{168}O_{10}$: C 80.05, H 10.26; found: C 80.01, H 10.39.

Data of **12**: Yellow-orange glassy product. UV/VIS (CH_2Cl_2): 271 (90210), 359 (sh, 52210), 388 (67090), 419 (sh, 50270). IR (CH_2Cl_2): 2202 (C≡C), 1718 (C=O). ^1H-NMR ($CDCl_3$, 200 MHz): 0.89 (*m*, 36 H); 1.26 (*m*, 216 H); 1.77 (*m*, 24 H); 4.02 (*m*, 24 H); 5.15 (*s*, 8 H); 7.31 (*s*, 4 H); 7.33 (*s*, 4 H); 7.36 (*m*, 6 H); 7.47 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.09; 22.68; 26.09; 26.16; 29.38; 29.70; 30.37; 31.93; 63.95; 64.11; 69.12; 73.36; 73.47; 82.55; 87.34; 87.92; 89.54; 108.09; 108.18; 121.01; 123.95; 124.05; 127.68; 128.48; 129.83; 131.48; 132.50; 142.56; 142.68; 152.84; 165.73; 165.82. FAB-MS: 3098.5 (21, M^+), 2424 (41, $[M-(C_{12}H_{25}O)_3C_6H_2CO_2]^+$), 1749 (100, $[M-2(C_{12}H_{25}O)_3C_6H_2CO_2]^+$). Anal. calc. for $C_{204}H_{326}O_{20}$: C 79.07, H 10.60; found: C 79.01, H 10.40.

Monomer **11**, *Dimer* **12**, *and (5*E*,11*E*,17*E*)-1,22-Diphenyl-5,6,11,12,17,18-hexakis{{[3,4,5-tris(dodecyloxy)benzoyl]oxy}methyl}docosa-5,11,17-triene-1,3,7,9,13,15,19,21-octayne (=(2*E*,8*E*,14*E*)-2,15-Bis(4-phenylbut-1,3-diynyl)-3,8,9,14-tetrakis{{[3,4,5-tris(dodecyloxy)benzoyl]oxy}methyl}hexadeca-2,8,14-triene-4,6,10,12-tetrayne-1,16-diyl Bis[3,4,5-tris(dodecyloxy)benzoate];* **13**). As described above, with CuCl (200 mg, 2.02 mmol), TMEDA (2 ml, 13.20 mmol), phenylacetylene (70 mg, 0.69 mmol), **10** (1.00 g, 0.69 mmol), and CH_2Cl_2 (150 ml) for 18 h. CC (SiO_2) eluting with hexane/CH_2Cl_2 4:1 gave 1,4-diphenylbuta-1,3-diyne, with hexane/CH_2Cl_2 2:1 **11** (173 mg, 15%), with hexane/CH_2Cl_2 4:3 → 1:1 **12** (203 mg, 19%), and with hexane/CH_2Cl_2 1:1 → 1:2 **13** (130 mg, 12%).

Data of **13**: Brown-orange liquid crystal (clearing temp. 40°). UV/VIS (CH_2Cl_2): 273 (117850), 396 (sh, 69310), 413 (71310). IR ($CHCl_3$): 2205 (C≡C), 1715 (C=O). ^1H-NMR ($CDCl_3$, 200 MHz): 0.88 (*m*, 54 H); 1.25 (*m*, 324 H); 1.74 (*m*, 36 H); 3.98 (*m*, 36 H); 5.12 (*s*, 8 H); 5.16 (*s*, 4 H); 7.28 (*s*, 8 H); 7.32 (*s*, 4 H); 7.35 (*m*, 6 H); 7.42 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.09; 22.88; 26.15; 26.22; 29.38; 29.55; 29.70; 30.37; 31.93; 63.85; 63.95; 64.10; 69.12; 73.35; 73.45; 77.19; 82.27; 82.97; 87.15; 87.99 (2 C); 89.67; 108.07; 108.18; 123.88; 124.04; 127.01; 127.17; 128.39; 128.48; 129.34; 129.88; 132.22; 132.49; 142.56; 142.71; 152.83; 165.66 (2 C); 165.79. FAB-MS: 4547 (6, M^+), 3872 (10, $[M-(C_{12}H_{25}O)_3C_6H_2CO_2]^+$), 3197 (40, $[M-2(C_{12}H_{25}O)_3C_6H_2CO_2]^+$), 2522 (100, $[M-3(C_{12}H_{25}O)_3C_6H_2CO_2]^+$). Anal. calc. for $C_{298}H_{484}O_{30}$: C 78.72, H 10.73; found: C 78.86, H 10.65.

