An Efficient Synthesis of Liquid Crystalline Gigantocycles Combining Banana-Shaped and Rod-Like Mesogenic Units

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Abstract: The synthesis of monodisperse gigantocycles with 63, 87, and 147 ring atoms on the gram scale is described. These molecules were assembled from terphenylene derivatives and long, flexible chains which were mainly aliphatic, with terminal alkyne groups. The latter allowed for ring formation through oxidative alkyne dimerization in high yield (80–87%). The combination of a rod-like and a banana-shaped mesogen connected by flexible chains within the backbone of a ring gives rise to nematic and smectic mesophases.

Keywords: Glaser coupling · liquid crystals · macrocycles

Introduction

Cyclic molecules play an important role as components of supramolecular systems such as rotaxanes and catenanes,[1] and as hosts for ions and molecules in host–guest complexes.[2] They are also examples of materials that undergo self-organisation and thus exhibit mesophases.[3–7] Furthermore, huge cycles are of interest because they are macromolecules with a special topology.[8–10] Efficient syntheses allowing for easy variation of ring size and addition of different functionalities, and thus having a broad sphere of application are therefore highly desirable. Herein we describe a versatile synthesis for functionalized, monodisperse, huge cyclic molecules on the gram scale. Our synthetic strategy is exemplified by the synthesis of the gigantocycles **9** and **17** containing up to 147 ring atoms.

Characteristic features of the cycles **9** and **17** are a banana-shaped moiety carrying inward and outward oriented functionalities. These are a 4-hydroxybenzoate substituted with two tolane moieties, and the rod-like unit 1,4-bis(4-ethynylphenyl)butadiyne. These units are linked through chains which are long, flexible, and mainly aliphatic with a different length in each of the three cycles **9a**, **b**, and **17**. The tail-to-tail attachment of rod-like mesogens through flexible chains within a ring can result in mesomorphic cyclic compounds.[4–7] Indeed, the cycles **9a**, **b**, and **17** were found to be thermotropic liquid crystalline compounds showing nematic and smectic phases. The cycles **9** and **17** are unique in so far as they combine mesogenic units of very different shape, that is a banana-shaped[11] and a rod-like mesogen.

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Results and Discussion

Synthesis

The main criterions for the design of the synthesis were the feasibility of preparing the building blocks on a multi-gram scale and a cyclization reaction giving high yields. The latter is imperative for a reaction sequence of broader relevance. These considerations resulted in the design of the ring precursors **8a**, **b**, and **16** and the choice of the oxidative alkyne dimerization as the cyclization reaction.

Synthesis of the ring precursors 8a, b and 16: The ring precursors **8a**, **b** and **16** were assembled from terphenylene **6**[12] and the long, flexible chains **5a**, **b** and **14** (Schemes 1 and 2). For the preparation of the chains **5** and **14** the long ω-alkynols **3** and **11** were required as the key building blocks. Convenient starting compounds for such alkynols are either ω-bromoalkanols or 1-bromoalkanes.

For the shortest alkynol **11** we used 11-bromoundecanol which was silylated to give **10** and subsequently converted into

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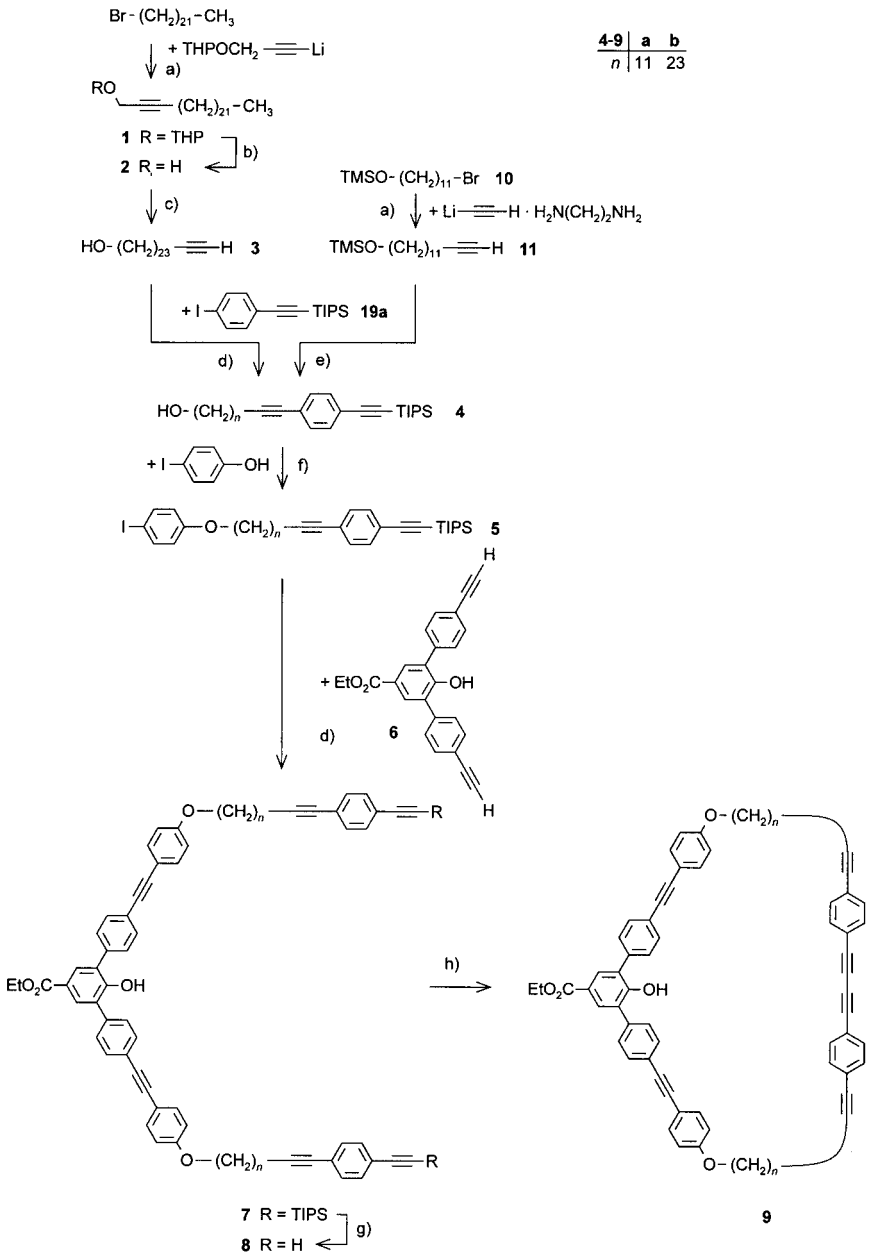

Scheme 1. a) 1,3-Dimethyl-1,3-diazacyclohexan-2-on, THF; b) TsOH, MeOH, THF; c) Li, 1,3-diaminopropane, KO*t*Bu; d) $[Pd(PPh_3)_2Cl_2]$, CuI, piperidine; e) 1) $[Pd(PPh_3)_2Cl_2]$, CuI, piperidine, 2) HCl, MeOH, diethyl ether; f) diisopropyl azodicarboxylate, PPh_3, THF; g) nBu_4NF, THF; h) CuCl, $CuCl_2$, pyridine.

