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# Synthesis of Alkylene-Bridged Diphenyl-Oligoynes

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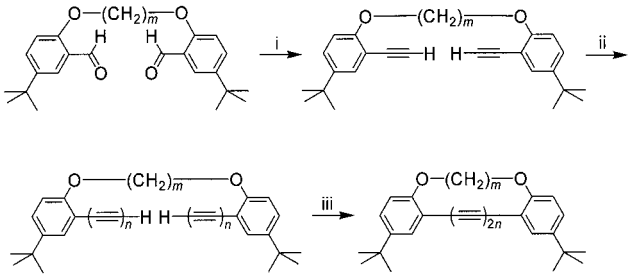
**Keywords:** Alkynes / Macrocycles / Oligoynes

A general synthesis route for the preparation of oligoynes stabilized by alkylene bridges is reported. The corresponding macrocycles contain oligoynes with up to eight conjugated triple bonds. The stabilization of the conjugated sp-oligoyne rods was achieved by bulky terminal phenylic endcaps spanning the alkylene chain to isolate the individual acetylenic rods and to avoid polymerization. Alkylene chains with up to 40 methylene groups were employed. The two terminal acetylene functions were introduced prior to the oligoyne elongation by twofold introduction of additional $C_2$-acetylene or $C_4$-butadiyne building blocks. The final step was the intramolecular acetylene coupling upon which very large macrocycles with up to 62 ring members containing segregated sp-, $sp^2$- and $sp^3$-segments were formed.


## Introduction

The investigation of very long oligoynes[1–5] has recently received increasing attention.[6–12] Conjugated oligoynes represent unique building blocks for the design and construction of new molecular architectures such as molecular wires.[8,11] Furthermore, oligoynes have been investigated as model systems for the hypothetical polymeric sp carbon allotrope "carbyne" $–(C{\equiv}C)_x–$.[7,8,13,14] The synthesis of carbyne remains a great challenge. This is due to the fact that the stability of oligoynes decreases considerably with increasing sp-carbon-chain length. A major pathway for the decomposition of long oligoynes is intermolecular crosslinking and polymerization. The smaller the intermolecular distance between the oligoynes is, the easier is the polymerization.[15] As a consequence, strategies for the stabilization of oligoynes have been developed by introducing building blocks at the termini in order to prevent a close approach of the individual alkyne chains. Examples are the use of bulky end-groups, such as dendrimers,[7] as well as the wrapping of the sp-chains by alkylene bridges spanning the organometallic termini.[8,11] For example, the synthesis of polyynes containing up to ten triple bonds, which span two redox-active rhenium fragments as protective units, was described by Gladysz and co-workers[16] by applying classical hetero- and homocoupling techniques. The same group also reported the first structurally characterized hexayne connecting two platinum metal complex fragments.[8,11,14] We recently developed 3,5-dihydroxyphenyl endcaps as protecting groups in the synthesis of α,ω-diphenylpolyynes with up to ten conjugated triple bonds.[7] The phenolic groups represented anchor groups for sterically demanding Frechét-type dendrimers and bulky silyl moieties. Diplatinum-endcap-protected oligoynes from tetrayne to hexayne rod lengths were recently prepared,[8,11] and the opposite terminal transition-metal endcaps additionally bridged with two long and flexible alkane (polymethylene) chains. Depending on the bridge's length, the flexible chains twisted around the central carbon rod and could adopt double-stranded helical conformations.[8,11]

We report here on the first approach of stabilizing purely organic endcapped oligoynes by long alkylene brigdes consisting of up to 40 methylene groups linking the corresponding phenyl termini. The basic idea for this synthesis was the initial preparation of the two alkyne termini connected by the alkylene linker followed by the subsequent construction of the oligoyne chains starting from both termini by formation of the first two acetylene functions. After the successive elongation of the oligoyne chains using various acetylene coupling methods the synthesis of the stabilized oligoynes is completed by an intramolecular alkyne homocoupling reaction (Scheme 1).




Scheme 1. Schematic representation of the preparation of oligoyne macrocycles starting with the protecting diphenyl termini. i) Formation of the acetylenic termini, ii) alkyne elongation and iii) macrocyclization.

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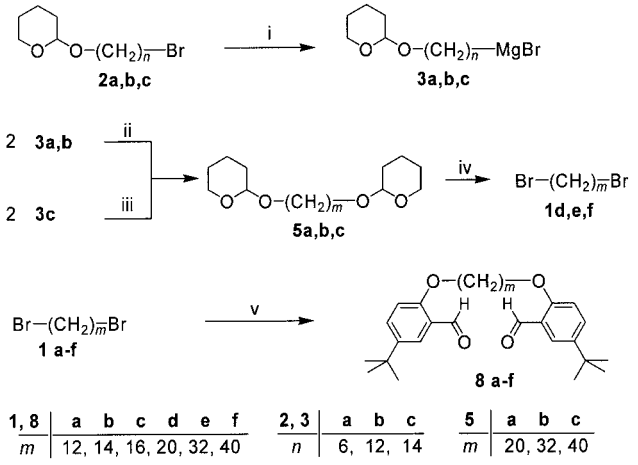
## Results and Discussion

### The Synthesis of the Protecting Units

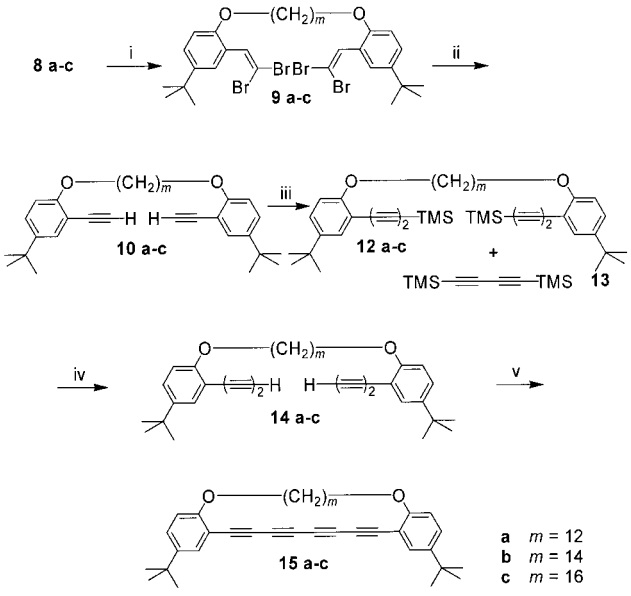
For the protection of 1,3,5,7-tetrayne rods, oligomethylene bridges with 12, 14 and 16 methylene groups were selected for the synthesis of the corresponding macrocycles. Longer alkylene bridges with 20, 32 and 40 carbon atoms were used for the protection of the long 1,3,5,7,9,11-hexayne carbon rods in the hexayne macrocycles. The starting compounds 1,12-dibromododecane (**1a**), 1,14-dibromotetradecane (**1b**) and 1,16-dibromohexadecane (**1c**) (**1a**–**c**, $m$ = 12, 14, 16) were obtained by conventional reduction of the corresponding dicarboxylic acids and subsequent bromination with HBr. The required α,ω-dibromoalkanes **1d**–**f** with chain lengths of $C_{20}$, $C_{32}$ and $C_{40}$ were prepared according to a method of Gladysz et al.:[9] ω-Tetrahydropyranyloxyalkyl bromides **2a**–**c** were transformed into the corresponding Grignard reagents **3a**–**c** ($n$ = 6, 12, 14). Two molecules each of the organomagnesium compound **3a**,**b** and **3c** were linked with 1,8-diiodooctane (**4**) and 1,12-dibromododecane (**1a**) under $Li_2CuCl_4$ catalysis, respectively, and the bis-THP ethers **5a**–**c** ($m$ = 20, 32, 40) were obtained (Scheme 2). Subsequent bromination with 2,4,4,6-tetrabromocyclohexadienone (**6**) according to the method of Tanaka and Oritani[17] led to the corresponding α,ω-dibromoalkanes **1d**–**f** ($m$ = 20, 32, 40). To assemble the stabilizing bis(benzaldehyde) units **8a**–**f** ($m$ = 12, 14, 16, 20, 32, 40), two molecules of 5-*tert*-butyl-2-hydroxybenzaldehyde (**7**)[18] were bridged with the α,ω-dibromoalkanes **1a**–**f** in DMF/$K_2CO_3$ and isolated by precipitation at –30 °C (Scheme 2).




Scheme 2. Synthesis of the protecting oligomethylene-bridged diphenyl termini **8a**–**f**. i) Mg, THF, heat; ii) I–$(CH_2)_8$–I (**4**), $Li_2CuCl_4$, THF, –20 °C; iii) Br–$(CH_2)_{12}$–Br (**1a**), $Li_2CuCl_4$, THF, –20 °C; iv) 2,4,4,6-tetrabromocyclohexa-2,5-dienone (**6**), $PPh_3$, $CH_2Cl_2$; v) 5-*tert*-butyl-2-hydroxybenzaldehyde (**7**), $K_2CO_3$, DMF, 80 °C.

### Synthesis of Dioxacycloalkatetrayne Macrocycles 15a–c

The carbonyl olefination of the bis(aldehydes) **8a**–**c** according to Corey and Fuchs[19] yields the bis-1,1-dibromo-2-phenylethenes **9a**–**c**, which upon elimination with LDA gave the bis-terminal diynes α,ω-bis(4-*tert*-butyl-2-ethynylphenyloxy)alkanes **10a**–**c** ($m$ = 12, 14, 16) in 95–85% yield (Scheme 3). The yields decreased with increasing chain length. Elongation of the two terminal alkyne functions of **10a**–**c** by cross-coupling with an excess of TMS–acetylene (**11**) under Hay[20] homocoupling conditions led to the formation of the TMS-protected terminal bis(diynes) **12a**–**c**. The excess of **11** prevented intramolecular self-coupling of the starting materials **10**; however, a large amount of the dimer coupling product 1,4-bis(trimethylsilyl)-1,3-butadiyne (**13**) was formed, which had to be separated by column chromatography. From the subsequent deprotection of **12** with $K_2CO_3$ in wet THF/$CH_3OH$ the bis(diynes) α,ω-bis(2-butadiynyl-4-*tert*-butylphenyloxy)alkanes **14a**–**c** were obtained. As **14a**–**c** decomposed rapidly during isolation, characterization was abandoned, and after a short aqueous workup and drying, the compounds were immediately employed for macrocylization by homocoupling according to Hay.[20] The coupling reaction was performed in high dilution in order to suppress dimerization and polymerization. With yields of < 10%, relative to the TMS derivatives **12a**–**c**, the dibenzocycloalkanetetrayne macrocycles **15a**–**c** were obtained (Scheme 3). The tetraynes **15a**–**c** appeared to be stable and had been dried and kept in high vacuum for hours without decomposition; in solution they remained stable for several months.




Scheme 3. Synthesis of the macrocyclic α,ω-diphenyltetraynes **15a**–**c**. i) $PPh_3$, $CBr_4$, $CH_2Cl_2$; ii) LDA, –80 °C; iii) excess of H–C≡C–TMS (**11**), TMEDA, CuCl, $O_2$, acetone; iv) $K_2CO_3$, MeOH, THF; v) TMEDA, CuCl, $O_2$, acetone, high dilution. Yields: **15a** (7%), **15b** (8%) and **15c** (1.3%).

All compounds as well as the intermediates of the synthesis were fully characterized by $^1$H- and $^{13}$C NMR spectroscopy, IR and UV/Vis spectroscopy, mass spectrometry and elemental analysis. The NMR spectra of the target tetrayne macrocycles **15** revealed the expected $C_{2v}$ symmetry. The NMR spectra of the $C_{14}$-bridged derivative **15b** are

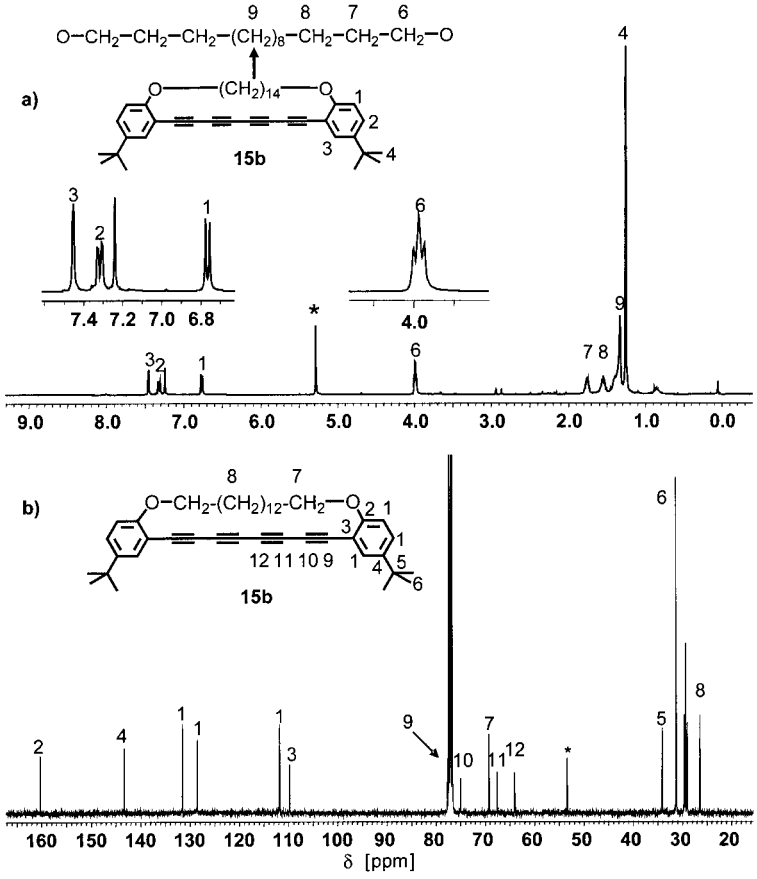



Figure 1. a) $^{1}H$ NMR spectrum (400 MHz, $CDCl_3$, 25 °C) and b) $^{13}C$ NMR spectrum (100.5 MHz, $CDCl_3$, 25 °C) of the 28-membered tetrayne macrocycle **15b** (* = solvent).

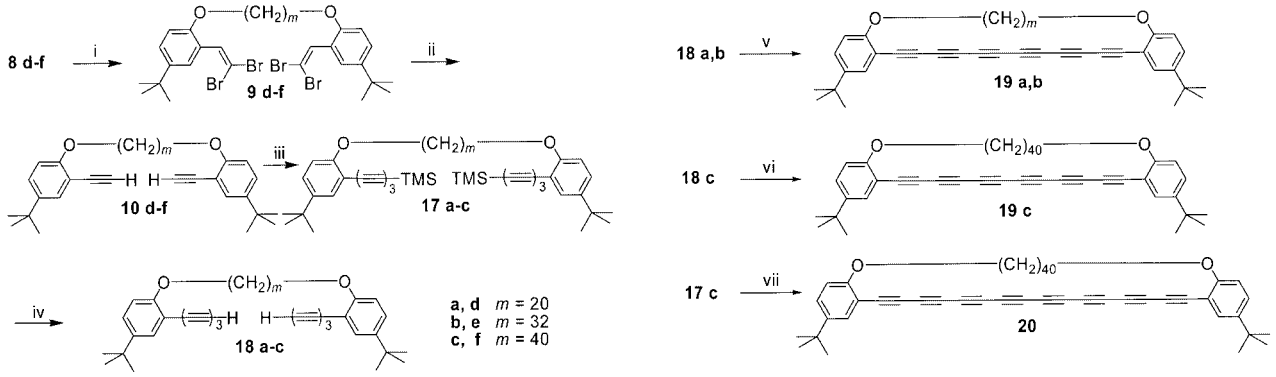
shown as representative examples in Figure 1. The signal for the two magnetically equivalent O–$CH_2$ groups (H6) appear as one triplet at $\delta$ = 4 ppm. The assignment of the signals of the phenyl H atoms was achieved by the analysis of their coupling multiplicities. The twelve methylene groups were observed as a group of partially resolved signals (H7, H8, H9), as well as the intensive peak of the hydrogen atoms from the *tert*-butyl methyl groups, all between $\delta$ = 1–2 ppm (H4 in Figure 1, a). All the signals for the sp-alkyne C atoms in the $^{13}C$ NMR spectra of the tetraynes **15** are well resolved and appear between $\delta$ = 60 to 80 ppm (Figure 1, b). Six signals were found for the aromatic C atoms (C1, C2, C3 and C4) and could be assigned groupwise by means of a DEPT spectrum. The $^{13}C$ signals of the methylene bridge C atoms appear in the range between $\delta$ = 25–34 ppm, where also the signals of the *tert*-butyl groups are located. The ether O–$CH_2$ (C7) methylene groups appear as one singlet at $\delta$ = 69.3 ppm.

The UV/Vis spectra of the different tetrayne macrocycles **15a**–**c** were almost identical, the wavelengths of the π-π*-transitions found in the alkyne region between 350–450 nm (see below).

### Synthesis of Dioxacycloalkanehexayne Macrocycles 19a–c

Similar to the syntheses of the tetraynes **15a**–**c** (Scheme 3), the carbonyl olefination of the bis(benzaldehydes) **8d**–**f** gave the bis(1,1-dibromoolefins) α,ω-bis[2-(2,2-dibromoethenyl)-4-*tert*-butylphenyloxy]alkanes **9d**–**f** (Scheme 4). Upon elimination with LDA the terminally unsaturated α,ω-bis(4-*tert*-butyl-2-ethynylphenyloxy)alkanes **10d**–**f** were obtained. The subsequent sp-elongation with 1-TMS-1,3-butadiyne under homocoupling conditions gave only very low yields, similar to the syntheses of **12** (Scheme 3). However, the cross-coupling of **10d**–**f** with 1-bromo-4-(trimethylsilyl)buta-1,3-diyne (**16**) gave rise to the formation of TMS-protected terminal bis(triynes) **17a**–**c** in reasonable yields (63%, 21% and 11%). The (trimethylsilyl)-butadiyne **16** was obtained upon treatment of 1,4-bis(trimethylsilyl)butadiyne (**13**) with MeLi/LiBr and $AgNO_3$/NBS in two steps.[14] From subsequent deprotection of **17a**–**c** with $K_2CO_3$/MeOH/THF the terminal bis(triynes) α,ω-bis(2-butadiynyl-4-*tert*-butylphenyloxy)alkanes **18a**–**c** were obtained. Because of their labile nature, they were immediately allowed to react without further characterization. Final macrocylization by homocoupling of **18a**,**b** with TMEDA, CuCl, $O_2$ in high dilution (3.8 mM) in acetone according to Hay[20] gave the 38-membered and the 50-membered dioxacycloalkanehexayne macrocycles **19a** and **19b**, respectively, with yields up to 33% (Scheme 4). Attempts to elongate the bis(triyne) **18c** with 1-bromo-4-(trimethylsilyl)butadiyne (**16**) to a bis(pentayne) by a Pd-catalyzed coupling reaction similar to a Sonogashira coup-




Scheme 4. Synthesis of macrocyclic α,ω-diphenylhexaynes **19a**–**c** and octayne **20**. i) $PPh_3$, $CBr_4$, $CH_2Cl_2$; ii) LDA, –80 °C; iii) Br–C≡C–C≡C–TMS (**16**), BuLi, THF, 0 °C; CuCl, pyridin; iv) $K_2CO_3$, MeOH, THF, v) TMEDA, CuCl, $O_2$, acetone; vi) [$Pd(PPh_3)_2Cl_2$], CuI, $NEt_3$, $CH_2Cl_2$, 0 °C Br–C≡C–C≡C–TMS (**16**) (diluted, 3 mmol); vii) $K_2CO_3$, [$Pd(PPh_3)_2Cl_2$], CuI, $NEt_3$, $CH_2Cl_2$, 0 °C, Br–C≡C–C≡C–TMS (**16**) (concentrated, 30 mmol). Yields: **19a** (33%), **19b** (18%), **19c** (58%), and **20** (1.1%).