*(2*E*)-2,3-Bis[(trimethylsilyl)ethynyl]but-2-ene-1,4-diyl Dioctadecanoate* (**14**). As described for **5**, with DCC (2.99 g, 14.51 mmol), DMAP (161 mg, 1.32 mmol), stearic acid (4.13 g, 14.16 mmol), **8** (1.85 g, 6.59 mmol), and CH_2Cl_2 (150 ml) for 12 h. CC (SiO_2, hexane/CH_2Cl_2 2:1) yielded **14** (4.51 g, 84%). Colorless crystals. M.p. 50°. IR (CH_2Cl_2): 2149 (C≡C), 1737 (C=O). ^1H-NMR ($CDCl_3$, 200 MHz): 0.20 (*s*, 18 H); 0.89 (*t*, $J=6.5$, 6 H); 1.26 (*m*, 56 H); 1.62 (*m*, 4 H); 2.36 (*t*, $J=7.5$, 4 H); 4.87 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): −0.30; 14.09; 22.68; 24.91; 29.19; 29.29; 29.35; 29.44; 29.66; 31.90; 34.19; 64.49; 99.57; 108.95; 127.91; 173.19. Anal. calc. for $C_{50}H_{92}Si_2O_4$: C 73.83, H 11.40; found: C 73.73, H 11.49.

*(2*E*)-2,3-Diethynylbut-2-ene-1,4-diyl Dioctadecanoate* (**15**). At 0°, 1M Bu_4NF in THF (11.4 ml, 11.40 mmol) was added to a stirred soln. of **14** (4.40 g, 5.41 mmol) in wet THF (100 ml). After 3 h, sat. aq. NH_4Cl soln. (100 ml) was added and the THF evaporated. The resulting aq. layer was extracted twice with CH_2Cl_2 and the combined org. phase washed with H_2O, dried ($MgSO_4$), and evaporated. CC (SiO_2, hexane/CH_2Cl_2 2:1) yielded **15** (2.21 g, 61%). Colorless solid that turned slowly black in the neat state. M.p. 64°. IR ($CHCl_3$): 3301 (≡C−H), 2105 (C≡C), 1737 (C=O). ^1H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, $J=7$, 6 H); 1.26 (*m*, 56 H); 1.65 (*m*, 4 H); 2.37 (*t*, $J=7.5$, 4 H); 3.60 (*s*, 2 H); 4.92 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.09; 22.68; 24.88; 29.09; 29.25; 29.35; 29.44; 29.66; 31.91; 34.07; 63.44; 78.49; 90.12; 128.19; 173.29.

*(5*E*)-1,10-Diphenyl-5,6-bis{[(1-oxooctadecyl)oxy]methyl}dec-5-ene-1,3,7,9-tetrayne* (*(2*E*)-2,3-Bis(4-phenylbut-1,3-diynyl)but-2-ene-1,4-diyl Dioctadecanoate*; **16**) *and* *(5*E*,11*E*)-1,16-Diphenyl-5,6,11,12-tetrakis{[(1-oxooctadecyl)oxy]methyl}hexadeca-5,11-diene-1,3,7,9,13,15-hexayne* (**17**). As described for **11**/**12**, with CuCl (100 mg, 1.01 mmol), TMEDA (1 ml, 6.60 mmol), phenylacetylene (305 mg, 2.99 mmol), **15** (200 mg, 0.299 mmol), and CH_2Cl_2 (70 ml) for 2 h. CC (SiO_2) eluting with hexane/CH_2Cl_2 4 : 1 gave 1,4-diphenylbuta-1,3-diyne, with hexane/CH_2Cl_2 3 : 2 **16** (66 mg, 25%), and with hexane/CH_2Cl_2 1 : 1 **17** (11 mg, 5%).