O-silylated 12-tridecynol **11**. For the substitution, we employed ethynyllithium in 1,3-dimethyl-1,3-diazacyclohexan-2-on (*N*,*N*′-dimethyl-*N*,*N*′-propylene urea, DMPU),[13, 14] thereby avoiding toxic HMPA which is still most often used as a co-solvent.[15, 16] The rather low yield (57%) of **11** is attributed to the formation of silylated tetracos-12-yn-1,24-diol which resulted from disubstitution of the ethyne with the bromoalkane.[17]

The corresponding longer alkynol, pentacos-24-ynol (**3**), was obtained from 1-bromodocosane. Reaction with the lithium salt of THP-protected propargyl alcohol gave compound **1** which was deprotected to give pentacos-2-ynol (**2**). Isomerization of **2** in a suspension of the lithium salt of 1,3-diaminopropane and KO*t*Bu in 1,3-diaminopropane[18] gave alkynol **3**. This alkyne isomerization reaction (Zipper reaction) yielded the alkynol **3** and about 30% of alkanes[19] carrying neither a hydroxyl nor an alkyne functionality. Most of these alkanes were removed by column chromatography and subsequent recrystallization. When NaH/diaminopropane[20, 21] was used as the isomerization agent, about 50% of non-functionalized alkanes were formed besides the intended product **3**. Other conditions such as KH/diaminopropane[22] and $NaNH_2$/diaminopropane[23] were tested only once and gave incomplete conversions. Experiments to improve the workup procedure revealed the sensitivity of the product towards transformation into an enyne with characteristic signals in the ^1H NMR spectrum at $\delta = 5.08$, 4.63, and 1.77.[24] Although this by-product was formed only in small amounts (1–3%, estimated by ^1H NMR spectroscopy), we were not successful in removing it by chromatography and recrystallization from hexane. This structural impurity was retained in the products during the following synthetic steps. To avoid the formation of this enyne, careful control of the temperature during aqueous workup turned out to be the crucial factor.

Pd/Cu-catalyzed coupling of the alkynol **3** or the silylated alkynol **11** with 1-iodo-4-(triisopropylsilylethynyl)benzene (**19a**) and, in the case of **11**, subsequent O-desilylation, gave the long chains **4a**, **b** with a protected, terminal arylalkyne moiety. Finally derivatization of **4a**, **b** with 4-iodophenol using the Mitsunobu reaction[25] gave the chains **5a**, **b**.

For the synthesis of the longest chain **14** we used the synthetic transformations of the preparation of **5b** starting from **3** in a repeated sequence (Scheme 2). Intermediate **4b** was attached to 2,6-dimethyl-4-iodophenol. The iodo functionality of product **12** was used to extend the molecule with alkynol **3**. Subsequent Mitsunobu reaction with 4-iodophenol gave **14**. 2,6-Dimethyl-4-iodophenol was chosen instead of 4-iodophenol as the link between the two alkynols in order to increase the solubility of the final long chain. Additionally, the signal of the aromatic protons of the dimethylphenol moiety

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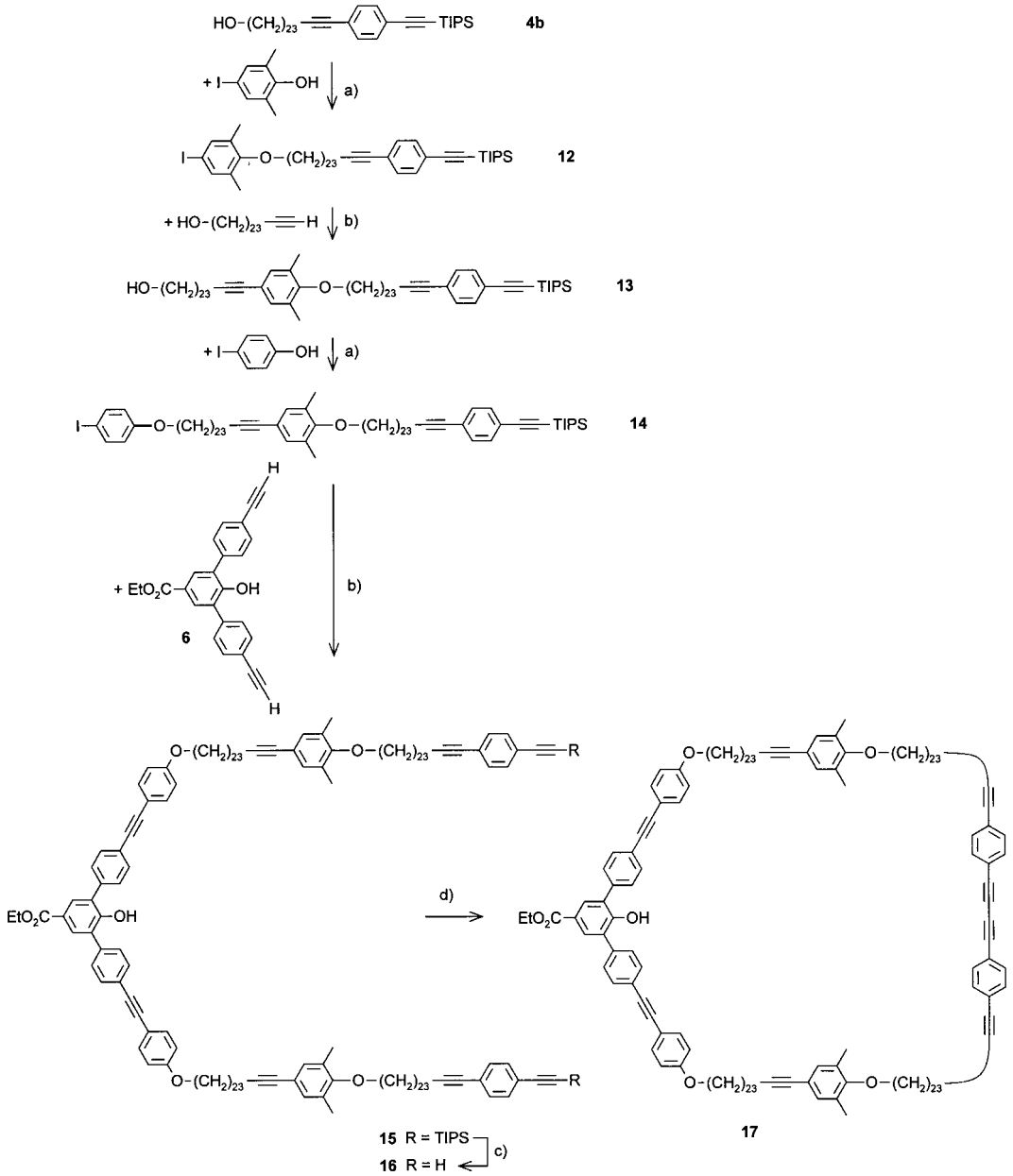

Scheme 2. a) Diisopropyl azodicarboxylate, PPh_3, THF; b) $[Pd(PPh_3)_2Cl_2]$, CuI, piperidine; c) $n$$Bu_4NF$, THF; d) CuCl, $CuCl_2$, pyridine, 1,2-dichlorobenzene.

appears well separated from others in the ^1H NMR spectra and hence offers the advantage of having an additional NMR probe within the molecule. We expect to be able to extend the reaction sequence for even larger chains by repeating alternately the two synthetic steps, Mitsunobu and alkynyl-aryl coupling. Alternatively, this should be possible using a divergent-convergent approach comprising of desilylation of the compounds with terminal hydroxyl functionalities, such as **4b** and **13**, and subsequent coupling of the products with compounds carrying an iodo substituent and a silylated terminal alkyne moiety, such as **12** and **14**.