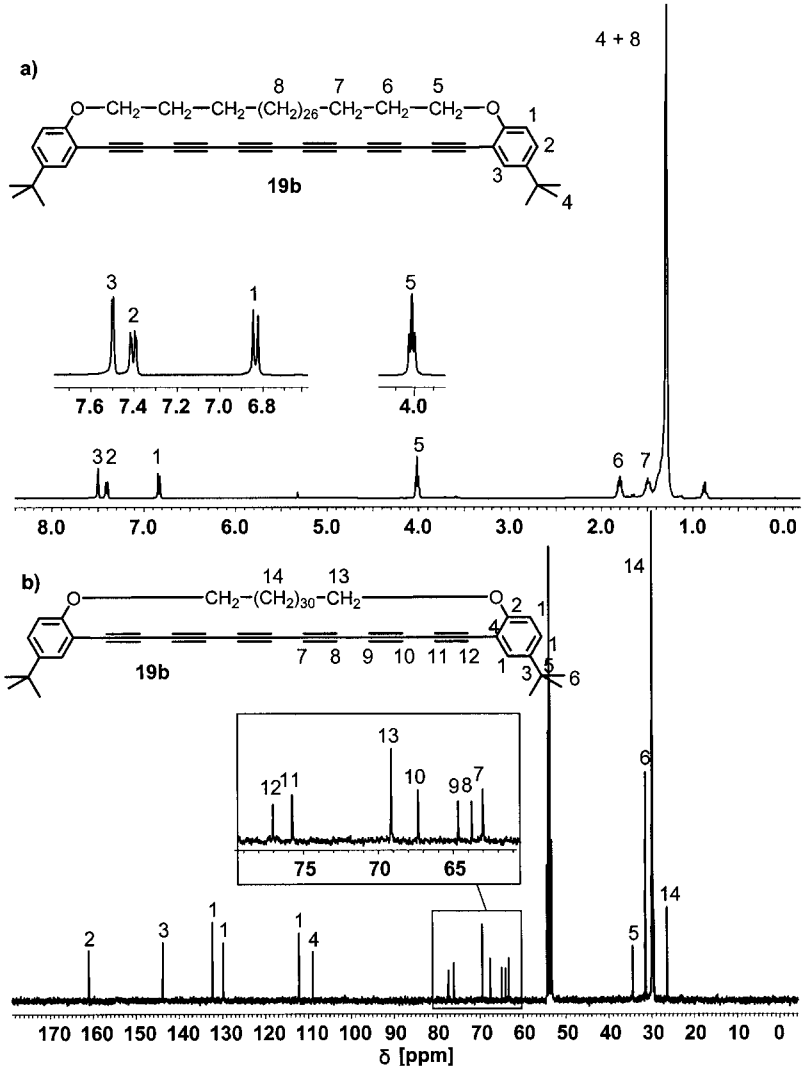
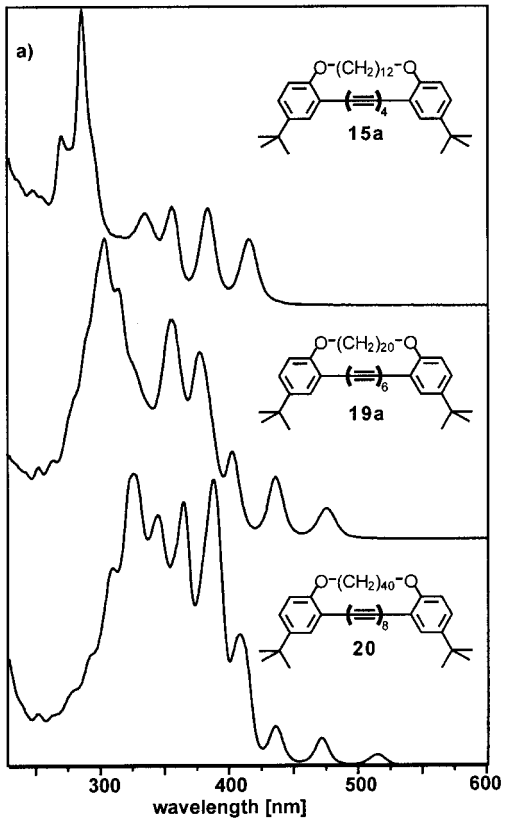



Figure 2. a) $^1H$ NMR spectrum (400 MHz, $CDCl_3$, 25 °C) and b) $^{13}C$ NMR (100.5 MHz, $CDCl_3$, 25 °C) spectrum of the 50-membered hexayne macrocycle **19b**.

ling[21] failed. Performing this reaction in high dilution (3 mM), we obtained the 58-membered macrocycle **19c** in 58% yield as the intramolecular coupling product. By the same transformation in tenfold higher concentration (30 mM) and with a larger amount of Pd catalyst (0.009 equiv.), the 62-membered dioxacycloalkaneoctayne macrocycle **20** was obtained as the main coupling product in 1% yield only, and characterized by mass spectrometry and UV/Vis spectroscopy (Scheme 4). The hexayne macrocycles **19a**–**c** were extraordinarily stable and were dried and stored over days. All the three target compounds **19a**–**c** as well as the corresponding intermediates were completely characterized by $^1$H and $^{13}$C NMR spectroscopy, IR and UV/Vis spectroscopy, mass spectrometry and elemental analysis. The NMR spectra of the ring-closed hexaynes **19a**–**c** also reveal the expected $C_{2v}$ symmetry as do those of the above-mentioned tetraynes **15a**–**c**. As an example, the NMR spectra of hexayne **19b** are shown in Figure 2. The $^{13}$C NMR spectra (Figure 2, b) showed the expected six signals (C7–C12) between $\delta$ = 63 and 78 ppm, which are due to the alkyne C atoms. The signal for the O–$CH_2$ C atom (C13) appears at $\delta$ = 69 ppm.

The UV/Vis spectra of the different hexaynes **19a**–**c** are almost identical to each other, irrespective of the oligomethylene chain length. The comparison of the UV spectra of the hexaynes with those of the shorter tetraynes and the longer sp-chain octayne **20** shows an increasing bathochromic shift of the corresponding absorption bands with increasing lengths of the sp-carbon chain. This reflects the typical behaviour of oligoynes[4,6,7,13b] and is caused by the narrowing of the HOMO–LUMO gap of oligoynes with increasing sp-chain length (Figure 3, a).[6,7,13b]



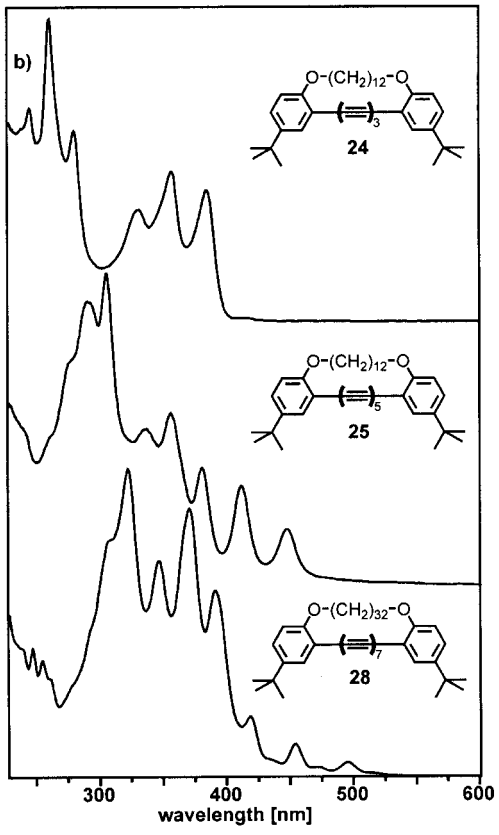



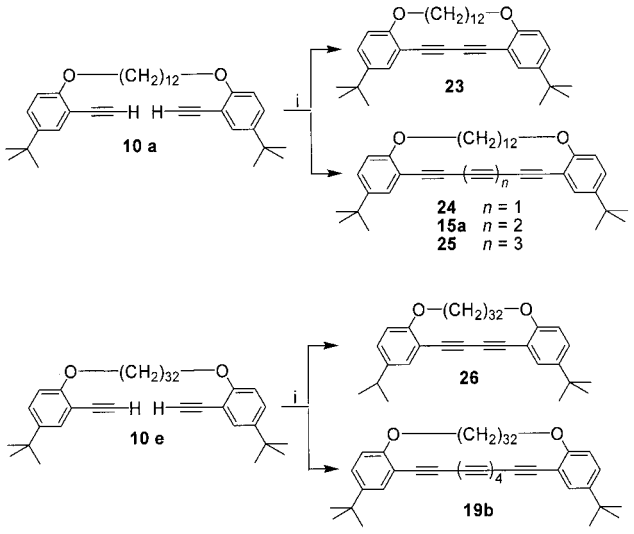

Figure 3. Comparative UV/Vis spectra of a) the tetrayne **15a**, hexayne **19a** and octayne macrocycle **20**, and b) the triyne **24**, pentayne **25** and heptayne macrocycle **28**.

### Palladium-Catalyzed Coupling Reactions

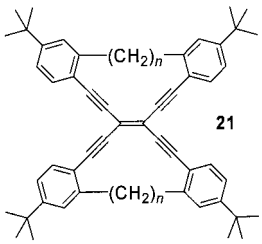
In an attempt to prepare the condensed bis(macrocyclic) structures **21** by introducing tetraiodoethene (**22**) into two molecules of the bis(acetylene) **10a** under palladium catalysis, the formation of the monomacrocyclic diyne **23**, triyne **24**, tetrayne **15a** and the pentayne **25** was observed (0.4%, 3.8%, 1.6% yield and traces, respectively) (Scheme 5) instead of the expected bis-coupled tetraethynylethene product **21**. An optimum total yield and product distribution was obtained using catalytical amounts of CuI and [$Pd(PPh_3)_2Cl_2$] and 4 equiv. of tetraiodoethene (**22**). Inspite of the low yields, the individual oligoynes could be separated by column chromatography. The compounds **23**, **24** and **15a** were completely characterized by $^1$H and $^{13}$C NMR spectroscopy, IR and UV spectroscopy and mass spectrometry; **25** was characterized by UV/Vis and mass spectrometry only. In order to obtain longer oligoyne structures, the $C_{32}$-bridged **10e** was treated with tetraiodoethene (**22**) under similar conditions. Only the intramolecular homocoupling product dioxacyclodotetracontadiyne **26** and the corresponding hexayne **19b** could be isolated by column chromatography in macroscopic quantities (5 and 3% yield, respectively) (Scheme 5). The corresponding $C_{32}$-

bridged triyne, tetrayne and pentayne macrocycles were detected in traces only.

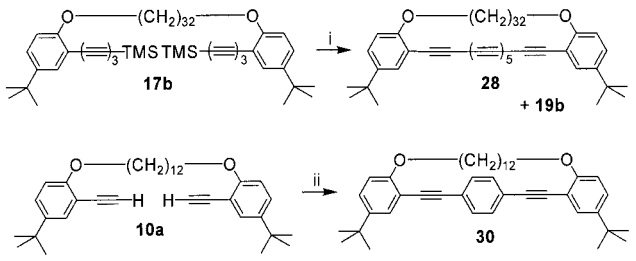



Scheme 5. Palladium-catalyzed coupling with tetraiodoethene (**22**). i) $[Pd(PPh_3)_2Cl_2]$, CuI, $I_2C{=}CI_2$ (**22**), $NEt_3$, $CH_3CN$, column chrom. Yields: **23** (0.4%), **24** (3.8%), **15a** (1.6%), **25** (traces), **26** (5%) and **19b** (3%).




It was assumed that diiodoacetylene (**27**), obviously formed from tetraiodoethene (**22**), was the active coupling reagent in the transformations described above. Carrying out palladium-catalyzed coupling of **27** with the bis(triyne) **17b**, besides the intramolecularly coupled hexayne **19b** and traces of the corresponding octayne, the bis-heterocoupling product heptayne **28** was isolated in a yield of 11% as an orange solid (Scheme 6). Similarly to diiodoacetylene (**27**), dihalogen-substituted aromatic compounds like the diiodobenzene **29** can be inserted between two terminal triple bonds according to a Sonogashira coupling reaction.[16] Treatment of the bis-ethynylbenzene **10a** with 1,4-diiodobenzene (**29**) at 50 °C in the presence of $[Pd(PPh_3)_2Cl_2]$, CuI and $NEt_3$ afforded the *p*-phenylene-interlinked macrocycle **30** as a white solid in 26% yield (Scheme 6). This last reaction opens synthetic routes to a defined interruption of the sp-conjugation of oligoynes and consequently to tune the spectroscopic and electronic features of polyynes.

As in the case of the tetrayne **15a**, hexayne **19a** and the octayne **20** (Figure 3, a), respectively, the electronic absorption spectra of the triyne **23**, pentayne **24** and heptayne **28** reveal a successive bathochromic shift of the π,π*-transitions (≈ 350–450 nm) with increasing number of triple bonds (Figure 3, b).




Scheme 6. Paladium-catalyzed coupling with diiodoacetylene (**27**) and 1,4-diiodobenzene (**29**) to obtain heptadiyne **28** and diethynylbenzene **30**. i) $[Pd(PPh_3)_2Cl_2]$, CuI, I–C≡C–I (**27**), $NEt_3$, $CH_2Cl_2$. Yield: **28** (11%); ii) $[Pd(PPh_3)_2Cl_2]$, CuI, I–$C_6H_4$–I (**29**), $NEt_3$, $CHCl_3$. Yield: **30** (26%).

## Conclusion

We have presented a method for the stabilization of oligoynes by very long alkylene chains with up to 40 methylene groups linking the phenyl termini of the carbon rods. At the same time we provided an access to a new class of very large macrocyclic molecules containing segregated sp-, $sp^2$- and $sp^3$-segments. The final macrocyclization step is an alkyne homocoupling-type reaction. Despite their conjugated triple-bond systems, the products formed exhibited enhanced stability against moisture and air exposure. They were dried and stored for days, and no decomposition was observed in solution. These oligoyne macrocycles are not only interesting with respect to their model character of the linear carbon allotrope carbyne. They present also new building blocks for even more elaborated molecular architectures, which could be obtained by applying classical and modern synthesis methods in the field of acetylene chemistry.[22] Work along these lines is currently under way in our laboratory.

## Experimental Section

### General Remarks

**Chemicals:** All chemicals were obtained from Aldrich, Fluka, Sigma, Acros Organics and Lancaster, the solvents purified by distillation. All reactions were carried out under protective atmosphere and in dry solvents. Thin Layer Chromatography (TLC): Riedel-de Haën silica gel 60 $F_{254}$ aluminum foils, detection: UV lamp or 10% aqueous $KMnO_4$ solution. High-Performance Liquid Chromatography (HPLC): Shimadzu Liquid Chromatograph LC-8A, Diode Array Detector SPD-M 10A, UV Detector SPD-M 10A, Auto Injector Sil-10A, Selection Valve VFCV-10AL, Fraction Collector FRC-10A. Analytical Columns: Cosmosil. Preparative Columns: Cosmosil. NMR Spectra: JEOL JNM EX 400, JEOL JNM GX 400 and JEOL 500. The chemical shifts are given in [ppm] relative to TMS. The spin coupling patterns are indicated as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and br. (broad, for unresolved signals). UV/Vis Spectra: Shimadzu UV-3102 PC, UV/Vis-NIR Scanning Spectrophotometer. IR Spectra: Bruker FT-IR Vector 22, KBr pellets or thin film (NaCl plates).

Mass Spectra: Micromass Zabspec, FAB (LSIMS) mode (3-nitrobenzyl alcohol). Elementary analysis (C, H, N) succeeded by combustion and gas chromatographical analysis with an EA 1110 CHNS analyser (CE Instruments).