Data of **16**: Pale yellow crystals. M.p. 92°. UV/VIS (CH_2Cl_2): 242 (33290), 258 (36550), 360 (44480), 384 (sh, 34690). IR (CH_2Cl_2): 2221 ($C\equiv C$), 1737 ($C=O$). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 6.5, 6 H); 1.26 (*m*, 56 H); 1.70 (*m*, 4 H); 2.42 (*t*, *J* = 7.5, 4 H); 4.96 (*s*, 4 H); 7.38 (*m*, 6 H); 7.54 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.09; 22.68; 24.98; 29.19; 29.35; 29.47; 29.66; 31.90; 34.17; 63.56; 73.36; 76.45; 87.34; 88.24; 121.21; 128.48; 129.38; 129.69; 132.50; 173.32. Anal. calc. for $C_{60}H_{84}O_4$: C 82.90, H 9.74; found: C 83.00, H 9.82.

Data of **17**: Yellow crystals. M.p. 111 – 113°. UV/VIS (CH_2Cl_2): 261 (32640), 385 (49370), 415 (sh, 38650). IR (CH_2Cl_2): 2203 ($C\equiv C$), 1740 ($C=O$). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*m*, 12 H); 1.26 (*m*, 112 H); 1.67 (*m*, 8 H); 2.40 (*t*, *J* = 7.5, 4 H); 2.41 (*t*, *J* = 7.5, 4 H); 4.92 (*s*, 8 H); 7.38 (*m*, 6 H); 7.54 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.09; 22.68; 24.91; 24.97; 29.17; 29.34; 29.51; 29.69; 31.90; 34.09; 34.13; 63.40; 63.47; 73.30; 76.23; 82.14; 86.96; 87.82; 89.03; 121.11; 128.36; 128.48; 129.79; 130.87; 132.53; 173.17; 173.23. Anal. calc. for $C_{104}H_{158}O_8$: C 81.30, H 10.37; found: C 81.29, H 10.51.

Monomer **16**, *Dimer* **17**, *and (5*E*,11*E*,17*E*)-1,22-Diphenyl-5,6,11,12,17,18-hexakis{[(1-oxooctadecyl)oxy]methyl}docosa-5,11,17-triene-1,3,7,9,13,15,19,21-octayne* (= *(2*E*,8*E*,11*E*)-3,8,9,14-Tetrakis{[(1-oxooctadecyl)oxy]methyl}-2,15-bis(4-phenylbut-1,3-diynyl)hexadeca-2,8,11-triene-4,6,10,12-tetrayne-1,6-diyl Dioctadecanoate*; **18**). As described for **11**/**12**, with CuCl (200 mg, 2.02 mmol), TMEDA (2 ml, 13.20 mmol), phenylacetylene (152 mg, 1.494 mmol), **15** (1.00 g, 1.494 mmol), and CH_2Cl_2 (150 ml) for 18 h. CC (SiO_2) eluting with hexane/CH_2Cl_2 4 : 1 gave 1,4-diphenylbuta-1,3-diyne, with hexane/CH_2Cl_2 3 : 2 **16** (112 mg, 9%), with hexane/CH_2Cl_2 1 : 1 **17** (58 mg, 5%), and with hexane/CH_2Cl_2 1 : 2 **18** (23 mg, 2%).