The long chains **5** and **14** were coupled with the terphenylene **6** in the presence of Pd/Cu salts to obtain, after desilylation, the ring precursors **8a**, **b** and **16**. Despite the great number of synthetic transformations, several grams of the cycle precursors were obtained in one batch, for example, 8–9 g of **8**.

Originally, the synthesis was pursued using trimethylsilyl (TMS) instead of triisopropylsilyl (TIPS) as the protecting group for the terminal alkyne moiety of **4**, **5**, and **7**. However, with this much cheaper protecting group two distinct side reactions were noted. One side reaction occurred during the synthesis of compound **19**, which is the coupling partner of the alkynols **3** and **11** in the reaction to obtain **4**. Compound **19** was prepared in a two-step process from 1-bromo-4-iodobenzene (Scheme 3): First, coupling of 1-bromo-4-iodobenzene with trialkylsilylethyne gave **18**.[26] Secondly, exchange of the bromo substituent of **18** for an iodo substituent by halogen metal exchange gave **19**. The coupling of 1-bromo-4-iodobenzene with trimethylsilylethyne gave **18b** contaminated with

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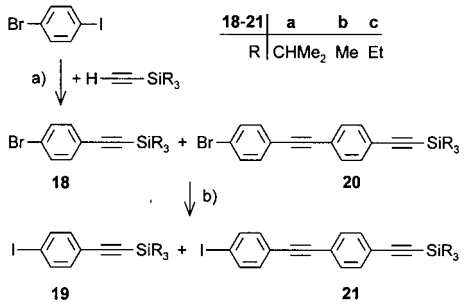
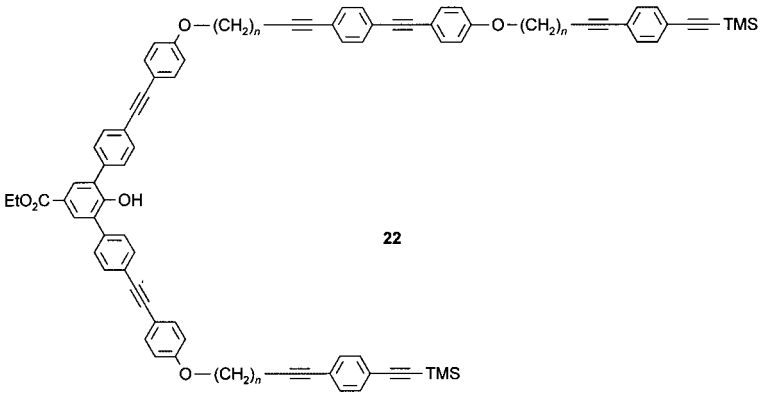


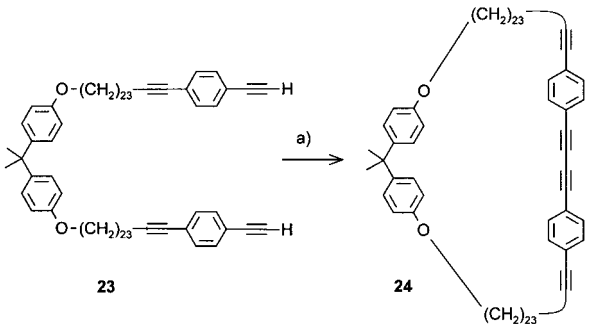
Scheme 3. a) $[Pd(PPh_3)_2Cl_2]$, CuI, piperidine (for **18a**) or diethylamine (for **18b**, **c**); b) 1) BuLi, THF, 2) 1,2-diodoethane or iodine.

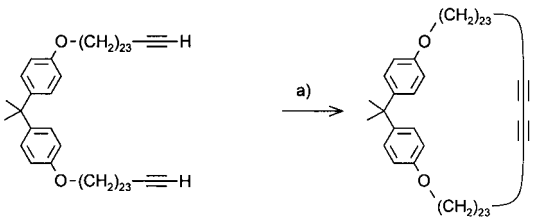
4-bromo-4′-(trimethylsilylethynyl)tolane (**20b**) in amounts of usually 0.5–3 mol%.[27a] Because **20b** has the same reactive groups as **18b**, all compounds derived from **18b**, such as **19b**, or **4(TMS)** (**4** carrying TMS instead of TIPS groups), contained small amounts of molecules which are extended by an ethynylenephenylene moiety, as proven by NMR spectroscopy and field desorption mass spectrometry (FD-MS).[27b] Exchanging the base and solvent piperidine for triethylamine in the preparation of **18b** did not improve the situation. All solvents had been dried prior to use. The amount of this kind of side reaction could be significantly reduced when triethylsilyl (TES) was used instead of TMS. Only occasionally traces of chain-extended products (<1% according to ^{1}H NMR and FD-MS spectra) were found. With TIPS as the protecting group the by-product **20a** was avoided.



The second side reaction when using TMS as the protecting group for the terminal alkyne moiety occurred upon attachment of the chains **5(TMS)** to terphenylene **6**. This gave compound **22** with chains approximately twice as long as the intended product **7**. The presence of **22** and of corresponding compounds derived from **22** upon further transformations according to Scheme 1 was proven through FD-MS spectra which show in addition to a dominant signal of the $[M]^+$ signal of **7b(TMS)**, **8b** and **9b**, a signal of low intensity at $[M+539]^+$. Corresponding ^{1}H NMR spectra reveal an additional signal at 6.84 ppm which is assigned to the two protons ortho to the oxygen atom of the phenol ring of the chain-extending moiety. From this signal's intensity, the amount of the by-product was estimated to be 3–6 mol%. For the formation of **22** we assume that piperidine partially deprotonates the phenolic compounds **6** and **7**. The resulting phenolates desilylate the compound **7(TMS)** and the released terminal alkyne moiety couples with the iodo component **5(TMS)** giving **22**. Careful chromatography permitted removal of this by-product, unfortunately at the expense of a substantial amount of product. Although the desilylation that causes the side products is a rather slow process and can be reduced by short reaction times (90 min) to an extent that the by-product is not detected anymore by ^{1}H NMR spectroscopy or FD-MS, the possibility of desilylation and subsequent chain extension renders this step unreliable. Through the use of the more stable alkyne protecting groups TES or TIPS, the "long chain extension" could be completely avoided.