**Synthesis of the Protective Bis(benzaldehyde) Units 8a–f**

**α,ω-Dibromoalkanes 1a–f**

**1,12-Dibromododecane (1a), 1,14-Dibromotetradecane (1b), 1,16-Dibromohexadecane (1c) and 1,20-Dibromoeicosane (1d):** The α,ω-dibromoalkanes **1a**–**c** were obtained by conventional reduction of the corresponding dicarboxylic acids with $LiAlH_4$ and subsequent bromination with HBr. 1,20-Dibromoeicosane (**1d**) was yielded from 1-bromo-6-(tetrahydropyranyloxy)hexane (**2a**) by reaction with Mg turnings to the organomagnesium compound **3a** and subsequent Grignard reaction with 1,8-diiodooctane (**4**) according to ref.[9] The bis-THP ether **5a** was converted into **1d** by bromination with tetrabromohexadienone **6** according to Tanaka and Oritani.[9,17]

**1,32-Bis(tetrahydropyranyloxy)dotriacontane (5b):**[9] Magnesium turnings (2.54 g, 104.48 mmol) together with dry THF were placed in a 1-L three-necked flask, so that the metal was covered by the solvent. Under vigorous stirring thoroughly dried 1-bromo-6-(tetrahydropyranyloxy)dodecane (**2b**) (2.50 g, 7.16 mmol) was added, while the mixture became warm and turbid. Immediately further **2b** (25.22 g, 72.26 mmol), diluted in 330 mL dry THF, was added dropwise, so that the solvent was kept at calm boiling temperature. When the addition was complete, the solution of **3b** was heated for 2 h under reflux and subsequently cooled to –15 °C. A 0.2 M solution of $Li_2CuCl_4$ (6.7 mL, 1.34 mmol) in THF and 1,8-diiodooctane (**4**, 11.35 g, 31.01 mmol), dissolved in THF (40 mL), were added. After 30 min the cooling bath was removed, and the reaction mixture was stirred for additional 18 h. To the resulting dark suspension a saturated aqueous solution of ammonium acetate (350 mL) was added and stirred for another 30 min. The layers were separated and the aqueous layer extracted twice with diethyl ether (200 mL each). The combined organic layers were washed twice with water (300 mL each), dried with $Na_2SO_4$ and concentrated to dryness. The crude product was dissolved in boiling THF (140 mL) and crystallized after cooling to 4 °C. **5b** was isolated as a white powder (15.32 g, 76%). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 4.51 (m, 2 H, C*H*), 3.82–3.80 (m, 2 H, C$H_2$), 3.67–3.62 (m, 2 H, C$H_2$), 3.44–3.43 (m, 2 H, C$H_2$), 3.35–3.27 (m, 2 H, C$H_2$), 1.80–1.70 (m, 2 H, C$H_2$), 1.64–1.63 (m, 2 H, C$H_2$), 1.54–1.45 (m, 12 H, C$H_2$), 1.18 (br. s, 56 H, C$H_2$) ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 98.8 (2 C, *C*H), 67.7 (2 C, *C*$H_2$), 62.3 (2 C, *C*$H_2$), 30.8 (2 C, *C*$H_2$), 29.8 (2 C, *C*$H_2$), 29.7 (22 C, *C*$H_2$), 29.6 (2 C, *C*$H_2$), 29.5 (2 C, *C*$H_2$), 26.2 (2 C, *C*$H_2$), 25.5 (2 C, *C*$H_2$), 19.7 (2 C, *C*$H_2$) ppm. IR (KBr): $\tilde{\nu}$ =2960, 2848, 2788, 2655, 1465, 1442, 1352, 1315, 1260, 1207, 1197, 1127, 1073, 1030, 980, 907, 872, 813, 722, 669, 576, 543 cm$^{-1}$. $C_{42}H_{82}O_4$ (651.08): calcd. C 77.47, H 12.69; found C 77.57, H 12.84.

**1,40-Bis(tetrahydropyranyloxy)tetracontane (5c):** According to the synthesis of **5b**, magnesium turnings (1.56 g, 64.18 mmol) were treated with 1-bromo-14-(tetrahydropyranyloxy)tetradecane (**2c**) (2.00 g, 5.31 mmol). Additional THP ether **2c** (18.39 g, 48.79 mmol) in THF (160 mL) was added and the mixture kept at reflux. When the addition was complete, the solution of **3c** was heated and cooled as described in the paragraph above for **5b**. Subsequent treatment with a 0.2 M solution of $Li_2CuCl_4$ in THF (4.1 mL, 0.82 mmol) and 1,12-dibromododecane (**1a**, 5.93 g, 18.08 mmol) after stirring for 18 h led to bis-THP ether **5c**. After workup with an aqueous solution of ammonium acetate, extraction with $CH_2Cl_2$ (150 mL each, twice), washing with water (250 mL) and saturated aqueous NaCl solution (250 mL), drying with $Na_2SO_4$ and evaporation of the solvent followed. The remaining crude mixture was dissolved in THF (140 mL) under reflux, and by subsequent cooling to 4 °C, the pure product **5c** crystallized as a white powder (7.57 g, 55%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 4.55 (m, 2 H, C*H*), 3.88–3.812 (m, 2 H, C$H_2$), 3.73–3.68 (m, 2 H, C$H_2$), 3.49–3.45 (m, 2 H, C$H_2$), 3.38–3.33 (m, 2 H, C$H_2$), 1.85–1.78 (m, 2 H, C$H_2$), 1.73–1.66 (m, 2 H, C$H_2$), 1.59–1.50 (m, 12 H, C$H_2$), 1.23 (br. s, 72 H, C$H_2$) ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 98.8 (2 C, *C*H), 67.7 (2 C, *C*$H_2$), 62.3 (2 C, *C*$H_2$), 30.9 (2 C, *C*$H_2$), 29.9 (2 C, *C*$H_2$), 29.8 (30 C, *C*$H_2$), 29.7 (2 C, *C*$H_2$), 29.6 (2 C, *C*$H_2$), 26.4 (2 C, *C*$H_2$), 25.6 (2 C, *C*$H_2$), 19.8 (2 C, *C*$H_2$) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2923, 2853, 1470, 1357, 1265, 1129, 1073, 1032, 972, 905, 872, 813, 722 cm$^{-1}$. $C_{50}H_{98}O_4$ (763.28): calcd. C 78.67, H 12.94; found C 78.64, H 13.07.

**1,32-Dibromodotriacontane (1e):** Triphenylphosphane (7.78 g, 29.70 mmol) was dissolved in $CH_2Cl_2$ (16 mL), cooled to 0 °C, and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (**6**, 12.18 g, 29.70 mmol) was added and the mixture stirred for 30 min. When the yellow color almost had disappeared, bis-THP ether **5b** (4.39 g, 6.75 mmol) was added and the reaction mixture was stirred for another 14 h at room temp. Subsequently the solvent was distilled off, and the remaining solid crude product was heated in ethanol (100 mL) under reflux for 1 h until all substances got dissolved. When cooling to 4 °C, the pure dibromoalkane **1e** crystallized (3.90 g, 95%) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 3.39 (t, $^3J$ = 6.9 Hz, 4 H, OC$H_2$), 1.83 (m, 4 H, OCH$_2$C$H_2$), 1.39 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.23 (s, 52 H, C$H_2$) ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 34.1 (2 C, *C*$H_2$), 32.8 (2 C, *C*$H_2$), 29.7 (18 C, *C*$H_2$), 29.6 (2 C, *C*$H_2$), 29.5 (2 C, *C*$H_2$), 29.4 (2 C, *C*$H_2$), 28.8 (2 C, *C*$H_2$), 28.2 (2 C, *C*$H_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2851, 1470, 1303, 1268, 1235, 1202, 1008, 719, 643 cm$^{-1}$. $C_{32}H_{64}Br_2$ (608.66): calcd. C 63.14, H 10.60; found C 62.73, H 10.49.

**1,40-Dibromotetracontane (1f):** Similar to the synthesis of **1e**, a mixture of triphenylphosphane (4.69 g, 17.90 mmol) and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (**6**, 7.34 g, 17.90 mmol) in $CH_2Cl_2$ (45 mL) was treated with bis-THP ether **5c** (3.10 g, 4.07 mmol). After stirring for 16 h and work up as for **1e** in boiling ethanol (650 mL), the product **1f** crystallized as a white powder (2.80 g, 96%). $^1$H NMR (400 MHz, $CDCl_3$, 40 °C): $\delta$ = 3.38 (t, $^3J$ = 6.8 Hz, 4 H, Br–C$H_2$), 1.83 (m, 4 H, Br–CH$_2$–C$H_2$), 1.45 (m, 4 H, BrCH$_2$CH$_2$C$H_2$), 1.24 (s, 68 H, C$H_2$) ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 50 °C): $\delta$ = 33.9 (2 C, Br*C*H$_2$), 32.9 (2 C, BrCH$_2$*C*H$_2$), 29.7 (22 C, *C*$H_2$), 29.5 (2 C, *C*$H_2$), 28.7 (2 C, *C*$H_2$), 28.2 (2 C, *C*$H_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2929, 2850, 1468, 1195, 1115, 724, 646, 544 cm$^{-1}$. $C_{40}H_{80}Br_2$ (720.87): calcd. C 66.65, H 11.19; found C 66.23, H 10.99.

**Bis(benzaldehydes) 8a–f**

**1,12-Bis(4-*tert*-butyl-2-formylphenyloxy)dodecane (8a):** To a solution of 5-*tert*-butyl-2-hydroxybenzaldehyde (**7**)[18] (10.00 g, 56.18 mmol) in DMF (250 mL) $K_2CO_3$ (23.15 g, 167.75 mmol) was added. To the resulting yellow suspension 1,12-dibromododecane (**1a**, 9.21 g, 28.08 mmol) was added and heated to 80 °C. The course of the reaction was monitored by means of TLC ($CH_2Cl_2$, $R_f$ = 0.55). After 16 h the mixture was cooled to room temp. and diethyl ether (300 mL) and water (250 mL) was added. The organic layer was separated, the aqueous phase was extracted twice with diethyl ether (250 mL each) and the combined organic phases washed with water (300 mL). After drying with $Na_2SO_4$ the solvent was distilled off in vacuo and the remaining crude mixture dissolved in boiling diethyl ether (600 mL). Upon cooling, the product **8a** crystallized as a white solid (11.02 g, 75%). $^1$H NMR (400 MHz,

$CDCl_3$, 25 °C): $\delta$ = 10.49 (s, 2 H, C*H*O), 7.82 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.54 (dd, $^4J$ = 2.7 Hz, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 6.89 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 4.03 (t, $^3J$ = 6.4 Hz, 4 H, OC$H_2$), 1.81 (m, 4 H, OCH$_2$C$H_2$), 1.46 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.24–1.35 (m, 12 H, C$H_2$) and 1.28 [s, 18 H, C(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 189.9 (2 C, *C*HO), 159.4 (2 C, Ar*C*), 143.1 (2 C, Ar*C*), 133.0 (2 C, Ar*C*H), 124.4 (2 C, Ar*C*H), 124.1 (2 C, Ar*C*), 112.2 (2 C, Ar*C*H), 68.6 (2 C, O*C*H$_2$), 34.3 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 29.6 (4 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 26.2 (2 C, *C*H$_2$), 26.1 (2 C, *C*H$_2$) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2921, 2852, 1681, 1607, 1579, 1497, 1471, 1415, 1388, 1364, 1292, 1266, 1246, 1191, 1138, 1098, 1042, 1001, 934, 819, 733, 679, 651, 600, 570 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 256, 329 nm. MS (FAB): *m*/*z* = 523 [M$^+$]. $C_{34}H_{50}O_4$ (522.74): calcd. C 78.12, H 9.64; found C 77.94, H 9.94.

**1,14-Bis(4-*tert*-butyl-2-formylphenyloxy)tetradecane (8b):** According to the same procedure as applied for the synthesis of **8a**, 5-*tert*-butyl-2-hydroxybenzaldehyde (**7**) (5.00 g, 28.09 mmol) was treated with 1,14-dibromotetradecane (**1b**, 5.00 g, 14.04 mmol) in DMF (100 mL). After heating for 16 h (TLC control: $CH_2Cl_2$/hexane,1:1, $R_f$ = 0.23) and cooling, water (200 mL) and $CH_2Cl_2$ (200 mL) was added. The aqueous layer was extracted with $CH_2Cl_2$ (200 mL) and the combined organic layers washed and dried. After work up similar as for **8a**, from boiling diethyl ether (200 mL) and cooling to –30 °C the white solid **8b** crystallized (5.76 g, 75%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 10.47 (s, 2 H, C*H*O), 7.82 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.54 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 6.89 (d, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 4.03 (t, $^3J$ = 6.4 Hz, 4 H, OC$H_2$), 1.81 (m, 4 H, OCH$_2$C$H_2$), 1.44 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.33–1.25 (m, 16 H, C$H_2$), 1.28 [s, 18 H, C(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 190.2 (2 C, *C*HO), 159.6 (2 C, Ar*C*), 143.3 (2 C, Ar*C*), 133.1 (2 C, Ar*C*H), 124.6 (2 C, Ar*C*H), 124.2 (2 C, Ar*C*), 112.3 (2 C, Ar*C*H), 68.6 (2 C, O*C*H$_2$), 34.2 [2 C, *C*(CH$_3$)$_3$], 31.3 [6 C, C(*C*H$_3$)$_3$], 29.6 (4 C, *C*H$_2$), 29.5 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 26.1 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2920, 2850, 1680, 1608, 1579, 1498, 1471, 1414, 1389, 1364, 1295, 1266, 1246, 1191, 1139, 1098, 1047, 1014, 935, 835, 819, 731, 679, 651, 600, 571 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 256, 330 nm. MS (FAB): *m*/*z* = 551 [M$^+$]. $C_{36}H_{54}O_4$ (550.79): calcd. C 78.50, H 9.88; found C 78.07, H 9.88.

**1,16-Bis(4-*tert*-butyl-2-formylphenyloxy)hexadecane (8c):** According to the synthesis of **8a**, a mixture of the hydroxybenzaldehyde **7** (1.00 g, 5.60 mmol), 1,16-dibromohexadecane (**1c**, 1.08 g, 2.81 mmol) and $K_2CO_3$ (2.33 g, 16.88 mmol) was heated for 16 h at 80 °C (TLC monitoring: $CH_2Cl_2$/hexane, 7:3, $R_f$ = 0.33). After addition of additional dibromohexadecane **1c** (54 mg, 0.14 mmol) and heating for two more hours, working up succeeded with diethyl ether and water (150 mL each). The aqueous layer was separated, extracted with diethyl ether (3 × 100 mL), and the combined organic phases were washed with water (2 × 200 mL) and saturated aqueous NaCl solution (200 mL). After drying with $Na_2SO_4$ the final purification was performed by column chromatography (silica gel, $CH_2Cl_2$/hexane, 1:1 → 7:3), and the white solid **8c** (1.26 g, 78%) was isolated. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 10.49 (s, 2 H, C*H*O), 7.82 (d, $^4J$ = 2.7 Hz, 2 H, Ar*H*), 7.54 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 6.89 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 4.03 (t, $^3J$ = 6.4 Hz, 4 H, OC$H_2$), 1.81 (m, 4 H, OCH$_2$C$H_2$), 1.46 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.24–1.33 (m, 12 H, C$H_2$), 1.28 [s, 18 H, C(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 189.9 (2 C, *C*HO), 159.5 (2 C, Ar*C*), 143.1 (2 C, Ar*C*), 133.00 (2 C, Ar*C*H), 124.5 (2 C, Ar*C*H), 124.1 (2 C, Ar*C*), 112.2 (2 C, Ar*C*H), 68.6 (2 C, O*C*H$_2$), 34.3 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 29.7 (2 C, *C*H$_2$), 29.67 (4 C, *C*H$_2$), 29.65 (2 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 29.2 (2 C, *C*H$_2$), 26.2 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2951, 29120, 2850, 1679, 1608, 1579, 1498, 1472, 1414, 1389, 1364, 1295, 1266, 1246, 1192, 1140, 1098, 1053, 1020, 987, 935, 909, 839, 824, 729, 679, 652, 601, 571, 501 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 256, 329 nm. MS (FAB): *m*/*z* = 579 [M$^+$]. $C_{38}H_{58}O_4$ (578.84): calcd. C 78.84, H 10.10; found C 78.44, H 10.01.

**1,20-Bis(4-*tert*-butyl-2-formylphenyloxy)eicosane (8d):** The bis(benzaldehyde) **8d** was obtained in analogy of the synthesis of **8c**, from 1,20-dibromoeicosane (**1d**, 2.97 g, 6.75 mmol), 5-*tert*-butyl-2-hydroxybenzaldehyde (**7**, 2.40 g, 13.49 mmol) and $K_2CO_3$ (5.58 g, 40.43 mmol) in DMF (60 mL). After a reaction time of 18 h, TLC monitoring (ethyl acetate/petroleum ether, 5:95, $R_f$ = 0.21) revealed complete transformation. The mixture was cooled and water (250 mL) and diethyl ether (250 mL) were added. After separating the layers, the aqueous layer was extracted with diethyl ether (three times, 150 mL each), and the combined ether phases were washed with water (twice, 300 mL each) and saturated aqueous solution of NaCl (300 mL). After drying with $Na_2SO_4$, the solvent was distilled off and the crude mixture dissolved in boiling diethyl ether (40 mL). After subsequent cooling to –30 °C the product **8d** crystallized as a white powder (3.63 g, 85%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 10.60 (s, 2 H, C*H*O), 7.64 (d, $^4J$ = 2.2 Hz, 2 H, Ar*H*), 7.37 (dd, $^4J$ = 2.2 Hz, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 6.71 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 3.85 (t, $^3J$ = 6.3 Hz, 4 H, OC$H_2$), 1.61 (m, 4 H, OCH$_2$C$H_2$), 1.28 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.10 (br. s, 52 H, C$H_2$), 1.06 [s, 18 H, C(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 190.2 (2 C, *C*HO), 159.6 (2 C, Ar*C*), 143.3 (2 C, Ar*C*), 133.1 (2 C, Ar*C*H), 124.6 (2 C, Ar*C*H), 124.2 (2 C, Ar*C*), 112.3 (2 C, Ar*C*H), 68.5 (2 C, O*C*H$_2$), 34.2 [2 C, *C*(CH$_3$)$_3$], 31.3 (8 C, *C*H$_2$), 29.7 [6 C, C(*C*H$_3$)$_3$], 29.6 (2 C, *C*H$_2$), 29.5 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 26.0 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3442, 2961, 2920, 2850, 2754, 1680, 1606, 1580, 1497, 1468, 1413, 1389, 1366, 1292, 1265, 1243, 1192, 1138, 1099, 1028, 935, 820, 722, 679, 651, 600, 568 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 256, 330 nm. MS (FAB): *m*/*z* = 636 [M]$^+$. $C_{42}H_{66}O_4$ (634.95): calcd. C 79.44, H 10.48; found C 79.47, H 10.57.