Data of **18**: Yellow-orange crystals (m.p. 80° – liquid-crystalline phase – clearing temp. 120°). UV/VIS (CH_2Cl_2): 261 (31980), 395 (49240), 411 (sh, 50440). IR (CH_2Cl_2): 2203 ($C\equiv C$), 1741 ($C=O$). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.88 (*m*, 18 H); 1.26 (*m*, 168 H); 1.64 (*m*, 12 H); 2.39 (*m*, 12 H); 4.89 (*s*, 4 H); 4.92 (*s*, 8 H); 7.38 (*m*, 6 H); 7.53 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.05; 14.10; 22.68; 22.97; 23.73; 24.89; 24.97; 28.90; 29.18; 29.35; 29.51; 29.70; 30.34; 31.91; 34.03; 34.13; 63.36; 63.47; 68.13; 73.30; 76.20; 81.85; 82.59; 86.83; 87.66; 87.92; 89.19; 121.11; 128.16; 128.50; 128.77; 129.82; 130.85; 132.54; 173.08; 173.14; 173.23. Anal. calc. for $C_{148}H_{232}O_{12}$: C 80.67, H 10.61; found: C 80.41, H 10.39.

REFERENCES

[1] K. Müllen, G. Wegner, 'Electronic Materials: The Oligomer Approach', Wiley-VCH, Weinheim, 1998; F. Diederich, Y. Rubin, *Angew. Chem., Int. Ed.* **1992**, *31*, 1101; F. Diederich, *Nature (London)* **1994**, *369*, 199; J. M. Tour, *Chem. Rev.* **1996**, *96*, 537; R. E. Martin, F. Diederich, *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1350; P. F. Van Hutten, V. V. Krasnikov, G. Hadziioannou, *Acc. Chem. Res.* **1999**, *32*, 257; F. Garnier, *Acc. Chem. Res.* **1999**, *32*, 209; J.-L. Brédas, J. Cornil, D. Beljonne, D. A. Dos Santos, Z. Shuai, *Acc. Chem. Res.* **1999**, *32*, 267; J. L. Segura, N. Martin, *J. Mater. Chem.* **2000**, *10*, 2403; U. H. F. Bunz, *Chem. Rev.* **2000**, *100*, 1605; J. Roncali, *Acc. Chem. Res.* **2000**, *33*, 147; J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791.

[2] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem., Int. Ed.* **1998**, *37*, 402 and ref. cit. therein; Y. Shirota, *J. Mater. Chem.* **2000**, *10*, 1; U. Mitschke, P. Bäuerle, *J. Mater. Chem.* **2000**, *10*, 1471; M. T. Bernius, M. Insbasekaran, J. O'Brien, W. Wu, *Adv. Mater.* **2000**, *12*, 1737.

[3] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science (Washington, D.C.)* **1995**, *270*, 1789; M. Granström, K. Petrisch, A. C. Arias, A. Lux, M. R. Anderson, R. H. Friend, *Nature (London)* **1998**, *395*, 257.

[4] J.-F. Nierengarten, J.-F. Eckert, J.-F. Nicoud, L. Ouali, V. Krasnokov, G. Hadziioannou, *Chem. Commun.* **1999**, 617; J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, S.-G. Liu, L. Echegoyen, F. Barigelletti, N. Armaroli, V. Krasnikov, G. Hadziioannou, *J. Am. Chem. Soc.* **2000**, *122*, 7467.

[5] L. Ouali, V. Krasnikov, U. Stalmach, G. Hadziioannou, *Adv. Mater.* **1999**, *11*, 1515; L. S. Roman, M. R. Andersson, T. Yohannes, O. Inganäs, *Adv. Mater.* **1997**, *9*, 1164; A. Sakamoto, O. Nakamura, G. Yoshimoto, M. Tasumi, *J. Phys. Chem. A* **2000**, *104*, 4198; G. Padmanaban, S. Ramakrishnan, *J. Am. Chem. Soc.* **2000**, *122*, 2244; T.-Q. Nguyen, I. B. Martini, J. Liu, B. J. Schwartz, *J. Phys. Chem. B* **2000**, *104*, 237 and ref. cit. therein.