Cyclization: The cyclization is most often the bottleneck in the synthesis of cyclic molecules and, therefore, calls for special attention. The oxidative alkyne dimerization (Glaser coupling)[29] can be a very efficient reaction for the formation of cyclic molecules. Most often it is employed in the formation of rather stiff rings.[30] However, a few remarkable results have been reported on very large cycles,[31, 32] also named gigantocycles,[7, 31] that are conformationally flexible. Several different reaction conditions for cyclization through alkyne dimerization can be found in the literature.[29–37] However, very little systematic or comparative work has been done.[36, 37] A comparison of the reaction conditions described for different kinds of alkynes made us assume that Cu^+/Cu^{2+} in pyridine is well suited for arylethynes, while Cu^+ in the presence of TMEDA and oxygen is well suited for aliphatic alkynes. The same conclusion is suggested by the kinetic studies of Hay[36] and Bohlmann.[37] A comparison of the cyclization of **23** and **25** in pyridine with Cu^+/Cu^{2+} as catalyst and agent[35] (Scheme 4) showed a dramatic influence of the substituent at the terminal ethyne groups. A solution of compound **23** or **25** dissolved in pyridine was slowly added to a suspension of the copper salts in pyridine. After complete addition the reaction mixture was stirred for 1–4 d. In the case of **23**, which has two aryl substituted terminal ethyne groups, the cyclic monomer **24** was formed almost exclusively as can be deduced from the size-exclusion chromatogram (Figure 1a). Cyclic compounds have a smaller hydrodynamic volume than the corresponding ring precursors. Therefore, the elution time of the cyclic compound is longer than that of the corresponding acyclic starting material. Cyclic and non-cyclic oligomers are expected at shorter elution times due to their larger hydrodynamic volume. The reaction of **23** was quantitative. The ^{1}H NMR spectrum shows no signal for an alkyne proton. However, applying the same conditions to the reaction of **25**—which has two alkyl substituted terminal ethyne groups—gave mostly oligomers and polymers (Fig-





Scheme 4. a) CuCl, $CuCl_2$, pyridine.

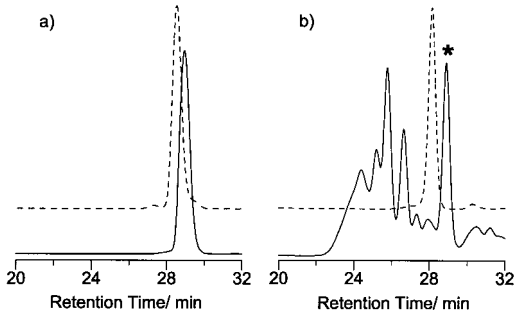


Figure 1. Size exclusion chromatograms of the starting materials **23** (a) or **25** (b) (– – –) and the crude products of cyclization (——). * denotes the signal arising from **26**.

ure 1 b) besides some cyclic monomer **26**. A substantial part of the material was insoluble, probably due to its high molecular weight. On top of this, the reaction was incomplete as shown by ^{1}H NMR spectroscopy. The spectra show the characteristic signals of the CH_2–C≡C–H moiety, a triplet at 1.93 ppm and a doublet of a triplets at 2.18 ppm. From this comparative study it is concluded that under the chosen conditions aryl substituted alkynes react faster than alkyl subsituted ones. Due to a fast reaction, the concentration of the aryl alkyne **23** is always kept below the critical concentration for intermolecular reactions. The alkyl alkyne **25**, however, accumulates over the course of the addition due to a comparatively slow reaction, finally allowing for competing intermolecular reactions.

The efficient cyclization of **23** was very promising for the preparation of our cyclic target molecules **9a**, **b** and **17**. Indeed, slow addition of the ring precursors **8a**, **b** and **16** to a suspension of CuCl and $CuCl_2$ in pyridine gave predominantly the cyclic monomers **9a**, **b** and **17**, respectively. The success of this procedure can be clearly seen from the size-exclusion chromatograms of the crude products (Figure 2). The giganto-

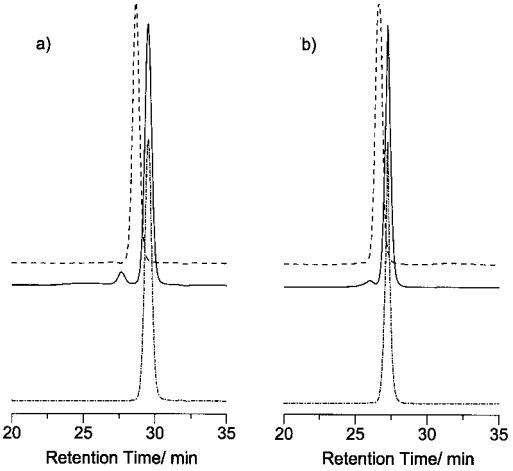


Figure 2. Representative size exclusion chromatograms of the starting materials **8a** (a) and **16** (b) (– – –), the crude product of cyclization (——), and the purified products **9a** (a) and **17** (b) (•–•–•), respectively.

cycles **9a**, **b** and **17** consisting of 63, 87, or 147 ring atoms were isolated by usual column chromatography in 80–87% yield as monodisperse compounds in amounts of 0.8–2.6 g in one batch. They are very soluble in THF, CH_2Cl_2, and $CHCl_3$.

Thermal characterization of the cyclic molecules 9 and 17 and of structurally related compounds: The cycles **9a**, **b** and **17** and structurally related compounds were investigated using polarizing microscopy and differential scanning calorimetry (DSC). Microscopy of compound **9b** revealed that in the first heating scan **9b** undergoes a crystal–crystal transition at 143–145 °C. At 151 °C it melts into a birefringent fluid phase with a *schlieren* texture, as typical for nematic phases (Figure 3). The transition from the nematic phase to the isotropic

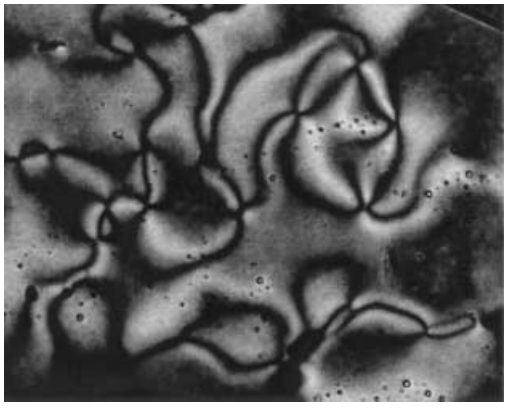


Figure 3. Optical photomicrograph (crossed polarizers) of the texture of macrocycle **9b** at 150 °C.

liquid takes place at 161 °C. This phase transition is completely reversible crystallization can be supercooled and sets in at 115 °C. Second and further heating scans revealed a crystal-crystal transition at 132–134 °C and a crystal-nematic transition at 142 °C. The DSC traces (Figure 4) are in agreement with these observations. Remarkably, the enthalpy of the nematic-isotropic transition is very small (0.2 kJ mol^{-1}).