**1,32-Bis(4-*tert*-butyl-2-formylphenyloxy)dotriacontane (8e):** 5-*tert*-Butyl-2-hydroxybenzaldehyde (**7**, 2.90 g, 16.28 mmol), dissolved in DMF (150 mL), and 1,32-dibromodotriacontane (**1e**, 4.95 g, 8.14 mmol) was heated to 80 °C to complete dissolution. After addition of $K_2CO_3$ (6.78 g, 49.14 mmol) and stirring for 15 h, water (250 mL) and $CH_2Cl_2$ (250 mL) were added and the layers were allowed to separate. The aqueous layer was extracted with $CH_2Cl_2$ (twice, 200 mL each), the organic phases combined, washed with water (twice, 250 mL each) and dried with $Na_2SO_4$. After filtering off the $Na_2SO_4$, the solution was concentrated and the crude mixture redissolved in boiling diethyl ether (350 mL). After cooling the solution to –30 °C, **8e** was isolated by precipitation as a white powder (5.90 g, 90%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 10.49 (s, 2 H, C*H*O), 7.83 (d, $^4J$ = 2.2 Hz, 2 H, Ar*H*), 7.54 (dd, $^4J$ = 2.2 Hz, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 6.89 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 4.03 (t, $^3J$ = 6.3 Hz, 4 H, OC$H_2$), 1.81 (m, 4 H, OCH$_2$C$H_2$), 1.44 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.29 [s, 18 H, C(C$H_3$)$_3$], 1.23 (br. s, 52 H, C$H_2$) ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 190.2 (2 C, *C*HO), 159.6 (2 C, Ar*C*), 143.2 (2 C, Ar*C*), 133.1 (2 C, Ar*C*H), 124.6 (2 C, Ar*C*H), 124.2 (2 C, Ar*C*), 112.2 (2 C, Ar*C*H), 68.5 (2 C, O*C*H$_2$), 34.2 [2 C, *C*(CH$_3$)$_3$], 31.3 [6 C, C(*C*H$_3$)$_3$], 29.9 (22 C, *C*H$_2$), 29.6 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.2 (2 C, *C*H$_2$), 26.0 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3442, 2919, 2849, 2758, 1680, 1608, 1579, 1498, 1472, 1414, 1389, 1364, 1295, 1266, 1245, 1192, 1138, 1098, 1036, 1008, 934, 909, 834, 819, 721, 678, 651, 600, 570 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 251, 330 nm. MS (FAB): *m*/*z* = 804 [M]$^+$. $C_{54}H_{90}O_4$ (803.26): calcd. 80.74, H 11.29; found 80.21, H 11.46.

**1,40-Bis(4-*tert*-butyl-2-formylphenyloxy)tetracontane (8f):** The diphenyl ether **8f** was was obtained by heating 1,40-dibromotetracontane (**1f**, 81 g, 5.29 mmol) and 5-*tert*-butyl-2-hydroxybenzaldehyde (**7**, 1.88 g, 10.58 mmol) in DMF (80 mL) at 90 °C. After the addition of $K_2CO_3$ (4.41 g, 31.96 mmol) and heating for 18 h, TLC analysis ($CH_2Cl_2$/hexane, 1:1, $R_f$ = 0.33) revealed complete conversion. The mixture was cooled to room temperature, treated with water (300 mL) and $CH_2Cl_2$ (300 mL), and the layers were allowed to separate. The aqueous layer was extracted with $CH_2Cl_2$ (twice, 150 mL each), the combined $CH_2Cl_2$ phases were washed with water (twice, 350 mL each) and dried with $Na_2SO_4$ according to the preparation of **8e**. The solvent was removed and the remaining solid was dissolved in 1 L of boiling diethyl ether. By precipitation at –30 °C, product **8f** was obtained (4.37 g, 90%) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 10.49 (s, 2 H, C*H*O), 7.83 (d, $^4J$ = 2.2 Hz, 2 H, Ar*H*), 7.54 (dd, $^4J$ = 2.2 Hz, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 6.89 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 4.03 (t, $^3J$ = 6.3 Hz, 4 H, OC$H_2$), 1.81 (m, 4 H, OCH$_2$C$H_2$), 1.45 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.29 [s, 18 H, C(C$H_3$)$_3$], 1.23 (br. s, 68 H, C$H_2$) ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 189.9 (2 C, *C*HO), 159.5 (2 C, Ar*C*O), 143.1 [2 C, Ar*C*C(CH$_3$)$_3$], 133.0 (2 C, Ar*C*H), 124.5 (2 C, Ar*C*H), 124.1 (2 C, Ar*C*CHO), 112.2 (2 C, Ar*C*H), 68.6 (2 C, OCH$_2$), 34.3 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 29.8 (30 C, *C*H$_2$), 29.7 (2 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 29.2 (2 C, *C*H$_2$), 26.2 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3450, 2963, 2919, 2850, 2756, 1680, 1606, 1497, 1473, 1389, 1365, 1263, 1192, 1097, 1027, 1008, 804, 719 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 255, 330 nm. MS (FAB): *m*/*z* = 916 [M]$^+$. $C_{62}H_{106}O_4$ (915.47): calcd. C 81.34, H 11.67; found C 80.77, H 11.80.

**Synthesis of Tetrayne Macrocycles 15a–c**

**1,12-Bis[4-*tert*-butyl-2-(2,2-dibromoethenyl)phenyloxy]dodecane (9a):** $CBr_4$ (19.90 g, 59.94 mmol) was dissolved in $CH_2Cl_2$ (100 mL) and the solution cooled to 0 °C. $PPh_3$ (31.41 g, 119.88 mmol) was added to this cold solution. Subsequently, a solution of **8a** (7.12 g, 13.62 mmol) in $CH_2Cl_2$ (200 mL) was added dropwise, and the reaction was completed after 10 min (TLC monitoring: $CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.68). Water (250 mL) and $CH_2Cl_2$ (250 mL) was added and the layers separated. The aqueous layer was extracted three times with $CH_2Cl_2$ (100 mL each) and the organic layers were combined. After drying with $Na_2SO_4$ and column chromatography ($CH_2Cl_2$/hexane, 2:8) a clear and colorless oil was isolated (10.79 g, 95%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.74 (d, $^4J$ = 2.5 Hz, 2 H, Ar*H*), 7.61 (s, 2 H, Br$_2$C=C*H*), 7.27 (dd, $^3J$ = 8.6 Hz, $^4J$ = 2.5 Hz, 2 H, Ar*H*), 6.76 (d, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 3.94 (t, $^3J$ = 6.5 Hz, 4 H, OC$H_2$), 1.77 (m, 4 H, OCH$_2$C$H_2$), 1.43 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.39–1.21 (m, 12 H, C$H_2$), 1.29 [s, 18 H, C(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 153.9 (2 C, Ar*C*), 142.6 (2 C, Ar*C*), 133.4 (2 C, Br$_2$*C*=CH), 126.4 (4 C, Ar*C*H u. Ar*C*), 123.8 (2 C, Ar*C*), 111.1 (2 C, Ar*C*H), 88.9 (2 C, Br$_2$C=*C*H), 68.5 (2 C, OCH$_2$), 34.2 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 29.6 (4 C, C$H_2$), 29.3 (2 C, C$H_2$), 29.2 (2 C, *C*H$_2$), 26.1 (2 C, *C*H$_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 3031, 2928, 2855, 1606, 1578, 1494, 1468, 1392, 1363, 1303, 1251, 1201, 1136, 1105, 1025, 938, 900, 843, 812, 737, 673, 623, 603, 581 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 306, 258 nm. MS (FAB): *m*/*z* = 834 [M$^+$]. $C_{36}H_{50}Br_4O_2$ (834.42): calcd. C 51.82, H 6.04, found C 51.89, H 6.24.

**1,14-Bis[4-*tert*-butyl-2-(2,2-dibromoethenyl)phenyloxy]tetradecane (9b):** In analogy to the synthesis of **9a**, the dibromostyrene **9b** was obtained from $CBr_4$ (15.43 g, 46.48 mmol) in $CH_2Cl_2$ (80 mL), $PPh_3$ (24.35 g, 92.94 mmol) and the dropwise addition of a solution of **8b** (5.56 g, 10.11 mmol) in $CH_2Cl_2$ (100 mL) at 0 °C (TLC: $CH_2Cl_2$, $R_f$ = 0.87). Working up succeeded with $CH_2Cl_2$ (200 mL) and water (300 mL), washing with water (twice, 400 mL), drying with $Na_2SO_4$ and column chromatography (silica gel, $CH_2Cl_2$/hexane, 1:1). The bridged distyryl compound **9b** was isolated as a colorless oil (8.30 g, 9.63 mmol). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.74 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.61 (s, 2 H, Br$_2$C=C*H*), 7.27 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.5 Hz, 2 H, Ar*H*), 6.76 (d, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 3.93 (t, $^3J$ = 6.6 Hz, 4 H, OC$H_2$), 1.77 (m, 4 H, OCH$_2$C$H_2$), 1.41 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.24–1.33 (m, 16 H, C$H_2$), 1.27 [s, 18 H, C(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 153.9 (2 C, Ar*C*), 142.5 (2 C, Ar*C*), 133.4 (2 C, Ar*C*H), 126.4 (4 C, Ar*C*H and Br$_2$C=*C*H), 123.8 (2 C, Ar*C*), 111.1 (2 C, Ar*C*H), 88.9 (2 C, Br$_2$*C*=CH), 68.5 (2 C, OCH$_2$), 34.2 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 29.7 (4 C, *C*H$_2$), 29.6 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.2 (2 C, *C*H$_2$), 26.1 (2 C, *C*H$_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 2926, 2854, 1606, 1577, 1494, 1468, 1392, 1363, 1304, 1251, 1201, 1136, 1106, 1026, 939, 900, 842, 811, 737, 673, 629, 603, 581 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 259, 307 nm. MS (FAB): *m*/*z* = 862 [M$^+$]. $C_{38}H_{54}Br_4O_2$ (862.48): calcd. C 52.92, H 6.31; found C 52.45, H 6.84.

**1,16-Bis[4-*tert*-butyl-2-(2,2-dibromoethenyl)phenyloxy]hexadecane (9c):** The preparation of the $C_{16}$-bridged compound **9c** was achieved by preparing a mixture of $CBr_4$ (3.21 g, 9.67 mmol) in $CH_2Cl_2$ (16 mL) and $PPh_3$ (5.07 g, 19.34 mmol) at 0 °C. To this yellow-orange suspension a solution of **8c** (1.22 g, 2.10 mmol) in $CH_2Cl_2$ (25 mL) was added dropwise. After 20 min, the reaction was complete (TLC: $CH_2Cl_2$, $R_f$ = 0.70), and water (300 mL) and $CH_2Cl_2$ (150 mL) were added. The aqueous layer was extracted twice with $CH_2Cl_2$ (150 mL each), the combined organic layers dried with $Na_2SO_4$ and the product **9c** isolated by column chromatography (silica gel, $CH_2Cl_2$) as a white solid (1.86 g, quantitatively). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.74 (d, $^4J$ = 2.2 Hz, 2 H, Ar*H*), 7.61 (s, 2 H, Br$_2$C=C*H*), 7.27 (dd, $^3J$ = 8.8 Hz, $^4J$ = 2.2 Hz, 2 H, Ar*H*), 6.76 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 3.93 (t, $^3J$ = 6.3 Hz, 4 H, OC$H_2$), 1.77 (m, 4 H, OCH$_2$C$H_2$), 1.43 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.26–1.33 (m, 20 H, C$H_2$), 1.29 [s, 18 H, C(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 153.9 (2 C, Ar*C*), 142.5 (2 C, Ar*C*), 133.3 (2 C, Ar*C*H), 126.4 (4 C, Ar*C*H and Br$_2$C=*C*H), 123.8 (2 C, Ar*C*), 111.1 (2 C, Ar*C*H), 88.9 (2 C, Br$_2$*C*=CH), 68.5 (2 C, OCH$_2$), 34.2 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 29.7 (6 C, *C*H$_2$), 29.6 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.2 (2 C, *C*H$_2$), 26.1 (2 C, *C*H$_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 2925, 2854, 1606, 1578, 1494, 1468, 1392, 1363, 1304, 1252, 1202, 1137, 1106, 1027, 939, 901, 843, 811, 737, 673, 630, 603 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 259, 307 nm. MS (FAB): *m*/*z* = 890 [M$^+$]. $C_{40}H_{58}Br_4O_2$ (890.53): calcd. C 53.95, H 6.57; found C 52.78, H 6.12.

**1,12-Bis(4-*tert*-butyl-2-ethynylphenyloxy)dodecane (10a):** Diisopropylamine (4.80 g, 47.52 mmol) was dissolved in THF (120 mL), cooled to 0 °C, treated with a 1.6 M *n*-butyllithium solution (30 mL, 48.00 mmol) in hexane and stirred for 1 h. Subsequently, 100 mL of the resulting solution of LDA (0.30 M, 30.00 mmol) was added at –80 °C to **9a** (5.00 g, 6.00 mmol), dissolved in THF (120 mL). The reaction process was controlled by TLC ($CH_2Cl_2$/hexane, 1:1, $R_f$ = 0.49). After 30 min the cooling bath was removed and aqueous HCl (10%, 200 mL) and $CH_2Cl_2$ (200 mL) were added. After separating the layers the aqueous layer was extracted three times with $CH_2Cl_2$ (150 mL each). Then the organic layers were washed with water (200 mL) and dried with $Na_2SO_4$. A clear and colourless oil was isolated by column chromatography (silica gel, $CH_2Cl_2$/hexane, 1:1) (2.93 g, 95%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.45 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.28 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 6.78 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 3.99 (t, $^3J$ = 6.6 Hz, 4 H, OC$H_2$), 3.22 (s, 2 H, C≡C*H*), 1.80 (m, 4 H, OCH$_2$C$H_2$), 1.44 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.26 [br. s, 30 H, C$H_2$ and C(C$H_3$)$_3$]

ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 157.9 (2 C, Ar*C*), 142.8 (2 C, Ar*C*), 130.9 (2 C, Ar*C*H), 127.0 (2 C, Ar*C*), 111.6 (2 C, Ar*C*H), 110.8 (2 C, Ar*C*H), 80.7 (2 C, C≡*C*H), 80.3 (2 C, *C*≡CH), 68.9 (2 C, O*C*H$_2$), 34.1 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 29.7 (4 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 29.2 (2 C, *C*H$_2$), 26.0 (2 C, *C*H$_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 3316, 3289, 2926, 2856, 2111, 1741, 1602, 1498, 1467, 1393, 1363, 1266, 1204, 1139, 1104, 1019, 895, 814, 776, 721 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ [nm] = 241, 249, 305, 346 nm. MS (FAB): *m*/*z* = 515 [M$^+$]. $C_{36}H_{50}O_2$ (514.76): calcd. C 83.99, H 9.79; found C 84.18, H 10.11.

**1,14-Bis(4-*tert*-butyl-2-ethynylphenyloxy)tetradecane (10b):** The bis-(acetylene)-terminated compound **10b** was obtained from a solution of diisopropylamine (11.17 g, 110.59 mmol) in THF (280 mL) and a 1.6 M solution of *n*-butyllithium (69 mL, 110.40 mmol). The resulting 0.3 M LDA solution (230 mL, 69.00 mmol) was added dropwise to a solution of **9b** (8.18 g, 9.49 mmol) in THF (180 mL) at –80 °C. After 20 min (TLC: $CH_2Cl_2$/hexane, 3:7, $R_f$ = 0.28) no more starting material was observed. The cooling bath was removed and 200 mL 10% aqueous HCl, 100 mL water and 200 mL hexane were added. The aqueous layer was extracted with hexane (100 mL) and the combined organic layers washed three times with water (150 mL each) and dried with $Na_2SO_4$. Purification was achieved by column chromatography (silica gel, ethyl acetate/hexane, 1:9) and yielded **10b** as a clear oil (4.63 g, 90%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.44 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.28 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 6.78 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 3.99 (t, $^3J$ = 6.6 Hz, 4 H, OC*H*$_2$), 3.22 (s, 2 H, C≡C*H*), 1.80 (m, 4 H, OCH$_2$C*H*$_2$), 1.45 (m, 4 H, OCH$_2$CH$_2$C*H*$_2$), 1.32–1.25 (m, 16 H, C*H*$_2$), 1.26 [s, 18 H, C(C*H*$_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 158.0 (2 C, Ar*C*), 142.9 (2 C, Ar*C*), 131.0 (2 C, Ar*C*H), 127.1 (2 C, Ar*C*), 111.6 (2 C, Ar*C*H), 110.8 (2 C, Ar*C*H), 80.7 (2 C, C≡*C*H), 80.3 (2 C, *C*≡CH), 68.8 (2 C, O*C*H$_2$), 34.0 [2 C, *C*(CH$_3$)$_3$], 31.3 [6 C, C(*C*H$_3$)$_3$], 29.6 (4 C, *C*H$_2$), 29.5 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 25.9 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3315, 3288, 2926, 2855, 1603, 1500, 1468, 1393, 1363, 1270, 1140, 1105, 1021, 894, 813, 635 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 242, 250, 298, 306 nm. MS (FAB): *m*/*z* = 543 [M$^+$]. $C_{38}H_{54}O_2$ (542.81): calcd. C 84.08, H 10.03; found 83.91, H 9.89.

**1,16-Bis(4-*tert*-butyl-2-ethynylphenyloxy)hexadecane (10c):** To a solution of diisopropylamine (2.58 g, 25.56 mmol) in THF (64 mL) a 1.6 M solution of *n*-butyllithium (6 mL, 25.60 mmol) in hexane was added at 0 °C. From the resulting 0.31 M LDA solution, 50 mL (15.50 mmol) were added to a solution of **5c** (1.84 g, 2.07 mmol) in THF (50 mL). By TLC monitoring (TLC: ethyl acetate/hexane, 1:9, $R_f$ = 0.45) it was demonstrated that the reaction was completed after 30 min. The reaction mixture was worked up with aqueous HCL solution (10%, 150 mL) and $CH_2Cl_2$ (150 mL). After separating the two layers, the aqueous layer was extracted three times with $CH_2Cl_2$ (100 mL each), and the combined organic phases washed with water (250 mL). Drying of the $CH_2Cl_2$ solution with $Na_2SO_4$ and subsequent column chromatography (silica gel, ethyl acetate/hexane, 1:9) gave **10c** as a white solid (1.00 g, 85%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.44 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.27 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 6.78 (d, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 3.99 (t, $^3J$ = 6.6 Hz, 4 H, OC*H*$_2$), 3.22 (s, 2 H, C≡C*H*), 1.80 (m, 4 H, OCH$_2$C*H*$_2$), 1.44 (m, 4 H, OCH$_2$CH$_2$C*H*$_2$), 1.32–1.24 (m, 20 H, C*H*$_2$), 1.26 [s, 18 H, C(C*H*$_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 158.0 (2 C, Ar*C*), 143.0 (2 C, Ar*C*), 131.0 (2 C, Ar*C*H), 127.1 (2 C, Ar*C*), 111.7 (2 C, Ar*C*H), 110.9 (2 C, Ar*C*H), 80.7 (2 C, C≡*C*H), 80.3 (2 C, *C*≡CH), 68.9 (2 C, O*C*H$_2$), 34.0 [2 C, *C*(CH$_3$)$_3$], 31.3 [6 C, C(*C*H$_3$)$_3$], 29.7 (6 C, *C*H$_2$), 29.6 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 25.9 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3315, 3291, 2926, 2854, 1602, 1500, 1468, 1393, 1363, 1269, 1140, 1105, 1020, 894, 813, 635 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ [nm] = 241, 250, 298, 306 nm. MS (FAB): *m*/*z* = 571 [M$^+$]. $C_{40}H_{58}O_2$ (570.86): calcd. C 84.15, H 10.24; found C 83.79, H 10.20.