[6] L. Yu, Z. Bao, *Adv. Mater.* **1994**, *6*, 156 and ref. cit. therein; M. Altmann, V. Enkelmann, G. Lieser, U. H. F. Bunz, *Adv. Mater.* **1995**, *7*, 726; T. Maddux, W. Li, L. Yu, *J. Am. Chem. Soc.* **1997**, *119*, 844; B. P. Hoag, D. L. Gin, *Adv. Mater.* **1998**, *10*, 1546; A. Bacher, P. G. Benthley, D. D. C. Bradley, L. K. Douglas, P. A. Glarvey, M. Grell, K. S. Whitehead, M. L. Turner, *J. Mater. Chem.* **1999**, *9*, 2985; J.-F. Eckert, J.-F. Nicoud, D. Guillon, J.-F. Nierengarten, *Tetrahedron Lett.* **2000**, *41*, 6411.

[7] J.-F. Nierengarten, D. Guillon, B. Heinrich, J.-F. Nicoud, *Chem. Commun.* **1997**, 1233.

[8] F. Diederich, *Chem. Commun.* **2001**, 219.

[9] J. Anthony, C. Boudon, F. Diederich, J.-P. Gisselbrecht, V. Gramlich, M. Gross, M. Hobi, P. Seiler, *Angew. Chem., Int. Ed.* **1994**, *33*, 763; M. Schreiber, J. Anthony, F. Diederich, M. E. Spahr, R. Nesper, M. Hubrich, F. Bommeli, L. Degiorgi, P. Wachter, P. Kaatz, C. Bosshard, P. Günter, M. Colussi, U. W. Suter, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Adv. Mater.* **1994**, *6*, 786; A. M. Boldi, J. Anthony, V. Gramlich, C. B. Knobler, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 779; R. E. Martin, U. Gubler, V. Gramlich, C. Bosshard, J.-P. Gisselbrecht, P. Günter, M. Gross, F. Diederich, *Chem.–Eur. J.* **1997**, *3*, 1505; R. E. Martin, T. Mäder, F. Diederich, *Angew. Chem., Int. Ed.* **1999**, *38*, 817; R. E. Martin, U. Gubler, J. Cornil, M. Balakina, C. Boudon, C. Bosshard, J.-P. Gisselbrecht, F. Diederich, P. Günter, M. Gross, J.-L. Brédas, *Chem.–Eur. J.* **2000**, *6*, 3622; R. E. Martin, U. Gubler, C. Boudon, C. Bosshard, J.-P. Gisselbrecht, P. Günter, M. Gross, F. Diederich, *Chem.–Eur. J.* **2000**, *6*, 4400; M. J. Edelmann, M. A. Estermann, V. Gramlich, F. Diederich, *Helv. Chim. Acta* **2001**, *84*, 473; A. P. H. J. Schenning, J.-D. Arndt, M. Ito, A. Stoddart, M. Schreiber, P. Siemsen, R. E. Martin, C. Boudon, J.-P. Gisselbrecht, M. Gross, V. Gramlich, F. Diederich, *Helv. Chim. Acta* **2001**, *84*, 296.

[10] E. A. Shilov, I. V. Smirnov-Zamkov, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1951**, 32.

[11] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Nagihara, *Synthesis* **1980**, 627; 'Metal-Catalyzed Cross-Coupling Reactions', Eds. F. Diederich and P. J. Stang, Wiley-VCH, Weinheim, 1998.

[12] L. J. Matthias, *Synthesis* **1979**, 561.

[13] V. Percec, M. Lee, J. Heck, H. E. Blackwell, G. Ungar, A. Alvarez-Castillo, *J. Mater. Chem.* **1992**, *2*, 931.

[14] A. S. Hay, *J. Org. Chem.* **1962**, *27*, 3320; P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem., Int. Ed.* **2000**, *39*, 2632.

[15] J. Anthony, A. M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C. B. Knobler, P. Seiler, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 13.

[16] T. X. Neenan, M. R. Callstrom, L. M. Scarmoutzos, K. R. Stewart, G. M. Whitesides, V. R. Hoves, *Macromolecules* **1998**, *21*, 3525.

[17] J.-F. Nierengarten, M. Schreiber, F. Diederich, V. Gramlich, *New J. Chem.* **1996**, *20*, 1273.

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