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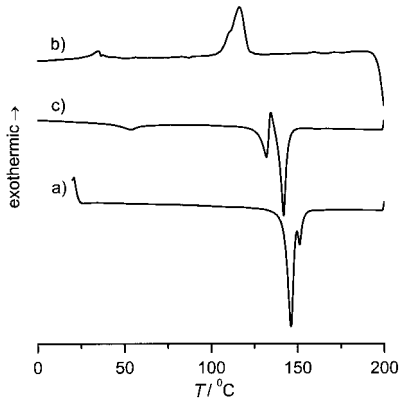

Figure 4. DSC of macrocycle **9b** with a scan rate of 10 K min^{-1}: a) first heating, b) cooling, c) second heating.

In contrast to **9b**, the smaller cycle **9a** has a very high melting point (201 °C) and shows only a monotropic nematic phase with a significantly lower clearing temperature (133 °C). Surprisingly, the extension of the flexible aliphatic ring segments of **9** enhances the stability of the nematic phase (compare compounds **9a** and **b**). The stability of nematic phases is usually reduced or the nematic phase is replaced by smectic phases with increasing length of terminal aliphatic chains.[38]

The largest cycle **17** exhibits a richer polymorphism than the macrocycles **9** (Figures 5 and 6). On slow cooling from the isotropic liquid state a nematic phase occurs at 113 °C ($\Delta H =$ 4.1 kJ mol^{-1}; Figure 6a, b), followed by a phase transition at

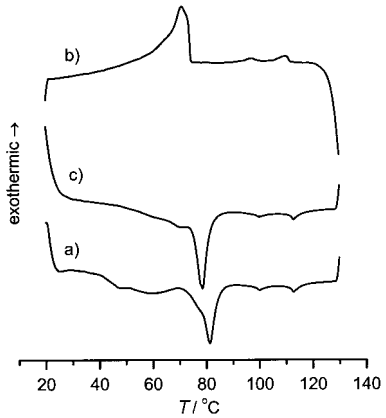

Figure 5. DSC of macrocycle **17** with a scan rate of 10 K min^{-1}: a) first heating, b) cooling, c) second heating.

99 °C ($\Delta H = 3.4$ kJ mol^{-1}). The latter phase transition is characterized by the occurrence of a fan-like texture (Figure 6c, d), which can be aligned homeotropically by shearing. These textural features indicate a smectic A-Phase (SmA) in which the molecules are organized in layers and the mesogenic units are aligned in average perpendicular to the smectic layer planes. On further cooling, at 81 °C (not detected with DSC), the fans become broken and birefringence occurs in the homeotropically aligned regions (Figure 6e, f) before the compound crystallizes at slightly lower temperatures. The birefringence of this low-temperature phase indicates that this mesophase is optically biaxial. It can only be observed in the cooling cycle, thus being a monotropic mesophase occurring below the melting point (81 °C). The other two mesophases are enantiotropic.

Macrocycle **17** was investigated additionally by means of X-ray diffraction. The nematic phase is characterised by two diffuse scatterings, one in the wide-angle region and the other in the small-angle region, as typical for nematic phases. In the SmA phase a sharp reflection corresponding to a layer thickness of $d = 7.4$ nm ($T = 95$ °C) is observed. The d value increases slightly (up to 7.5 nm at $T = 79$ °C) with decreasing temperature. The molecular length of $L = 8.3$ nm (measured at CPK models in the most stretched form) is in good agreement with the layer thickness d if the fluid state of the alkyl chains is taken into account. Assuming a maximal segregation of the aromatic and aliphatic building blocks in this smectic phase, the arrangement shown in Figure 7 is proposed. The banana-shaped units and the rod-like units lay side by side forming aromatic-rich layers separated by layers of the aliphatic parts of the macrocycles. The 4-ethynyl-2,6-dimethylphenoxy units, which interrupt the aliphatic parts of the macrocycle **17** are concentrated at the interfaces between neighboring layers. It is possible that these units form distinct sublayers that may additionally stabilise the smectic phase of **17**.

The optical biaxiality of the low temperature mesophase can result from a reduction of the rotational disorder of the banana-shaped units around their long axes which would lead to a biaxial SmA-phase (SmA_b)[39] or, alternatively, from a tilting of the banana-shaped and the rod-like units with respect to the layer normal (SmC).[40] Moreover, both can happen simultaneously with the additional possibility of a polar order of the banana-shaped units, leading to polar smectic phases (B2-type banana phases).[41] However, the rapid crystallization of this material and the failure to get sufficiently well oriented samples by alignment in a magnetic field inhibited a more detailed investigation of this mesophase. Nevertheless, the textural features of this biaxial mesophase are not typical for B2 phases or SmA_b phases, but more related to those of conventional SmC phases in which the calamitic cores adapt an in average uniformly tilted arrangement within the layers.

All three macrocyles **9a**, **b** and **17** contain two shape-persistent and therefore mesogenic units as part of the ring backbone: a rod-like and an angular or so called banana-shaped[11] moiety. At least one of these units must be essential for the mesomorphic behaviour because the corresponding hydrogenated (more flexible) macrocycle **28** is a comparatively low-melting ($T_m = 107$ °C) non-mesomorphic compound. To get an idea which of these moieties is essential for mesophase formation, we studied the thermal behaviour of the non-cyclic compounds **27a**, **b** as representatives incorporating the rod-like moiety and that of the non-cyclic compounds **7c**, **8a**, **b** and **16** as representatives containing a banana-shaped moiety. None of these compounds exhibit a liquid crystalline phase. Because the isotropization temperature of the cycle **9b** ($T_{N-I} = 161$ °C) is higher than the melting points of all non-cyclic compounds **27a** ($T_m = 145$ °C), **27b** ($T_m = 125$ °C), **7c** ($T_m = 113$ °C), **8a** ($T_m = 132$ °C), **8b** ($T_m =$