**1,12-Bis[4-*tert*-butyl-2-(4-trimethylsilylbutadiynyl)phenyloxy]dodecane (12a):** CuCl (1.74 g, 17.58 mmol) and TMEDA (0.82 mg, 7.10 mmol) were dissolved in acetone (160 mL) and stirred for 50 min. Subsequently, the mixture was filtered several times until no more precipitating solid was found in the filtrate. The filter residues were washed with acetone (5 mL each). The dark green solution was added dropwise over a period of 30 min to a solution of (trimethylsilyl)acetylene (**11**; 2.29 g, 23.37 mmol) and **10a** (1.00 g, 1.95 mmol) in acetone (100 mL), through which oxygen was bubbled for 15 min. During the continuous bubbling of oxygen through the solution, small quantities of acetone were added in order to prevent thickening. Because there was still starting material detectable by TLC monitoring ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.32), an additional re-dosage of (trimethylsilyl)acetylene (**11**, 304 mg, 3.12 mmol) was added in three portions (76 mg, 76 mg and finally 152 mg). After 30 h stirring, to the resulting mixture HCl (10%, 120 mL), $H_2O$ (130 mL) and hexane (150 mL) were added. Subsequently, the two layers were separated, and the aqueous layer extracted with hexane (3 × 100 mL). The combined hexane layers were washed with aqueous HCl (10%, 100 mL) and water (2 × 100 mL), and dried with $Na_2SO_4$. By column chromatography (silica gel, $CH_2Cl_2$/cyclohexane, 1:9) **12a** was obtained as a white solid (772 mg, 56%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.43 (d, $^4J$ = 2.6 Hz, 2 H, Ar–*H*), 7.27 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 6.75 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 3.97 (t, $^3J$ = 6.7 Hz, 4 H, OC*H*$_2$), 1.79 (m, 4 H, OCH$_2$C*H*$_2$), 1.45 (m, 4 H, OCH$_2$CH$_2$C*H*$_2$), 1.28–1.39 (m, 12 H, C*H*$_2$), 1.28 [18, H C(C*H*$_3$)$_3$], 0.21 [s, 18 H, Si(C*H*$_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 159.1 (2 C, Ar*C*), 143.0 (2 C, Ar*C*), 131.6 (2 C, Ar*C*H), 127.7 (2 C, Ar*C*H), 111.7 (2 C, Ar*C*H), 110.3 (2 C, Ar*C*), 90.4 (2 C, SiC≡*C*C≡*C*), 88.4 (2 C, SiC≡*C*C≡C), 77.2 (2 C, SiC≡*C*), 74.3 (2 C, Si*C*≡C), 69.0 (2 C, O*C*H$_2$), 34.0 [2 C, *C*(CH$_3$)$_3$], 31.3 [6 C, C(*C*H$_3$)$_3$], 29.9–26.3 (10 C, *C*H$_2$), –0.34 [6 C, Si(*C*H$_3$)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2961, 2927, 2855, 2204, 2099, 1729, 1601, 1519, 1499, 1466, 1391, 1364, 1283, 1250, 1157, 1075, 1041, 846, 815, 762, 735, 669 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 288, 317, 328 nm. MS (FAB): *m*/*z* = 707 [M$^+$]. $C_{46}H_{66}O_2Si_2$ (707.17): calcd. C 78.13, H 9.41; found C 77.83, H 9.21.

**1,14-Di{4-*tert*-butyl-2-[4-(trimethylsilyl)butadiynyl]phenyloxy}-tetradecane (12b):** A filtered solution of CuCl (11.14 g, 11.52 mmol) in acetone (80 mL) and TMEDA (545 mg, 4.70 mmol) was added dropwise to a solution of **10b** (0.70 g, 1.29 mmol) and **11** (1.38 g, 14.08 mmol) as for the synthesis of **12a** (TLC control: $CH_2Cl_2$/hexane, 3:7, $R_f$ = 0.49). After 18 h additionally 50 mL of the Cu/TMEDA solution and (trimethylsilyl)acetylene (**11**, 1.38 g, 14.08 mmol) were added. After a total of 24 h an aqueous solution of HCl (10%, 10 mL), water (60 mL) and hexane (100 mL) was added to the mixture. Extraction and washings with hexane (3 × 100 mL), aqueous HCl (10%, 70 mL) and drying was performed like with **12a**. By column chromatography a yellow solid **12b** was obtained (568 mg, 60%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.43 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.27 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 6.75 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 3.97 (t, $^3J$ = 6.6 Hz, 4 H, OC*H*$_2$), 1.79 (m, 4 H, OCH$_2$C*H*$_2$), 1.44 (m, 4 H, OCH$_2$CH$_2$C*H*$_2$), 1.33–1.25 (m, 16 H, C*H*$_2$), 1.24 [s, 18 H, C(C*H*$_3$)$_3$], 0.20 [s, 18 H, Si(C*H*$_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 159.1 (2 C, Ar*C*), 143.1 (2 C, Ar*C*), 131.6 (2 C, Ar*C*H), 127.8 (2 C, Ar*C*H), 111.7 (2 C, Ar*C*H), 110.3 (2 C, Ar*C*), 90.4 (2

C, SiC≡CC≡*C*), 88.4 (2 C, SiC≡C*C*≡C), 77.2 (2 C, SiC≡*C*), 74.3 (2 C, Si*C*≡C), 69.0 (2 C, O*C*$H_2$), 34.0 [2 C, *C*($CH_3$)$_3$], 31.3 [6 C, C(*C*$H_3$)$_3$], 29.7 (2 C, *C*$H_2$), 29.6 (2 C, *C*$H_2$), 29.5 (2 C, *C*$H_2$), 29.4 (2 C, *C*$H_2$), 29.1 (2 C, *C*$H_2$), 25.9 (2 C, *C*$H_2$), –0.6 [6 C, Si(*C*$H_3$)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2961, 2925, 2853, 2203, 2099, 1601, 1499, 1466, 1392, 1364, 1284, 1250, 1156, 1040, 846, 816, 762, 636 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 256, 271, 288, 316, 328 nm. MS (FAB): *m*/*z* = 735 [$M^+$]. $C_{48}H_{70}O_2Si_2$ (735.22): calcd. C 78.41, H 9.60; found C 77.91, H 9.74.

**1,16-Bis[4-*tert*-butyl-2-(4-trimethylsilylbutadiynyl)phenyloxy]hexadecane (12c):** CuCl (1.86 g, 18.80 mmol) and TMEDA (0.87 g, 7.52 mmol) were dissolved in acetone (150 mL) and the solution stirred for 1 h. Subsequently, the mixture was filtered and washed with acetone as for **12a**. This solution was slowly added to a solution of **10c** (1.09 g, 2.01 mmol) and **11** (2.15 g, 22.00 mmol) in acetone (90 mL). Oxygen was passed through the reaction mixture and the reaction progress monitored by TLC ($CH_2Cl_2$/hexane, 4:6, $R_f$ = 0.69). During the following 24 h, additional four portions (2 × 0.59 g, 6.02 mmol each and 2 × 0.28 g, 2.85 mmol each) of **11** were added. Work up was performed with aqueous HCl (10%, 140 mL), water (140 mL), hexane (200 mL), two extractions with hexane (150 mL each), washings with HCl (10%, 200 mL) and water (2 × 250 mL) and drying ($Na_2SO_4$) as for compound **12a**. Column chromatography (silica gel, $CH_2Cl_2$/hexane, 2:8) yielded 616 mg (40%) of a white solid **12c**. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.43 (d, $^4J$ = 2.5 Hz, 2 H, Ar*H*), 7.27 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.5 Hz, 2 H, Ar*H*), 6.75 (d, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 3.97 (t, $^3J$ = 6.7 Hz, 4 H, OC$H_2$), 1.79 (m, 4 H, OC$H_2$C$H_2$), 1.44 (m, 4 H, OC$H_2$C$H_2$C$H_2$), 1.33–1.24 (m, 20 H, C$H_2$), 1.24 [s, 18 H, C(C$H_3$)$_3$], 0.20 [s, 18 H, Si(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 159.1 (2 C, Ar*C*), 143.1 (2 C, Ar*C*), 131.6 (2 C, Ar*C*H), 127.8 (2 C, Ar*C*H), 111.7 (2 C, Ar*C*H), 110.3 (2 C, ArC), 90.4 (2 C, SiC≡CC≡*C*), 88.4 (2 C, SiC≡C*C*≡C), 77.2 (2 C, SiC≡*C*), 74.3 (2 C, Si*C*≡C), 69.0 (2 C, O*C*$H_2$), 34.0 [2 C, *C*($CH_3$)$_3$], 31.3 [6 C, C(*C*$H_3$)$_3$], 29.7 (6 C, *C*$H_2$), 29.6 (2 C, *C*$H_2$), 29.3 (2 C, *C*$H_2$), 29.1 (2 C, *C*$H_2$), 25.9 (2 C, *C*$H_2$), –0.3 [6 C, Si(*C*$H_3$)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2961, 2926, 2852, 2204, 2099, 1601, 1499, 1467, 1391, 1364, 1284, 1250, 1157, 1039, 847, 815, 761, 636 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 256, 271, 288, 316, 328 nm. MS (FAB): *m*/*z* = 764 [$M^+$]. $C_{50}H_{74}O_2Si_2$ (763.27): calcd. C 78.67, H 9.77; found C 77.98, H 9.55.

**1,12-Bis(2-butadiynyl-4-*tert*-butylphenyloxy)dodecane (14a):** A spatulum tip of $K_2CO_3$ was added to TMS-protected **12a** (750 mg, 1.06 mmol), dissolved in a 1:1 mixture of wet $CH_3OH$ and THF. After 10 min no more starting material was observed (TLC: $CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.30), and subsequently water (50 mL), aqueous HCl (10%, 30 mL) and hexane (100 mL) were added. The reaction mixture was extracted with hexane twice (70 mL each) and the combined organic layers dried with $Na_2SO_4$. The remaining solution was concentrated to a few mL and immediately transformed to the tetrayne **15a**. MS (FAB): *m*/*z* = 563 [$M^+$].

**1,14-Bis(2-butadiynyl-4-*tert*-butylphenyloxy)tetradecane (14b):** To a solution of the TMS-protected butadiynyl derivative **12b** (180 mg, 0.24 mmol) in wet $CH_3OH$ (3 mL) and THF (4 mL) a minute amount of $K_2CO_3$ was added. By means of TLC monitoring ($CH_2Cl_2$/hexane, 3:7, $R_f$ = 0.38), after 1 h no more starting material was detected. Then aqueous HCl (10%, 15 mL), water (15 mL) and hexane (45 mL) were added. The layers were separated and the aqueous layer was extracted twice with hexane (50 mL each). The combined hexane layers were dried with $Na_2SO_4$. The clear and colorless solution obtained was carefully concentrated to 10 mL and immediately applied for the subsequent transformation. MS (FAB): *m*/*z* = 591 [$M^+$].

**1,16-Bis(2-butadiynyl-4-*tert*-butylphenyloxy)hexadecane (14c):** To a solution of **12c** (567 mg, 0.74 mmol) in a 1:1 mixture of $CH_3OH$/THF (10 mL) a spatulum tip of $K_2CO_3$ was added and the mixture stirred. After 1 h stirring no more starting material was observed (TLC control: ethyl acetate/hexane, 2:8, $R_f$ = 0.52). Subsequently, aqueous HCl (10%, 70 mL), water (45 mL) and hexane (140 mL) were added and the layers separated. The aqueous layer was extracted twice with hexane (140 mL each) and the combined organic phases dried with $Na_2SO_4$. The hexane solution was concentrated and immediately used without characterization.

**Dibenzo-dioxacycloalkanetetrayne Derivative 15a:** TMEDA (455 mg, 3.92 mmol) was added to a solution of CuCl (958 mg, 9.68 mmol) in acetone (50 mL) and the mixture stirred for 1 h. Subsequently, the reaction mixture was filtered several times. The hexane solution of **14a**, described above, was diluted with acetone (250 mL), and added dropwise to the filtrate, while a gentle stream of oxygen was passed through the solution. After a period of 15 h no more starting material was observed by TLC control ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.42), and aqueous HCl (10%, 50 mL), water (50 mL) and hexane (200 mL) were added. After separating the two layers, the aqueous layer was extracted twice with hexane (200 mL each) and the combined organic phases dried with $Na_2SO_4$. By column chromatography (silica gel, $CH_2Cl_2$/hexane, 2:8) the yellow product zone was separated and **15a** was isolated as a yellow oil (42 mg, 7% with respect to **12a**). $^1$H NMR (400 MHz, $CDCl_3$, 22 °C): $\delta$ = 7.42 (d, $^4J$ = 2.2 Hz, 2 H, Ar*H*), 7.32 (dd, $^4J$ = 2.2 Hz, $^3J$ = 8.6 Hz, 2 H, Ar*H*), 6.78 (d, $^3J$ = 8.6 Hz, Ar*H*), 3.99 (t, $^3J$ = 5.5 Hz, 4 H, OC$H_2$), 1.74 (m, 4 H, OC$H_2$C$H_2$), 1.56 (m, 4 H, OC$H_2$C$H_2$C$H_2$), 1.40–1.30 (m, 12 H, C$H_2$), 1.25 [s, 18 H, C–(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.50 MHz, $CDCl_3$, 25 °C): $\delta$ = 160.8 (2 C, Ar*C*), 143.5 (2 C, Ar*C*), 130.7 (2 C, Ar*C*H), 128.5 (2 C, Ar*C*H), 112.3 (2 C, Ar*C*H), 110.1 (2 C, Ar*C*), 77.6 [2 C, (ArC≡*C*C≡C)$_2$], 75.1 [2 C, (Ar*C*≡CC≡C)$_2$], 69.7 (2 C, O*C*$H_2$), 67.6 [2 C, (ArC≡C*C*≡C)$_2$], 64.0 (ArC≡CC≡*C*)$_2$) , 34.1 [2 C, *C*($CH_3$)$_3$], 31.3 [6 C, C(*C*$H_3$)$_3$], 30.3 (2 C, *C*$H_2$), 30.2 (2 C, *C*$H_2$), 30.1 (2 C, *C*$H_2$), 29.7 (2 C, *C*$H_2$), 26.9 (2 C, *C*$H_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 2963, 2922, 2853, 2152, 2048, 1599, 1499, 1466, 1386, 1362 1261, 1093, 1024, 805, 705, 624 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 286, 335, 356, 384, 416 nm. MS (FAB): *m*/*z* = 560 [$M^+$]. $C_{40}H_{48}O_2$ (560.78): calcd. C 85.67, H 8.63; found C 85.24, H 8.56.

**Dibenzo-dioxacycloalkanetetrayne Derivative 15b:** CuCl (400 mg, 4.00 mmol) and TMEDA (192 mg, 1.66 mmol) were dissolved in acetone (25 mL) and stirred for 1 h. Subsequently, the solution was filtered several times and the filter cake was rinsed each time with 3–4 mL of acetone. To this dark green solution the hexane solution of **14b** (see above), diluted with acetone (55 mL), was added dropwise over a period of 3 h. During this time, a gentle stream of oxygen was passed through the mixture. After the completion of the reaction (TLC control: ethyl acetate/hexane, 2:8; $R_f$ = 0.63) water (20 mL), aqueous HCl (10%, 20 mL) and hexane (60 mL) were added and the layers separated. The aqueous layer was extracted twice with hexane (50 mL each), the combined organic layers were washed with water (200 mL) and dried with $Na_2SO_4$. Colum chromatography allowed the isolation of the yellow product zone, and **15b** was isolated as a yellow oil (11 mg, 8% relative to **12b**). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.45 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.31 (dd, $^4J$ = 2.5 Hz, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 6.76 (d, $^3J$ = 8.8 Hz, Ar*H*), 3.99 (t, $^3J$ = 5.4 Hz, 4 H, OC$H_2$), 1.75 (m, 4 H, OC$H_2$C$H_2$), 1.53 (m, 4 H, OC$H_2$C$H_2$C$H_2$), 1.40–1.30 (m, 20 H, C$H_2$), 1.25 [s, 18 H, C–(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.50 MHz, $CDCl_3$, 25 °C): $\delta$ = 160.0 (2 C, Ar*C*), 143.2 (2 C, Ar*C*), 131.8 (2 C, Ar*C*H), 128.5 (2 C, Ar*C*H), 111.5 (2 C, Ar*C*H), 109.5 (2 C, Ar*C*), 77.6 [2 C, (Ar*C*≡*C*C≡C)$_2$], 75.2 [2 C, (ArC≡*C*C≡C)$_2$], 69.1 (2 C,

O*C*H$_2$), 67.7 [2 C, (ArC≡C*C*≡C)$_2$], 64.2 (ArC≡CC≡*C*)$_2$) , 34.1 [2 C, *C*(CH$_3$)$_3$], 31.3 [6 C, C(*C*H$_3$)$_3$], 29.7 (2 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.2 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 29.0 (2 C, *C*H$_2$), 26.3 (2 C, *C*H$_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 2963, 2922, 2852, 2151, 2047, 1598, 1498, 1466, 1387, 1363, 1261, 1096, 1022, 804, 704, 625 cm$^{-1}$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ = 286, 335, 355, 383, 415 nm. MS (FAB): *m*/*z* = 588 [M$^+$]. C$_{42}$H$_{52}$O$_2$ (588.83): calcd. C 85.66, H 8.90; found C 84.97, H 8.88.