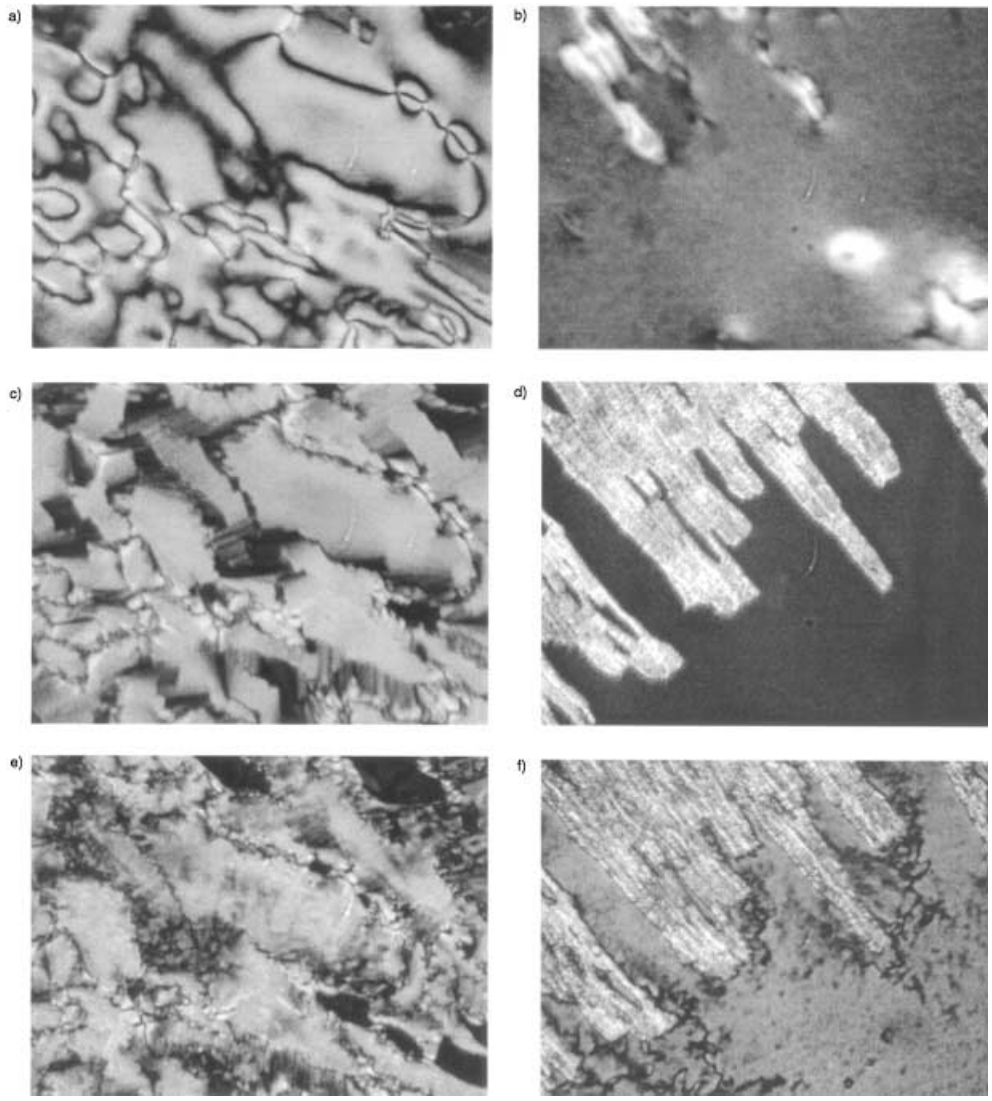

Figure 6. Optical photomicrographs (crossed polarizers) of the textures of macrocycle **17**: (a, b) nematic phase at 101 °C; (c, d) SmA-phase at 90 °C; (e, f) optically biaxial smectic phase (most probably SmC) at 81 °C.

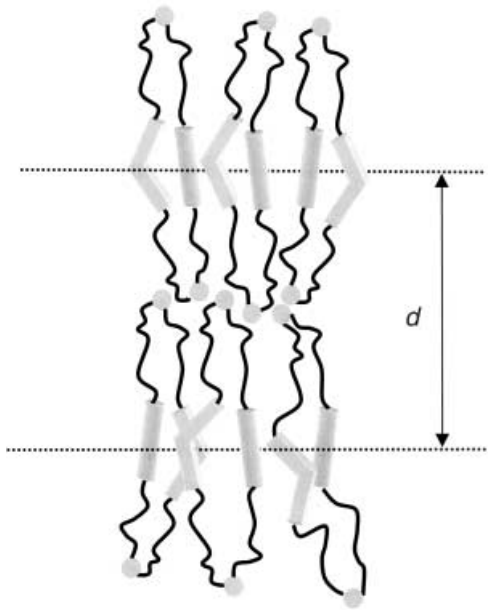

Figure 7. Proposed arrangement of macrocycle **17** in the SmA phase.

120 °C) including the ring precursor **16** ($T_m = 100$ °C) and no mesophase could be detected for any of these non-cyclic compounds, the mesophases of the cycle **9b** must be induced or significantly stabilised by the macrocyclic molecular structure. Accordingly, it is assumed that for the other cyclic compounds **9a** and **17** the cyclic molecular structure is essential for the formation of the liquid crystalline phases, too. The appearance of mesophases for the macrocycles but not for the non-cyclic model compounds is probably largely due to the reduced conformational flexibility of the rings in comparison to related open-chain compounds. Furthermore, the reduced difference in entropy between the isotropic and the LC state when comparing cyclic with non-cyclic compounds should additionally favor the formation of the liquid crystalline phases.[7b] With the investigated macrocycles nematic phases are predominant, even for macrocycles with very long aliphatic segments. Obviously the different shapes of the two mesogenic segments disturb the organisation of these units into distinct sublayers and thus favor the nematic phase.

The macrocycle **24**, incorporating as a banana-shaped unit the significantly smaller bisphenol A, directly melts into an

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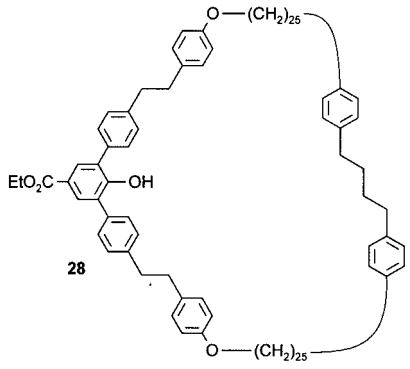

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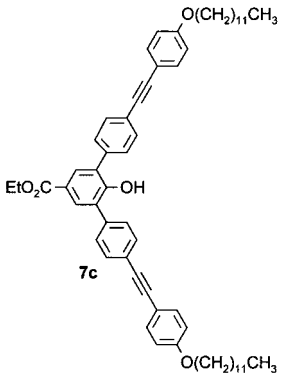

7c

27a $n = 5$
27b $n = 10$

isotropic liquid at 85 °C which rapidly crystallizes on cooling. Only upon very rapid cooling from the isotropic liquid state a rather fluid birefringent mesophase occurs at 43 °C, which immediately crystallizes. The very rapid crystallization did not allow for deciding unambiguously whether this is a true liquid crystalline or a disordered crystalline phase and prevents any further investigation of this phase. In the case of compound **24**, the mesophase stabilization provided by macrocyclization is obviously not sufficient to give rise to a stable liquid crystalline phase. Hence, the appropriate choice of the anisometric segments is also of great importance for the successful design of liquid crystalline macrocycles.

Conclusion

We have developed an efficient synthesis for monodisperse cyclic compounds with 63, 78, and 147 ring atoms. The final key step is the cyclization through oxidative dimerization of aryl ethyne groups. Although the gigantocycles **9a**, **b** and **17** show some rather special structural features, the reported synthetic strategy of these compounds gives a useful guideline for the preparation of gigantocycles with variations in ring size, building blocks and functional groups.

The unique combination of a banana-shaped and a rod-like moiety within a ring gives rise to unexpectedly stable nematic and smectic liquid crystalline phases. The cyclic molecular structure thereby seems to be essential for the formation of the liquid crystalline phases of the molecules under discussion. The covalent fixation of rigid segments with different shapes, which are highly incompatible with each other and therefore would not mix as individual molecules, could in the future lead to novel non-conventional mesophases. Additionally, the reported gigantocycles open the way to the preparation of liquid crystalline catenanes, a new class of supramolecular mesomorphic compounds.[42]

Experimental Section

General methods: All reactions were carried out under an inert atmosphere in dried Schlenk flasks. In the case of CC-coupling reactions, the solutions were degassed through several freeze-pump-thaw cycles prior to the addition of the catalysts. THF was dried over sodium/benzophenone and piperidine over CaH_2. $[Pd(PPh_3)_2Cl_2]$ was synthesized according to the literature,[43] however with 2.1 times the amount of methanol. For flash chromatography, silica gel was used. TLC was carried out on silica gel-coated aluminium foil (Merck $60F_{254}$). The petroleum ether used had a boiling range of 30–40 °C. The NMR spectra were recorded on a 300 MHz instrument at room temperature in $CDCl_3$ as solvent and internal standard. The assignment of the ^{13}C NMR signals is in accordance with Dept-135 measurements. The only exception is the signal of C≡**C**H. This signal does not appear in the DEPT spectrum, in common with our observations of a variety of compounds of the type ArC≡**C**H and AlkC≡**C**H.[44] The subscripts α, β, γ, δ, and ε refer to the aromatic rings. The hydroxybenzoate moiety is named α. The benzene unit closest to the hydroxybenzoate moiety is named β, the benzene unit connected with Ar_β by only one ethyne moiety is named γ, the benzene unit connected with Ar_γ by the alkane chain is named δ, and the residual benzene unit is named ε. For the numbering of the positions, the ethyl 4-hydroxybenzoate is considered as the substituted parent compound. Accordingly, the aromatic rings of the precursors **4**, **5**, **12**–**14** are named and numbered as if these chains were already attached to the core unit, ethyl 4-hydroxybenzoate. If not otherwise mentioned, melting points were determined in open capillaries and are not corrected. The temperatures for crystalline–crystalline, crystalline–liquid crystalline, and liquid crystalline–isotropic melt transitions were read at the maximum or minimum of the endothermic or exothermic peaks of the DSC traces. Terphenylene **6**[12] was obtained as described in the literature.

Pentacos-2-yn-1-ol (2): *n*BuLi (1.6 M, 102 mL, 163 mmol) in hexane was added dropwise (30 min) to a solution of 3-tetrahydropyranyloxyprop-1-yne (24.0 g, 171 mmol) in THF (230 mL) at −75 °C (bath temp). After stirring the reaction mixture for 0.5 h at −73 °C, DMPU (100 mL) was added dropwise (20 min), followed by the addition of solid, degassed 1-bromodocosane (50.10 g, 128.3 mmol). The cooling bath was removed and the reaction mixture was stirred 17.5 h at room temperature. The resulting suspension was cooled (ice bath) and quenched with water. The aqueous phase was extracted with diethyl ether. The combined organic phases were washed with 2 N HCl, water and finally with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was dissolved in 1,4-dioxane (400 mL) and methanol (200 mL), and toluenesulfonic acid monohydrate (2.0 g, 11 mmol) was added. Slowly, a precipitate formed. After stirring the reaction mixture for 4.5 h at room temperature, NaOH (2 N, 50 mL), and water (500 mL) were added, the precipitate was filtered off using a Büchner glass funnel, washed with water and methanol, and dried (P_4O_{10}, 0.01 mbar) to give **2** (43.1 g, 92 %). Recrystallization from ethanol (300 mL) gave **2** (40.3 g, 86 %) as a beige colored solid.[45] M.p. 77.0–77.9 °C; ^1H NMR: $\delta = 4.24$ (t, $^5J = 2.2$ Hz, 2H, H-1), 2.19 (tt, $^5J = 2.2$ Hz, $^3J = 7.0$ Hz, 2H, H-4), 1.56 (br s, 1H, OH), 1.49 (m, 2H, H-5), 1.4–1.2 (m, 38H, CH_2), 0.87 (t-shaped, 3H); ^{13}C NMR: $\delta = 86.7$, 78.3 (C≡C), 51.4 (CH_2OH), 31.9 (CH_2), 29.7–28.6 (7 signals, CH_2), 22.7, 18.7 (CH_2), 14.1

(CH_3); elemental analysis calcd (%) for $C_{25}H_{48}O$ (364.658): C 82.34, H 13.27; found: C 82.20, H 13.37.

Pentacos-24-yn-1-ol (3):[18] A mixture of lithium (2.90 g, 418 mmol) and 1,3-diaminopropane (200 mL; distilled from CaH_2) was heated to 70 °C until the blue color had disappeared (ca. 1 h). The reaction mixture was cooled to room temperature, KO*t*Bu (27.30 g, 243 mmol), and 30 min later solid **2** (25.31 g, 69.41 mmol) was added. The brown reaction mixture was kept at 40–45 °C for 24 h.[46] The reaction mixture was cooled (ice bath) and poured onto 5 N HCl (ca. 1 L) at such a rate that the temperature of the acidic solution did not exceed 21 °C. The brown precipitate was filtered off (Büchner glass funnel), suspended in water, filtered off again, washed with water, and dried (P_4O_{10}, 0.01 mbar). In most experiments filtering proceeds rather slowly, therefore washing was kept to a minimum giving a crude material full of salts. Column chromatography, first with petroleum ether to elute the non-polar side products, then with petroleum ether/CH_2Cl_2 1:1 *v*/*v* to elute undefined side products and finally with petroleum ether/diethyl ether 1:1 *v*/*v* to elute the product **3** (16.8 g).[47] The latter was recrystallized from hexane to give **3** (15.3 g, 61 %) as a colorless solid. The compound was made detectable by TLC with the aid of the ammonium salt of 8-anilinonaphthalin-1-sulfonic acid.[48] The isolated yields of other experiments varied between 40 and 75 %. M.p. 80.5–81.9 °C (lit.:[49] 76–78 °C); ^{1}H NMR: $\delta = 3.62$ (t, $J = 6.6$ Hz, 2 H, H-1), 2.16 (dt, $^4J = 2.6$ Hz, $^3J = 7.0$ Hz, 2 H, H-23), 1.92 (t, $J = 2.6$ Hz, 1 H, H-25), 1.53 (m, 4 H, H-2, -22), 1.24 (m, 42 H, CH_2); ^{13}C NMR: $\delta = 84.8$ (C-24), 68.0 (C-25),[50] 63.1 (C-1), 32.8, 29.7–28.5 (7 signals), 25.7, and 18.4 (CH_2); elemental analysis calcd (%) for $C_{25}H_{48}O$ (364.658): C 82.34, H 13.27; found: C 82.39, H 13.30.