**Dibenzo-dioxacycloalkanetetrayne Derivative 15c:** CuCl (1.41 g, 14.20 mmol) and TMEDA (0.68 g, 5.90 mmol) in acetone (90 mL) was stirred for 1 h and subsequently filtered repeatedly until no precipitation occurred anymore. The filter cake was rinsed with acetone (5 mL each) for each filtration cycle. Subsequently, the readily prepared hexane solution of **14c** (see above), diluted with acetone (200 mL), was added dropwise to this solution over a period of 2 h. During this period of time, a gentle stream of oxygen was bubbled through the solution. After 20 h by TLC control no more starting material was observed and a yellow product band occurred (TLC: ethyl acetate/hexane, 1:9; $R_f$ = 0.66). Water (60 mL), aqueous HCl (10%, 60 mL) and hexane (150 mL) were added to the reaction mixture and the layers separated. The aqueous layer was extracted twice with hexane (160 mL each) and the combined organic layers washed with aqueous HCl (10%, 100 mL) and water (200 mL), and dried with Na$_2$SO$_4$. By column chromatography (silica gel, ethyl acetate/hexane, 3:97) **15c** was isolated as a yellow oil (6 mg, 1.3%). $^1$H NMR (400 MHz, CDCl$_3$, 22 °C): $\delta$ = 7.46 (d, $^4J$ = 2.4 Hz, 2 H, Ar*H*), 7.31 (dd, $^4J$ = 2.6 Hz, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 6.75 (d, $^3J$ = 8.8 Hz, Ar*H*), 3.98 (t, $^3J$ = 5.7 Hz, 4 H, OC*H*$_2$), 1.77 (m, 4 H, OCH$_2$C*H*$_2$), 1.49 (m, 4 H, OCH$_2$CH$_2$C*H*$_2$), 1.38–1.23 (m, 16 H, C*H*$_2$), 1.25 [s, 18 H, C–(C*H*$_3$)$_3$] ppm. $^{13}$C NMR (100.50 MHz, CD$_2$Cl$_2$, 22 °C): $\delta$ = 160.0 (2 C, Ar*C*), 143.2 (2 C, Ar*C*), 131.8 (2 C, Ar*C*H), 128.5 (2 C, Ar*C*H), 111.5 (2 C, Ar*C*H), 109.5 (2 C, Ar*C*), 77.6 [2 C, (ArC≡*C*C≡C)$_2$], 75.2 [2 C, (Ar*C*≡CC≡C)$_2$], 69.1 (2 C, O*C*H$_2$), 67.6 [2 C, (ArC≡C*C*≡C)$_2$], 64.2 (ArC≡CC≡*C*)$_2$) , 34.1 [2 C, *C*(CH$_3$)$_3$], 31.3 [6 C, C(*C*H$_3$)$_3$], 29.7 (2 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.2 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 28.7 (2 C, *C*H$_2$), 26.3 (2 C, *C*H$_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 2925, 2854, 2196, 2126, 2073, 1737, 1600, 1499, 1466, 1363, 1263, 1150, 1133, 1101, 891, 813, 720, 626 cm$^{-1}$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ = 271, 286, 336, 357, 384, 416 nm. MS (FAB): *m*/*z* = 617 [M$^+$]. C$_{44}$H$_{56}$O$_2$ (616.89): calcd. C 85.66, H 9.15; found C 84.89, H 9.01.

**Synthesis of Hexayne Macrocycles 18a–c**

**1,20-Bis[4-*tert*-butyl-2-(2,2-dibromoethenyl)phenyloxy]eicosane (9d):** A solution of CBr$_4$ (7.23 g, 21.78 mmol) in CH$_2$Cl$_2$ (40 mL) was cooled to 0 °C and PPh$_3$ (11.41 g, 43.55 mmol) was added. To the resulting yellow suspension the bis(aldehyde) **8d** (3.00 g, 4.73 mmol), dissolved in CH$_2$Cl$_2$ (50 mL) was added and the cooling bath removed. After 30 min, when TLC control (CH$_2$Cl$_2$, $R_f$ = 0.82) showed complete transformation, water (400 mL) and CH$_2$Cl$_2$ (300 mL) were added. After separating the layers, the aqueous layer was extracted twice with CH$_2$Cl$_2$ (200 mL each). The combined organic layers were dried with Na$_2$SO$_4$. From column chromatography (silica gel, CH$_2$Cl$_2$), the pure product **9d** was obtained as a white solid (4.37 g, 98%). $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ = 7.75 (d, $^4J$ = 2.4 Hz, 2 H, Ar*H*), 7.61 (s, 2 H, C*H*CBr$_2$), 7.28 (dd, $^4J$ = 2.4 Hz, $^3J$ = 8.5 Hz, 2 H, Ar*H*), 6.76 (d, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 3.93 (t, $^3J$ = 6.5 Hz, 4 H, OC*H*$_2$), 1.77 (m, 4 H, OCH$_2$C*H*$_2$), 1.42 (m, 4 H, OCH$_2$CH$_2$C*H*$_2$), 1.29 (br. s, 28 H, C*H*$_2$), 1.25 [s, 18 H, C(C*H*$_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$, 25 °C): $\delta$ = 153.9 (2 C, Ar*C*), 142.6 (2 C, Ar*C*), 133.4 (2 C, Ar*C*H), 126.4 (4 C, Ar*C*H and Br$_2$C=*C*H), 123.8 (2 C, Ar*C*), 111.0 (2 C, Ar*C*H), 88.9 (2 C, Br$_2$*C*=CH), 68.5 (2 C, O*C*H$_2$), 34.2 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 29.7 (10 C, *C*H$_2$), 29.6 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.2 (2 C, *C*H$_2$), 26.1 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2959, 2922, 2850, 1606, 1494, 1467, 1391, 1363, 1305, 1251, 1138, 1106, 1018, 939, 901, 845, 812, 736, 673, 631, 581, 497 cm$^{-1}$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ = 259, 307 nm. MS (FAB): *m*/*z* = 946 [M$^+$]. C$_{44}$H$_{66}$Br$_4$O$_2$ (946.63): calcd. C 55.83, H 7.03; found C 56.28, H 7.37.

**1,32-Bis[4-*tert*-butyl-2-(2,2-dibromoethenyl)phenyloxy]dotriacontane (9e):** To a solution of CBr$_4$ (10.46 g, 31.51 mmol) in CH$_2$Cl$_2$ (65 mL) at 0 °C PPh$_3$ (16.51 g, 63.01 mmol) was added. To this yellowish suspension a solution of **8e** (5.50 g, 6.85 mmol) in CH$_2$Cl$_2$ (100 mL) was added dropwise and subsequently stirred for 30 min at 0 °C and for 30 min at room temperature. Subsequently, CH$_2$Cl$_2$ (300 mL) and water (300 mL) were added and the two layers separated. The organic layer was washed twice with water (300 mL each) and dried with Na$_2$SO$_4$. By column chromatography (silica gel 60, CH$_2$Cl$_2$/hexane, 1:1) the product **9e** was obtained as a white solid (7.38 g, 96.6%). $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ = 7.74 (d, $^4J$ = 2.3 Hz, 2 H, Ar*H*), 7.60 (s, 2 H, C*H*CBr$_2$), 7.27 (dd, $^4J$ = 2.3 Hz, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 6.76 (d, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 3.92 (t, $^3J$ = 6.4 Hz, 4 H, OC*H*$_2$), 1.78 (m, 4 H, OCH$_2$C*H*$_2$), 1.40 (m, 4 H, OCH$_2$CH$_2$C*H*$_2$), 1.29 [s, 18 H, C(C*H*$_3$)$_3$], 1.24 (br. s, 52 H, C*H*$_2$) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$, 25 °C): $\delta$ = 153.8 (2 C, Ar*C*), 142.4 (2 C, Ar*C*), 133.2 (2 C, Ar*C*H), 126.3 (2 C, Ar*C*H), 123.7 (4 C, Ar*C*H and Br$_2$C=*C*H), 111.0 (2 C, Ar*C*H), 88.9 (2 C, Br$_2$*C*=CH), 68.6 (2 C, O*C*H$_2$), 34.3 [2 C, *C*(CH$_3$)$_3$], 31.5 [6 C, C(*C*H$_3$)$_3$], 29.8 (22 C, *C*H$_2$), 29.7 (2 C, *C*H$_2$), 29.5 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 26.2 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2916, 2851, 1604, 1494, 1473, 1390, 1363, 1306, 1254, 1130, 1105, 1019, 939, 903, 844, 804, 717 cm$^{-1}$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ = 259, 307 nm. MS (FAB): *m*/*z* = 1114 [M$^+$]. C$_{56}$H$_{90}$Br$_4$O$_2$ (1114.94): calcd. C 60.33, H 8.14; found C 60.28, 8.15.

**1,40-Bis[4-*tert*-butyl-2-(2,2-dibromoethenyl)phenyloxy]tetracontane (9f):** PPh$_3$ (11.99 g, 45.78 mmol) was added to a solution of CBr$_4$ (7.60, 22.89 mmol) in CH$_2$Cl$_2$ (40 mL) at 0 °C. To the resulting yellow suspension the bis(aldehyde) **8f** (4.37 g, 4.78 mmol), dissolved in CH$_2$Cl$_2$ (180 mL), was added dropwise within 20 min. Subsequently, the cooling bath was removed and the progress of the reaction monitored by TLC (CH$_2$Cl$_2$/hexane, 2:8, $R_f$ = 0.50). After 1 h, CH$_2$Cl$_2$ (300 mL) and water (300 mL) were added and the layers separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (200 mL) and the combined organic layers washed twice with water (300 mL each). By column chromatography (silica gel, CH$_2$Cl$_2$/hexane, 2:8) the product **9f** was isolated (5.68 g, 97%) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ = 7.74 (d, $^4J$ = 2.3 Hz, 2 H, Ar*H*), 7.61 (s, 2 H, C*H*CBr$_2$), 7.27 (dd, $^4J$ = 2.3 Hz, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 6.76 (d, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 3.93 (t, $^3J$ = 6.4 Hz, 4 H, OC*H*$_2$), 1.77 (m, 4 H, OCH$_2$C*H*$_2$), 1.42 (m, 4 H, OCH$_2$CH$_2$C*H*$_2$), 1.29 [s, 18 H, C(C*H*$_3$)$_3$], 1.24 (br. s, 68 H, C*H*$_2$) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$, 25 °C): $\delta$ = 153.9 (2 C, Ar*C*), 142.6 (2 C, Ar*C*), 133.4 (2 C, Ar*C*H), 126.4 (4 C, Ar*C*H and Br$_2$C=*C*H), 123.8 (2 C, Ar*C*), 111.0 (2 C, Ar*C*H), 88.9 (2 C, Br$_2$*C*=CH), 68.5 (2 C, O*C*H$_2$), 34.2 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 29.7 (30 C, *C*H$_2$), 29.5 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 26.1 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2916, 2851, 1604, 1494, 1473, 1390, 1363, 1306, 1254, 1130, 1105, 1019, 939, 903, 844, 804, 717 cm$^{-1}$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ = 259, 307 nm. MS (FAB): *m*/*z* = 1227 [M$^+$]. C$_{64}$H$_{106}$Br$_4$O$_2$ (1227.15): calcd. C 62.64, H 8.71; found C 62.71 H: 8.70.

**1,20-Bis(4-*tert*-butyl-2-ethynylphenyloxy)eicosane (10d):** Diisopropylamine(2.626.37 mmol) and a 1.6 M solution of *n*-butyllithium

(16.54 mL, 26.46 mmol) in hexane were mixed and transferred into THF (66 mL) and stirred for 1 h. The resulting 0.3 M lithium diisopropylamide solution was given in a dropping funnel, and a few drops of the solution were added to a suspension of the tetrabromo compound **9d** (2.00 g, 2.11 mmol) in THF (30 mL) at –50 °C. When the suspended solid **9d** dissolved, the mixture was cooled to –80 °C and 28 mL of the LDA solution were added. The reaction process was monitored by TLC ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.09). After 20 min each, 8 mL (2.40 mmol) and two times 10 mL (3.00 mmol) of the LDA solution from above were added additionally to obtain a complete transformation. After allowing to warm to room temperature, an aqueous HCl solution (10%, 200 mL) and $CH_2Cl_2$ (200 mL) were added. The two phases were separated, and the aqueous layer extracted three times with $CH_2Cl_2$ (150 mL each). The combined organic layers were dried with $Na_2SO_4$ and by means of column chromatography (silica gel, $CH_2Cl_2$/hexane, 1:3) the product **10d** was obtained as a white solid (988 mg, 75%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.45 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.28 (dd, $^4J$ = 2.6 Hz, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 6.78 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 3.99 (t, $^3J$ = 6.6 Hz, 4 H, OC$H_2$), 3.22 (s, 2 H, ArC≡C–*H*), 1.80 (m, 4 H, OCH$_2$C$H_2$), 1.45 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.27 (s, 28 H, C$H_2$), 1.24 [s, 18 H, C(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 158.0 (2 C, Ar*C*), 143.0 (2 C, Ar*C*), 131.0 (2 C, Ar*C*H), 127.1 (2 C, Ar*C*H), 111.7 (2 C, Ar*C*H), 110.9 (2 C, Ar*C*C≡C), 80.7 (2 C, Ar*C*≡C), 80.3 (2 C, ArC≡*C*), 68.9 (2 C, O*C*H$_2$), 34.0 [2 C, *C*(CH$_3$)$_3$], 31.3 (10 C, *C*H$_2$), 29.7 [6 C, C(*C*H$_3$)$_3$], 29.6 (2 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 25.9 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3310, 3284, 2921, 2849, 2106, 1603, 1503, 1463, 1391, 1362, 1271, 1255, 1141, 1105, 1004, 891, 819, 725, 649, 635, 605 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 242, 250, 298, 306 nm. MS (FAB): *m*/*z* = 628 [M$^+$]. $C_{44}H_{66}O_2$ (626.97): calcd. C 84.29, H 10.61; found C 83.98, H 10.57.

**1,32-Bis(4-*tert*-butyl-2-ethynylphenyloxy)dotriacontane (10e):** To a solution of diisopropylamine (8.48 g, 84.01 mmol) in THF (210 mL) a solution of *n*-butyllithium in hexane (1.6 M, 52.5 mL, 84.01 mmol) was added at 0 °C and stirred for 1 h at this temperature. Under vigorous stirring, 140 mL of this LDA solution (42 mmol) were added rapidly dropwise to a solution of **9e** (7.38 g, 6.62 mmol) in THF (110 mL) at –80 °C. Than the reaction mixture was slowly warmed to room temperature, and subsequently HCl (10%, 200 mL) and $CH_2Cl_2$ were added. The separated aqueous layer was extracted twice with $CH_2Cl_2$ (200 mL each), and the combined organic phases were dried with $Na_2SO_4$. Purification by column chromatography (silica gel, $CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.25) delivered the product **10e** (3.28 g, 62%) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.44 (d, $^4J$ = 2.4 Hz, 2 H, Ar*H*), 7.28 (dd, $^4J$ = 2.4 Hz, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 6.78 (d, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 3.99 (t, $^3J$ = 6.6 Hz, 4 H, OC$H_2$), 3.22 (s, 2 H, ArC≡C*H*), 1.80 (m, 4 H, OCH$_2$C$H_2$), 1.46 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.26 [s, 18 H, C(C$H_3$)$_3$], 1.23 (br. s, 52 H, C$H_2$) ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 158.0 (2 C, Ar*C*), 142.9 (2 C, Ar*C*), 131.0 (2 C, Ar*C*H), 127.1 (2 C, Ar*C*H), 111.6 (2 C, Ar*C*H), 110.9 (2 C, Ar*C*C≡C), 80.7 (2 C, Ar*C*≡C), 80.3 (2 C, ArC≡*C*), 68.9 (2 C, O*C*H$_2$), 34.0 [2 C, *C*(CH$_3$)$_3$], 31.3 [6 C, C(*C*H$_3$)$_3$], 29.7 (22 C, *C*H$_2$), 29.6 (2 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 25.9 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3443, 3310, 3286, 2921, 2849, 2361, 1636, 1502, 1463, 1391, 1269, 1141, 1104, 819, 725, 635 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 242, 249, 298,305 nm. MS (FAB): *m*/*z* = 796 [M$^+$]. $C_{56}H_{90}O_2$ (795.28): calcd. C 84.57, H 11.41; found C 84.42, H 11.45.

**1,40-Bis(4-*tert*-butyl-2-ethynylphenyloxy)tetracontane (10f):** A solution of diisopropylamine (2.26 g, 22.38 mmol) in THF (56 mL) was cooled to 0 °C, treated with a 1.6 M solution of *n*-butyllithium (14 mL, 22.40 mmol) in hexane and stirred for 1 h. In the meantime, the tetrabromo compound **9f** (1.58 g, 1.29 mmol) was dissolved in THF (50 mL) and cooled to –20 °C (partially precipitating). To this resulting suspension 26 mL (7.95 mmol) of the 0.3 M LDA solution from above were added dropwise, and the solution warmed to room temperature over a period of 2 h. At a temperature of 10 °C the former white suspension became reddish and dark while turning clear. TLC control ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.23) proved complete conversion. Water (60 mL), aqueous HCl (10%, 150 mL) and $CH_2Cl_2$ (200 mL) were added and the two layers formed were separated. The aqueous layer was extracted twice with $CH_2Cl_2$ (200 mL each), and the combined organic layers were washed with water and dried with $Na_2SO_4$. By means of column chromatography (silica gel, $CH_2Cl_2$/hexane, 2:8) product **10f** was isolated (723 mg, 62%) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.44 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.28 (dd, $^4J$ = 2.6 Hz, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 6.78 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 3.99 (t, $^3J$ = 6.7 Hz, 4 H, OC$H_2$), 3.22 (s, 2 H, ArC≡C–*H*), 1.80 (m, 4 H, OCH$_2$C$H_2$), 1.44 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.27 [s, 18 H, C(C$H_3$)$_3$], 1.24 (br. s, 68 H, C$H_2$) ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 158.0 (2 C, Ar*C*), 142.9 (2 C, Ar*C*), 131.0 (2 C, Ar*C*H), 127.1 (2 C, Ar*C*H), 111.6 (2 C, Ar*C*H), 110.9 (2 C, Ar*C*C≡C), 80.7 (2 C, Ar*C*≡C), 80.3 (2 C, ArC≡*C*), 68.8 (2 C, O*C*H$_2$), 34.0 [2 C, *C*(CH$_3$)$_3$], 31.3 [6 C, C(*C*H$_3$)$_3$], 29.7 (30 C, *C*H$_2$), 29.6 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 25.9 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3443, 3310, 3286, 2921, 2849, 2361, 1636, 1502, 1463, 1391, 1269, 1141, 1104, 819, 725, 635 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 241, 249, 298,305 nm. $C_{64}H_{106}O_2$ (907.49): calcd. C 84.70, H 11.77; found C 84.33, H 11.85.

**1,20-Bis[4-*tert*-butyl-2-(6-trimethylsilylhexa-1,3,5-triynyl)phenyloxy]eicosane (17a):** The ethynyl derivative **10d** (300 mg, 0.48 mmol) was dissolved in dry and degassed THF (11 mL) at 0 °C. Subsequently the solution was treated with a 1.6 M solution of *n*-butyllithium (62 mL, 0.99 mmol) in hexane. After 60 min, CuCl (98 mg, 0.99 mmol) was added, and the mixture was warmed to room temperature. The resulting solution was diluted with pyridine (7 mL) and cooled again to 0 °C. Subsequently, a solution of 1-bromo-4-(trimethylsilyl)buta-1,3-diyne (**16**, 279 mg, 1.39 mmol) in THF (7 mL) was added and the heterocoupling reaction process controlled by TLC ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.32). After 20 min, another addition of **16** (undiluted, 106 mg, 0.52 mmol) followed. After a total of 60 min, aqueous HCl (10%, 40 mL), water (40 mL) and hexane (60 mL) were added. The two layers were separated, and the aqueous layer was extracted three times with hexane (60 mL each). The combined organic layers were dried with $Na_2SO_4$ and the product **17a** was isolated by column chromatography (silica gel, $CH_2Cl_2$/hexane, 2:8) as a white-yellowish solid (262 mg, 63%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.44 (d, $^4J$ = 2.5 Hz, 2 H, Ar*H*), 7.30 (dd, $^4J$ = 2.5 Hz, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 6.76 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 3.96 (t, $^3J$ = 6.5 Hz, 4 H, OC$H_2$), 1.78 (m, 4 H, OCH$_2$C$H_2$), 1.44 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.25 [s, 18 H, C(C$H_3$)$_3$], 1.24 (br. s, 28 H, C$H_2$), 0.20 [s, 18 H, Si(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 159.8 (2 C, ArC*C*O), 143.2 (2 C, Ar*C*C), 131.7 (2 C, Ar*C*H), 128.4 (2 C, Ar*C*H), 111.7 (2 C, Ar*C*H), 109.6 (2 C, Ar*C*), 88.7 (2 C,C≡CC≡C*C*≡CTMS), 88.4 (2 C, C≡CC≡CC≡*C*TMS), 77.2 (2 C, C≡*C*C≡CC≡CTMS), 74.5 (2 C, *C*≡CC≡CC≡CTMS), 69.0 (2 C, O*C*H$_2$), 67.0 (2 C, C≡C*C*≡CC≡CTMS), 62.2 (2 C, C≡CC≡*C*C≡CTMS), 34.1 [2 C, *C*(CH$_3$)$_3$], 31.3 [6 C, C(*C*H$_3$)$_3$], 29.7 (10 C, *C*H$_2$), 29.6 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.0 (2 C, *C*H$_2$), 25.9 (2 C, *C*H$_2$), –0.5 [6 C, Si(*C*H$_3$)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2925, 2854, 2184, 2165, 2073, 1600,1498, 1467, 1408, 1364, 1330, 1290, 1252, 1168, 1131, 1100, 1018, 925, 849, 760, 704, 662,

627 $cm^{-1}$. UV/Vis (hexane): $\lambda_{max}$ = 217, 223, 235, 248, 260, 287, 306, 314, 333, 354 nm. MS (FAB): *m*/*z* = 892 [$M^+$]. $C_{60}H_{82}O_2Si_2$ (891.44): calcd. C 80.84, H 9.27; found 80.54, H 9.12.

**1,32-Bis[4-*tert*-butyl-2-(6-trimethylsilylhexa-1,3,5-triynyl)phenyloxy]dotriacontane (17b):** A solution of **10e** (1.00 g. 1.26 mmol) in dry and degassed THF (32 mL) was cooled to 0 °C, treated with a 1.6 M solution of *n*-butyllithium in hexane (1.57 mL, 2.52 mmol) and stirred for 1 h at 0 °C. After removing the cooling bath, CuCl (249 mg, 2.52 mmol) was added and stirred for 90 min at room temperature, while an increasing turbidity and yellow coloration of the solution was observed. Subsequently the reaction mixture was concentrated to 10 mL at a rotatory pump vacuum and degassed pyridine (20 mL) was added. When the residing THF was removed in rotatory pump vacuo, a light green and almost clear solution remained, which was cooled to 0 °C and treated with a solution of 1-bromo-4-(trimethylsilyl)buta-1,3-diyne (**16**, 0.75 g, 3.73 mmol) in degassed THF (15 mL). The reaction process was controlled by TLC ($CH_2Cl_2$/hexane, 1:9, $R_f$ = 0.32). After 10 min aqueous HCl (10%, 200 mL), water (200 mL) and hexane (250 mL) were added and the phases separated. The aqueous phase was extracted twice with hexane (200 mL each) and the combined organic layers dried with $Na_2SO_4$. The product **17b** was obtained as a pale yellow solid (273 mg, 21%) by column chroamtography (silica gel, $CH_2Cl_2$/hexane, 1:9). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.44 (d, $^4J$ = 2.5 Hz, 2 H, Ar*H*), 7.30 (dd, $^4J$ = 2.5 Hz, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 6.76 (d, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 3.97 (t, $^3J$ = 6.5 Hz, 4 H, OC$H_2$), 1.78 (m, 4 H, OCH$_2$C$H_2$), 1.45 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.25 [s, 18 H, C(C$H_3$)$_3$], 1.24 (br. s, 52 H, C$H_2$), 0.20 [s, 18 H, Si(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 159.9 (2 C, Ar*C*O), 143.2 (2 C, Ar*C*C), 131.7 (2 C, Ar*C*H), 128.3 (2 C, Ar*C*H), 111.7 (2 C, Ar*C*H), 109.7 (2 C, Ar*C*), 88.7 (2 C,C≡CC≡C*C*≡CTMS), 88.4 (2 C, C≡CC≡CC≡*C*TMS), 77.2 (2 C, C≡*C*C≡CC≡CTMS), 74.5 (2 C, *C*≡CC≡CC≡CTMS), 69.0 (2 C, O*C*H$_2$), 67.0 (2 C, C≡C*C*≡CC≡CTMS), 62.2 (2 C, C≡CC≡*C*C≡CTMS), 34.1 [2 C, *C*(CH$_3$)$_3$], 31.3 [6 C, C(*C*H$_3$)$_3$], 29.7 (22 C, *C*H$_2$), 29.6 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 25.9 (2 C, *C*H$_2$), –0.5 [6 C, Si(*C*H$_3$)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 3444, 2923, 2850, 2353, 2187, 2167, 2075, 1601,1498, 1470, 1409, 1391, 1365, 1331, 1290, 1253, 1167, 1130, 1100, 1016, 925, 850, 760, 712, 662, 627, 493 $cm^{-1}$. UV/Vis (hexane): $\lambda_{max}$ = 216, 223, 235, 248, 260, 288, 304, 313, 331, 353 nm. MS (FAB): *m*/*z* = 1036 [$M^+$]. $C_{72}H_{106}O_2Si_2$ (1059.75): calcd. C 81.60, H 10.08; found C 81.22, H 10.41.

**1,40-Bis[4-*tert*-butyl-2-(6-trimethylsilylhexa-1,3,5-triynyl)phenyloxy]tetracontane (17c):** A suspension of the diyne **10f** (500 mg, 0.55 mmol) in degassed and dry THF (13 mL) was treated with a 1.61 M solution of butyllithium (0.71 mL, 1.13 mmol) in hexane at 0 °C. After 10 min the reaction was warmed to room temperature. After 50 min, additional CuCl (112 mg, 1.13 mmol) was added and a yellow-orange suspension was formed. Susequently, degassed pyridine (8 mL) was added and cooled to 0 °C. Finally, 1-bromo-4-(trimethylsilyl)buta-1,3-diyne (**16**, 320 mg, 1.59 mmol), dissolved in degassed THF (7 mL), was added and the reaction progress controlled by TLC ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.46). After 45 min, a second portion of 1-bromo-4-(trimethylsilyl)buta-1,3-diyne (**16**, 162 mg, 0.80 mmol) was added and the mixture stirred at room temperature for 18 h. Subsequently, water (60 mL), HCl (10%, 60 mL) and hexane (250 mL) were added and the black-brown solid tars removed by filtration. The two layers were separated, the upper organic layer was washed with water (500 mL) and dried with $Na_2SO_4$. The pure product **17c** was obtained by column chromatography (silica gel, $CH_2Cl_2$/hexane, 12:88) as a pale yellow solid (70 mg, 11%). $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 7.47 (d, $^4J$ = 2.4 Hz, 2 H, Ar*H*), 7.37 (dd, $^4J$ = 2.4 Hz, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 6.82 (d, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 4.00 (t, $^3J$ = 6.6 Hz, 4 H, OC$H_2$), 1.78 (m, 4 H, OCH$_2$C$H_2$), 1.44 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.27 (s, 68 H, C$H_2$), 1.26 [s, 18 H, C(C$H_3$)$_3$], 0.23 [s, 18 H, Si(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 160.3 (2 C, Ar*C*), 143.7 (2 C, Ar*C*C), 132.1 (2 C, Ar*C*H), 129.1 (2 C, Ar*C*H), 112.1 (2 C, Ar*C*H), 109.5 (2 C, Ar*C*), 89.5 (2 C,C≡CC≡C*C*≡CTMS), 88.2 (2 C, C≡CC≡CC≡*C*TMS), 77.2 (2 C, C≡*C*C≡CC≡CTMS), 75.1 (2 C, *C*≡CC≡CC≡CTMS), 69.4 (2 C, O*C*H$_2$), 67.2 (2 C, C≡C*C*≡CC≡CTMS), 62.1 (2 C, C≡CC≡*C*C≡CTMS), 34.4 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 30.1 (30 C, *C*H$_2$), 30.0 (2 C, *C*H$_2$), 29.7 (2 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 26.3 (2 C, *C*H$_2$), –0.5 [6 C, Si(*C*H$_3$)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 3448, 2922, 2849, 2186, 2167, 2074, 1600, 1498, 1470, 1409, 1390, 1364, 1331, 1290, 1253, 1166, 1130, 1100, 1015, 925, 892, 848, 815, 760, 720, 661, 627, 492 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 226, 238, 249, 262, 316, 334, 356 nm. $C_{80}H_{122}O_2Si_2$ (1171.96): calcd. C 81.98, H 10.49; found C 81.35, H 10.68.

**1,20-Bis[4-*tert*-butyl-2-(1,3,5-hexatriynyl)phenyloxy]eicosane (18a):** A spatulum tip of $K_2CO_3$ was added to a solution of **17a** (260 mg, 0.30 mmol) in a mixture of wet THF/MeOH (1:1, 4 mL). When after 30 min only one product was observed by TLC control ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.28), aqueous HCl (10%, 20 mL), water (20 mL) and hexane (50 mL) were added. After separating the layers, the aqueous layer was extracted twice with hexane (50 mL each) and the combined organic layers dried with $Na_2SO_4$. The clear, slightly yellow solution was concentrated to a few mL and immediately used for subsequent transformations to avoid decomposition.

**1,32-Bis[4-*tert*-butyl-2-(1,3,5-hexatriynyl)phenyloxy]dotriacontane (18b):** To a solution of **17b** (256 mg, 0.25 mmol) in a mixture of wet THF/MeOH (1:1, 8 mL) a minute amount of $K_2CO_3$ was added. By TLC control ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.31) already after 30 min the complete transformation was observed. Subsequently, aqueous HCl (10%, 20 mL), water (20 mL) and hexane (50 mL) were added and the two layers separated. The aqueous layer was extracted twice with hexane (50 mL each) and the combined organic layers were dried with $Na_2SO_4$. The resulting clear and colourless solution was concentrated at room temperature to 10 mL and directly used for further reactions. At complete dryness the product decomposed with black color within a few minutes.

**1,40-Bis[4-*tert*-butyl-2-(1,3,5-hexatriynyl)phenyloxy]tetracontane (18c):** A solution of **17c** (72 mg, 0.06 mmol) in a 1:1 mixture of non-dried THF/MeOH (10 mL) was treated with a spatulum tip of $K_2CO_3$. TLC control ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.35) showed complete conversion after 30 min. Subsequently, water (150 mL) and $CH_2Cl_2$ (150 mL) were added and the layers separated. The aqueous layer was extracted with $CH_2Cl_2$ (80 mL), the combined organic layers were washed with water (300 mL) and dried with $Na_2SO_4$. The slightly yellow solution was concentrated to a few mL and used directly for the next conversion without further characterization.

**Dibenzo-dioxacycloalkanehexayne Derivative 19a:** A solution of CuCl (495 mg, 5.00 mmol) and TMEDA (238 mg, 2.05 mmol) in acetone (30 mL) was stirred for 1 h and afterwards filtered three times. The filter residues were washed with 3–4 mL of acetone, each. A gentle stream of oxygen was passed through this dark violet solution for 15 min. Subsequently, the as-prepared hexane solution of **18a**, diluted with acetone (80 mL), was added dropwise over a period of 2.5 h. Afterwards, when no starting material was observed anymore by TLC monitoring ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.64), water (30 mL), aqueous HCl (10%, 30 mL) and hexane

(90 mL) were added and the two layers were allowed to separate. The aqueous layer was extracted twice with hexane (70 mL each) and the combined organic layers were washed twice with water (200 mL each) and dried with $Na_2SO_4$. The product **19a** was isolated (72 mg, 33%, relative to **17a**) as a yellow oil by column chromatography (silica gel, $CH_2Cl_2$/hexane, 1:9). $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 7.48 (d, $^4J$ = 2.4 Hz, 2 H, Ar*H*), 7.38 (dd, $^4J$ = 2.6 Hz, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 6.81 (d, $^3J$ = 8.8 Hz, Ar*H*), 4.00 (t, $^3J$ = 5.6 Hz, 4 H, OC$H_2$), 1.76 (m, 4 H, OCH$_2$C$H_2$), 1.52 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.39 (m, 4 H, C$H_2$), 1.30 [s, 18 H, C(C$H_3$)$_3$],1.26 (s, 24 H, C$H_2$) ppm. $^{13}$C NMR (100.50 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 161.2 (2 C, Ar*C*), 143.8 (2 C, Ar*C*), 132.0 (2 C, Ar*C*H), 129.7 (2 C, Ar*C*H), 112.2 (2 C, Ar*C*H), 109.0 (2 C, Ar*C*), 77.3 [2 C, (Ar*C*≡*C*C≡CC≡C)$_2$], 75.8 [2 C, (Ar*C*≡CC≡CC≡C)$_2$], 69.6 (2 C, O*C*H$_2$), 67.6 [2 C, (ArC≡C*C*≡CC≡C)$_2$], 64.9 [2 C, (ArC≡CC≡C*C*≡C)$_2$], 64.0 [(ArC≡CC≡*C*C≡C)$_2$], 63.2 [2 C, (ArC≡CC≡CC≡*C*)$_2$], 34.4 [2 C, *C*(CH$_3$)$_3$], 31.3 [8 C, C(*C*H$_3$)$_3$], 30.3 [2 C, *C*H$_2$], 30.2 (8 C, *C*H$_2$), 29.9 (2 C, *C*H$_2$), 29.7 (2 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 26.8 (2 C, *C*H$_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 2963, 2923, 2852, 2150, 2047, 1599, 1498, 1466, 1387, 1363, 1261, 1096, 1023, 804, 704, 625 cm$^{-1}$. MS (FAB): *m*/*z* = 720 [M$^+$]. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 254, 265, 306, 317, 357, 379, 404, 438, 477 nm. $C_{52}H_{64}O_2$ (721.03): calcd. C 86.61, H 8.95; found C 85.79, H 8.99.

**Dibenzo-dioxacycloalkanehexayne Derivative 19b:** A mixture of CuCl (495 mg, 5.00 mmol) and TMEDA (0.31 mL, 2.05 mmol) in acetone (30 mL) was stirred for 60 min. Subsequently, the suspension was filtered several times, until no precipitate was detected anymore. After each of the filtrations, the filter residue was rinsed with acetone (5 mL). The dark purple solution was flushed with oxygen for 15 min. Subsequently, the hexane solution of **18b**, diluted with acetone (80 mL), was added slowly and dropwise over a period of 2 h. After another 2 h of stirring the TLC control showed no more starting material ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.48), and water (30 mL), aqueous HCl (10%, 30 mL) and hexane (90 mL) were added and the layers allowed to separate. The aqueous layer was extracted twice with hexane (70 mL each), and the combined organic layers were washed twice with water (200 mL each) and dried with $MgSO_4$. By means of column chromatography (silica gel, $CH_2Cl_2$/hexane, 1:9) the yellow product zone was separated and **19b** was isolated (39 mg, 18%) as a yellow oil. $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 7.49 (d, $^4J$ = 2.4 Hz, 2 H, Ar*H*), 7.40 (dd, $^4J$ = 2.5 Hz, $^3J$ = 8.6 Hz, 2 H, Ar*H*), 6.83 (d, $^3J$ = 8.9 Hz, 2 H, Ar*H*), 4.01 (t, $^3J$ = 6.3 Hz, 4 H, O–C$H_2$), 1.80 (m, 4 H, OCH$_2$C$H_2$), 1.49 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.28 [s, 18 H, C(C$H_3$)$_3$], 1.27 (s, 52 H, C$H_2$) ppm. $^{13}$C NMR (100.50 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 161.0 (2 C, Ar*C*), 143.8 (2 C, Ar*C*), 132.3 (2 C, Ar*C*H), 129.8 (2 C, Ar*C*H), 112.5 (2 C, Ar*C*H), 108.9 (2 C, Ar*C*), 77.3 [2 C, (ArC≡*C*C≡CC≡C)$_2$], 76.0 [2 C, (Ar*C*≡CC≡CC≡C)$_2$], 69.4 (2 C, O*C*H$_2$), 67.6 [2 C, (Ar*C*≡C*C*≡CC≡C)$_2$], 64.9 [2 C, (ArC≡CC≡C*C*≡C)$_2$], 64.1 [(ArC≡CC≡*C*C≡C)$_2$], 63.3 [2 C, (ArC≡CC≡CC≡*C*)$_2$], 31.4 [2 C, *C*(CH$_3$)$_3$], 29.8 [6 C, C(*C*H$_3$)$_3$], 29.7 (24 C, *C*H$_2$), 29.6 (2 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 26.4 (2 C, *C*H$_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 2963, 2923, 2853, 2151, 2047, 1600, 1499, 1464, 1386, 1362, 1260, 1096, 1024, 806, 705, 625 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 304, 316, 357, 379, 404, 437, 477 nm. UV/Vis (hexane): $\lambda_{max}$ = 303, 311, 351, 373, 398, 431, 470 nm. MS (FAB): *m*/*z* = 888 [M$^+$]. $C_{64}H_{88}O_2$ (889.34): calcd. C 86.43, H 9.97; found C 86.40, H 9.66.

**Dibenzo-dioxacycloalkanehexayne Derivative 19c:** The hexane solution of **18c** was diluted with $CH_2Cl_2$ to a total of 20 mL and 1-bromo-4-(trimethylsilyl)buta-1,3-diyne (**16**, 50 mg, 0.250 mmol) was added at 0 °C. This mixture was added dropwise to a solution of triethylamine (0.1 mL), [Pd(PPh$_3$)$_2$Cl$_2$] (0.80 mg, 1.0·10$^{-3}$ mmol) and CuI (0.45 mg, 2.3·10$^{-3}$ mmol) in $CH_2Cl_2$ over a period of 2 h. After the addition was finished, TLC monitoring ($CH_2Cl_2$/hexane, 2:8) showed complete conversion. Only the hexayne **19c** ($R_f$ = 0.50) and no other products were observed. Water (120 mL) and $CH_2Cl_2$ were added and the layers separated. The aqueous layer was extracted with $CH_2Cl_2$ (50 mL) and the combined organic layers were washed with water (300 mL) and dried with $Na_2SO_4$. By column chromatography (silica gel, $CH_2Cl_2$/hexane, 1:9) the bright yellow-orange zone of **19c** was fractionated (35 mg, 58% relative to **17c**) as a yellow-orange oil. $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 7.49 (d, $^4J$ = 2.4 Hz, 2 H, Ar*H*), 7.40 (dd, $^4J$ = 2.6 Hz, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 6.83 (d, $^3J$ = 8.8 Hz, Ar*H*), 4.01 (t, $^3J$ = 6.3 Hz, 4 H, OC$H_2$), 1.79 (m, 4 H, OCH$_2$C$H_2$), 1.49 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.34–1.26 [m, 86 H, C(C$H_3$)$_3$ and C$H_2$] ppm. $^{13}$C NMR (100.50 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 161.0 (2 C, Ar*C*), 143.8 (2 C, Ar*C*), 132.2 (2 C, Ar*C*H), 129.7 (2 C, Ar*C*H), 112.1 (2 C, Ar*C*H), 108.9 (2 C, Ar*C*), 77.3 [2 C, (ArC≡*C*C≡CC≡C)$_2$], 76.0 [2 C, (Ar*C*≡CC≡CC≡C)$_2$], 69.4 (2 C, O*C*H$_2$), 67.6 [2 C, (ArC≡C*C*≡CC≡C)$_2$], 65.0 [2 C, (ArC≡CC≡C*C*≡C)$_2$], 64.0 [(ArC≡CC≡*C*C≡C)$_2$], 63.3 [2 C, (ArC≡CC≡CC≡*C*)$_2$], 34.4 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 29.9 (2 C, *C*H$_2$), 29.8 (2 C, *C*H$_2$), 29.7 (30 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 26.4 (2 C, *C*H$_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 2962, 2922, 2854, 2151, 2047, 1601, 1499, 1462, 1387, 1362, 1261, 1095, 1024, 805, 705, 624 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 263, 276, 288, 304, 354, 373, 399, 435, 476 nm. MS (FAB): *m*/*z* = 1001 [M$^+$]. $C_{72}H_{104}O_2$ (1001.55): calcd. C 86.34, H 10.47; found C 85.76, H 10.50.

**Dibenzo-dioxacycloalkaneoctayne Derivative 20:** The bis(trimethylsilyltriyne) **17c** (100 mg, 0.087 mmol) was deprotected with $K_2CO_3$ as described above for the bis(hexatriynes) **18a**–**c**. The resulting solution was diluted with $CH_2Cl_2$ to a total of 5 mL. Subsequently, 1-bromo-4-(trimethylsilyl)buta-1,3-diyne (**16**) was added. Over a period of 15 min, this mixture was added dropwise to a solution of [Pd(PPh$_3$)$_2$Cl$_2$] (0.7 mg, 0.99·10$^{-3}$ mmol), CuI (0.5 mg, 2.60·10$^{-3}$ mmol), triethylamine (727 mg, 7.20 mmol) and 1-bromo-4-(trimethylsilyl)buta-1,3-diyne (**16**, 83 mg, 0.413 mmol) in $CH_2Cl_2$ (3 mL) at 0 °C. The reaction progress was controlled by TLC ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.56). After every 22 h, [Pd(PPh$_3$)$_2$Cl$_2$] (1.0 mg, 1.40·10$^{-3}$ mmol) was added and after a total of 48 h, water (100 mL) and $CH_2Cl_2$ (100 mL) was added. The aqueous layer was separated and extracted twice with $CH_2Cl_2$ (50 mL each), the combined organic layers were washed three times with water (100 mL each) and dried with $Na_2SO_4$. By column chromatography (silica gel, $CH_2Cl_2$/hexane, 1:9) the yellow product zone of **20** was separated in a yield of 1 mg (0.95·10$^{-3}$ mmol, 1.1%). UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 292, 310, 326, 345, 364, 388, 409, 436, 472, 515 nm. MS (FAB): *m*/*z* = 1049 [M$^+$].

**Palladium-Catalyzed Coupling, Synthesis of Macrocyclic Oligoynes 23, 24, 15a and 25:** A solution of the bis(acetylene) **10a** (0.70 g, 1.36 mmol) in $CH_3CN$ (8 mL) was added dropwise to a solution of triethylamine (4.12 g, 40.80 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (9.5 mg, 13.6·10$^{-3}$ mmol), CuI (5.2 mg, 27.0·10$^{-3}$ mmol) and tetraiodoethene (**22**, 1.45 g, 2.72 mmol) in $CH_3CN$ (4 mL). After 3 h, when with TLC control ($CH_2Cl_2$/hexane, 3:7) only traces of the starting material were detectable, a saturated aqueous solution of $NH_4Cl$ (50 mL) and $CH_2Cl_2$ (100 mL) were added. Subsequently, both layers were separated, the aqueous layer extracted twice with $CH_2Cl_2$ (100 mL each) and the combined organic phases were washed three times with water (50 mL each) and dried with $Na_2SO_4$. By a two-fold separation with column chromatography on silica gel ($CH_2Cl_2$/hexane, 2:8 and 15:85) the diyne **23** (3 mg, 0.4%, $R_f$ = 0.25), triyne **24** (28 mg, 3.8%, $R_f$ = 0.32), tetrayne **15a** (12 mg, 1.6%, $R_f$ = 0.38)

and pentayne **25** (traces, $R_f$ = 0.43) were isolated ($R_f$-values determined in $CH_2Cl_2$/hexane, 3:7).

**Dibenzo-dioxacycloalkanediyne Derivative 23:** $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.51 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.28 (dd, $^3J$ = 8.8 Hz, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 6.77 (d, $^3J$ = 8.8 Hz, Ar*H*), 3.99 (t, $^3J$ = 6.2 Hz, 4 H, OC$H_2$), 1.80 (m, 4 H, OCH$_2$C$H_2$), 1.49 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.33 (br. s, 12 H, C$H_2$), 1.27 [s, 18 H, C(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.50 MHz, $CDCl_3$, 22 °C): $\delta$ = 158.2 (2 C, Ar*C*), 142.8 (2 C, Ar*C*), 131.6 (2 C, Ar*C*H), 127.2 (2 C, Ar*C*H), 111.3 (2 C, Ar*C*H), 110.9 (2 C, Ar*C*), 79.2 [2 C, (ArC≡*C*)$_2$], 77.4 [2 C, (Ar*C*≡C)$_2$], 68.8 (2 C, O*C*H$_2$), 34.1 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 28.9 (4 C, *C*H$_2$), 28.5 (2 C, *C*H$_2$), 27.8 (2 C, *C*H$_2$), 26.1 (2 C, *C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2927, 1502, 1252, 1151, 808 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 246, 262, 278, 335, 355 nm. MS (FAB): *m*/*z* = 512 [M$^+$]. $C_{36}H_{48}O_2$ (512.74): calcd. C 84.32, H 9.44; found C 83.86, H 9.50.

**Dibenzo-dioxacycloalkanetriyne Derivative 24:** $^1$H NMR (400 MHz, $CDCl_3$, 22 °C): $\delta$ = 7.47 (d, $^4J$ = 2.4 Hz, 2 H, Ar*H*), 7.30 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.5 Hz, 2 H, Ar*H*), 6.76 (d, $^3J$ = 8.8 Hz, Ar*H*), 3.99 (t, $^3J$ = 5.4 Hz, 4 H, OC$H_2$), 1.76 (m, 4 H, OCH$_2$C$H_2$), 1.56 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.36 (br. s, 12 H, C$H_2$), 1.26 [s, 18 H, C(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.50 MHz, $CDCl_3$, 22 °C): $\delta$ = 159.5 (2 C, Ar*C*), 143.0 (2 C, Ar*C*), 131.5 (2 C, Ar*C*H), 127.9 (2 C, Ar*C*H), 111.5 (2 C, Ar*C*H), 110.1 (2 C, Ar*C*), 77.7 [2 C, (ArC≡*C*C)$_2$], 75.8 [2 C, (Ar*C*≡CC)$_2$], 69.0 (2 C, O*C*H$_2$), 67.0 (2 C, ArC≡C*C*)$_2$, 34.2 [2 C, *C*(CH$_3$)$_3$], 31.4 [6 C, C(*C*H$_3$)$_3$], 29.2 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 28.9 (2 C, *C*H$_2$), 28.8 (2 C, *C*H$_2$), 26.5 (2 C, *C*H$_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 2927, 2856, 2195, 1599, 1498, 1466, 1390, 1365, 1275, 1147, 1049, 891, 816, 737, 627 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 246, 261, 281, 331, 358, 385 nm. MS (FAB): *m*/*z* = 536 [M$^+$]. $C_{38}H_{48}O_2$ (536.76): calcd. C 85.02, H 9.01; found C 84.99, H 8.99.

**Dibenzo-dioxacycloalkanepentayne Derivative 25:** UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 278, 292, 307, 337, 356, 382, 412, 448 nm. MS (FAB): *m*/*z* = 584 [M$^+$].

**Palladium-Catalyzed Coupling, Synthesis of Macrocyclic Oligoynes 26 and 19b:** A solution of the bis(acetylene) **10e** (200 mg, 0.25 mmol) in $CH_2Cl_2$ (8 mL) was added dropwise to a solution of triethylamine (4.12 g, 40.80 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (21 mg, 0.03 mmol), CuI (12 mg, 0.06 mmol) and tetraiodoethene (**22**, 804 mg, 1.51 mmol) in acetonitrile (4 mL). After 3 h, when by TLC control ($CH_2Cl_2$/hexane, 2:8) only traces of the starting material were detectable, a saturated aqueous solution of $NH_4Cl$ (50 mL) and $CH_2Cl_2$ (50 mL) were added. Subsequently, the layers were separated, the aqueous layer was extracted twice with $CH_2Cl_2$ (50 mL each) and the combined organic phases were washed three times with water (100 mL each) and dried with $Na_2SO_4$. By column chromatography on silica gel ($CH_2Cl_2$/hexane, 16:84) the diyne **26** (10 mg, 5%, white solid) and the hexayne **19b** (7 mg, 3%) were isolated.

**Dibenzo-dioxacycloalkanediyne Derivative 26:** $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 7.50 (d, $^4J$ = 2.8 Hz, 2 H, Ar*H*), 7.34 (dd, $^4J$ = 2.7 Hz, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 6.84 (d, $^3J$ = 8.8 Hz, Ar*H*), 4.04 (t, $^3J$ = 6.6 Hz, 4 H, OC$H_2$), 1.85 (m, 4 H, OCH$_2$C$H_2$), 1.49 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.39–1.25 (m, 52 H, C$H_2$), 1.29 [s, 18 H, C–(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.50 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 159.2 (2 C, Ar*C*), 143.6 (2 C, Ar*C*), 131.6 (2 C, Ar*C*H), 128.1 (2 C, Ar*C*H), 112.1 (2 C, Ar*C*H), 111.0 (2 C, Ar*C*), 79.6 [2 C, (ArC≡*C*)$_2$], 77.4 [2 C, (Ar*C*≡C)$_2$], 69.3 (2 C, O*C*H$_2$), 34.3 [2 C, *C*(CH$_3$)$_3$], 31.5 [6 C, C(*C*H$_3$)$_3$], 29.9 (12 C, *C*H$_2$), 29.8 (2 C, *C*H$_2$), 29.7 (2 C, *C*H$_2$), 29.6 (2 C, *C*H$_2$), 29.5 (2 C, *C*H$_2$), 29.4 (2 C, *C*H$_2$), 29.3 (2 C, *C*H$_2$), 29.2 (2 C, *C*H$_2$), 29.1 (2 C, *C*H$_2$), 26.3 (2 C, *C*H$_2$) ppm. UV/Vis (hexane): $\lambda_{max}$ = 246, 263, 278, 334, 356 nm. MS (FAB): *m*/*z* = 793 [M$^+$]. $C_{56}H_{88}O_2$ (793.26): calcd. C 84.79, H 11.18; found C 84.38, H 11.35.

**Palladium-Catalyzed Coupling, Synthesis of Macrocyclic Oligoynes 28 and 30**

**Dibenzo-dioxacycloalkaneheptayne Derivative 28:** To a solution of **17b** (82 mg, 0.079 mmol) in a mixture of wet methanol/THF (10 mL, 1:1) a minute amount of $K_2CO_3$ was added and the mixture stirred for 20 min. After this period, no more starting material was detected by TLC ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.25), and water (100 mL) and $CH_2Cl_2$ (100 mL) were added. After separating the organic layer, it was washed twice with water (300 mL each), dried with $Na_2SO_4$, concentrated in vacuo to about 5 mL and diluted with dry $CH_2Cl_2$ (13 mL). Diiodoacetylene (**27**, 132 mg, 0.474 mmol) was added to this solution, and the mixture added dropwise to a solution of [Pd(PPh$_3$)$_2$Cl$_2$] (0.6 mg, 0.85·10$^{-3}$ mmol), CuI (0.4 mg, 2.1·10$^{-3}$ mmol) and triethylamine (72 mg, 0.713 mmol) in $CH_2Cl_2$ (6 mL) at –35 °C. By TLC monitoring only the starting material was observed ($CH_2Cl_2$/hexane, 2:8). Subsequently, the reaction mixture was warmed to room temperature and stirred for 16 h. When no more starting material was detected by TLC ($CH_2Cl_2$/hexane, 2:8, $R_f$ = 0.30), hexane and water (100 mL each) were added. After separating the layers, the aqueous layer was extracted with hexane (50 mL) and the combined organic phases were washed twice with water (150 mL each). After drying with $Na_2SO_4$ the yellow product fraction was purified and separated from the simultanously formed hexayne **19b** by column chromatography ($CH_2Cl_2$/hexane, 1:9), yield 8 mg, 11% of the orange solid **28**. $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 7.49 (d, $^4J$ = 2.6 Hz, 2 H, Ar*H*), 7.40 (dd, $^4J$ = 2.6 Hz, $^3J$ = 8.8 Hz, 2 H, Ar*H*), 6.83 (d, $^3J$ = 8.9 Hz, 2 H, Ar*H*), 4.01 (t, $^3J$ = 6.2 Hz, 4 H, OC$H_2$), 1.80 (m, 4 H, OCH$_2$C$H_2$), 1.49 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.28 [s, 18 H, C(C$H_3$)$_3$], 1.27 (s, 52 H, C$H_2$) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 307, 324, 347, 372, 393, 419, 455, 496 nm. MS (FAB): *m*/*z* = 913 [M$^+$].

**Phenylenediyne Macrocycle 30:** A solution of **10a** (100.0 mg, 0.195 mmol) and 1,4-diiodobenzene (**29**, 64.2 mg, 0.195 mmol) in $CH_2Cl_2$ (15 mL) was added dropwise to a solution of [Pd(PPh$_3$)$_2$Cl$_2$] (1.4 mg, 1.94·10$^{-3}$ mmol), CuI (0.8 mg, 3.9·10$^{-3}$ mmol) and triethylamine (2 mL) in $CH_2Cl_2$ (15 mL) and stirred for 18 h. Only traces of starting material were detected by TLC control ($CH_2Cl_2$/hexane, 3:7, $R_f$ = 0.43), and a saturated aqueous solution of $NH_4Cl$ (50 mL) and $CH_2Cl_2$ (100 mL) were added. After separating the two layers, the aqueous layer was extracted twice with $CH_2Cl_2$ (100 mL each) and the combined organic layers were washed three times with water (50 mL each) and dried with $Na_2SO_4$. The phenylenediyne **30** was isolated as a white solid by column chromatography (silica gel, $CH_2Cl_2$/hexane, 3:7) in 26% (30 mg) yield. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.50 (s, 4 H, C≡CAr*H*C≡C) 7.47 (d, $^4J$ = 2.4 Hz, 2 H, Ar*H*), 7.28 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.4 Hz, 2 H, Ar*H*), 6.80 (d, $^3J$ = 8.7 Hz, 2 H, Ar*H*), 4.02 (t, $^3J$ = 5.2 Hz, 4 H, OC$H_2$), 1.78 (m, 4 H, OCH$_2$C$H_2$), 1.65 (m, 4 H, OCH$_2$CH$_2$C$H_2$), 1.37–1.30 (br., 12 H, C$H_2$), 1.29 [s, 18 H, C(C$H_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 157.8 (2 C, Ar*C*), 143.1 (2 C, Ar*C*), 131.3 (2 C, C≡CAr*C*HC≡C), 129.9 (2 C, Ar*C*H), 126.8 (2 C, Ar*C*H), 123.3 (2 C, C≡CAr*C*C≡C) 112.1 (2 C, Ar*C*), 111.5 (2 C, Ar*C*H), 92.8 (2 C, ArC≡*C*ArC), 88.3 (2 C, ArC*C*≡CArC), 68.9 (2 C, O*C*H$_2$), 34.1 [2 C, *C*(CH$_3$)$_3$], 31.4 [6C, C(*C*H$_3$)$_3$], 30.4 (2 C, *C*H$_2$), 30.0 (2 C, *C*H$_2$), 29.9 (2 C, *C*H$_2$), 29.7 (2 C, *C*H$_2$), 27.1 (2 C, *C*H$_2$) ppm. IR (NaCl): $\tilde{\nu}$ = 2957, 2923, 2853, 1740, 1618, 1595, 1499, 1466, 1406, 1386, 1363, 1341, 1289, 1259, 1162, 1096, 1026, 891, 810, 751, 737, 629, 545 cm$^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ [nm] = 227, 301, 344, 364 nm. MS (FAB): *m*/*z* = 588

[$M^+$]. $C_{42}H_{52}O_2$ (588.84): calcd. C 85.66, H 8.90; found C 85.14, H 8.94.

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