1-Bromo-4-(triisopropylsilylethynyl)benzene (18a): For a better control of the reaction the following procedure is recommended instead of the published one.[12] [$Pd(PPh_3)_2Cl_2$] (101 mg, 0.14 mmol) and CuI (537 mg, 2.82 mmol) were added to a degassed solution of 1-bromo-4-iodobenzene (40.00 g, 141 mmol) in piperidine (100 mL) and THF (150 mL). The flask was immersed in an ice bath and triisopropylsilylacetylene (35 mL, 156 mmol) was added within 30 min (the temperature of the reaction mixture was kept at 10–20 °C). The flask was left in the ice bath and the reaction mixture and cooling bath were allowed to slowly reach room temperature (ca. 3 h). The onset of the reaction can be seen due to the formation of a precipitate. Removing the cooling bath too early results in a sudden increase of the temperature. If the temperature of the reaction mixture rises above 30 °C, a substantial amount of 1,4-bis(triisopropylsilylethynyl)benzene is formed. After stirring the reaction mixture overnight at room temperature, diethyl ether and 2 N HCl were added. This is an exothermic reaction! The organic phase was washed twice with 2 N HCl and the combined aqueous phases were extracted with diethyl ether. The combined organic phases were dried ($MgSO_4$) and the solvent was removed in vacuo. Distillation (140–145 °C, 0.6 mbar) gave **18a** (39 g, 82 %) as a slightly yellow liquid. The compound slowly decomposed with formation of a precipitate, therefore storage under inert atmosphere in a freezer is recommended. For analytical data see the reference.[12]

1-Iodo-4-(triisopropylsilylethynyl)benzene (19a): 1.6 M *n*BuLi in hexane (63 mL, 101 mmol) was added dropwise (ca. 30 min) to a solution of **18a** (30.0 g, 88.9 mmol) in THF (400 mL) at −78 °C. After stirring the solution at −78 °C for 30 min, iodine (26.7 g, 105 mmol) was added as a solid. The cooling bath was removed and the reaction mixture was allowed to come to room temperature. Saturated aqueous $Na_2S_2O_3$ was then added. The aqueous phase was extracted with diethyl ether, the organic phase was washed with saturated aqueous $Na_2S_2O_3$ and dried ($MgSO_4$). Distillation (104–108 °C, 0.01 mbar) gave iodo compound **19a** (22 g, 64 %) as a reddish liquid. The product contained traces of the hydrolysis product (triisopropylsilylethynyl)benzene. ^{1}H NMR: $\delta = 7.62$ (half of AA′XX′, 2 H, H-2, -6), 7.18 (half of AA′XX′, 2 H, H-3, -5), 1.11 (apparent s, 21 H, C**H**(C**H**$_3$)$_2$); ^{13}C NMR: $\delta = 137.3$ (CH), 133.5 (CH), 123.0 (C-4), 106.0 (**C**≡CSi), 94.1 (C-1), 92.4 (C≡**C**Si), 18.6 (**C**H$_3$), 11.3 (Si**C**H).

25-[4-(2-Triisopropylsilylethynyl)phenyl]pentacos-24-yn-1-ol (4b): [$Pd(PPh_3)_2Cl_2$] (270 mg, 0.38 mmol) and CuI (146 mg, 0.77 mmol) were added to a solution of pentacos-24-yn-1-ol (**3**) (13.82 g, 37.90 mmol) and iodo compound **19a** (16.02 g, 41.68 mmol) in piperidine (200 mL). After 21 h at room temperature, the reaction mixture was cooled (ice bath) and poured into cold (ice bath) 5 N HCl (450 mL). The precipitate was filtered off, washed with water and dried (P_4O_{10}, vacuum). Flash chromatography (CH_2Cl_2, $R_f = 0.5$) gave **4b** (15.5 g, 66 %) as a colorless wax. M.p. 36.5–37.0 °C; ^{1}H NMR: $\delta = 7.36$, 7.29 (AA′XX′, 2 H each, ArH), 3.61 (t, $J =$ 6.6 Hz, 2 H, C**H**$_2$OH), 2.38 (t, $J = 7.0$ Hz, 2 H, C**H**$_2$C≡C), 1.55 (m, 4 H, C**H**$_2$CH$_2$OH, C**H**$_2$CH$_2$C≡C), 1.5–1.2 (m, 38 H, CH_2), 1.10 (apparent s, 21 H, C**H**(C**H**$_3$)$_2$); ^{13}C NMR: $\delta = 131.8$, 131.3 (CH$_\delta$), 124.1, 122.5 (C$_\delta$-4, C$_\delta$-1), 106.8 (**C**≡CSi), 92.5 (CH$_2$**C**≡C), 92.0 (C≡**C**Si), 80.4 (CH$_2$C≡**C**), 63.1 ($HOCH_2$), 32.8, 29.7–28.7 (7 signals), 25.7, 19.5 (CH_2), 18.6 (CH_3), 11.3 (CH); elemental analysis calcd (%) for $C_{42}H_{72}OSi$ (621.123): C 81.22, H 11.68; found: C 81.24, H 11.72.

4-{25-[4-(2-Triisopropylsilylethynyl)phenyl]pentacos-24-yn-1-yloxy}-1-iodobenzene (5b): Diisopropyl azodicarboxylate (5.3 mL, 26.9 mmol) was added to a cooled (ice bath) solution of alkynol **4b** (13.90 g, 22.37 mmol), 4-iodophenol (5.91 g, 26.9 mmol), and PPh_3 (7.05 g, 26.9 mmol) in THF (250 mL). The reaction is slightly exothermic. After 27 h (the reaction needs less time for completion) at room temperature, the solvent was removed in vacuo. Flash chromatography (petroleum ether/CH_2Cl_2 1:1 *v*/*v*, $R_f = 0.96$) gave **5b** (16.3 g). The product was dissolved in CH_2Cl_2 (40 mL) and this solution was added to ethanol (300 mL). The precipitate which formed was isolated and washed with ethanol to give **5b** (15.6 g 85 %) as a colorless solid. M.p. 70.8–72.0 °C; ^{1}H NMR: $\delta = 7.52$ (half of AA′XX′, 2 H, H$_\gamma$-2, -6), 7.36, 7.29 (AA′XX′, 2 H each, H$_\delta$), 6.65 (half of AA′XX′, 2 H, H$_\gamma$-3, -5), 3.88 (t, $J = 6.6$ Hz, 2 H, OCH_2), 2.38 (t, $J = 7.0$ Hz, 2 H, CH_2C≡C), 1.74 (m, 2 H, OCH$_2$C**H**$_2$), 1.56 (m, 2 H, C**H**$_2$CH$_2$C≡C), 1.5–1.2 (m, 38 H, CH_2), 1.10 (apparent s, 21 H, C**H**(C**H**$_3$)$_2$); ^{13}C NMR: $\delta = 159.1$ (C$_\gamma$-4), 138.2 (C$_\gamma$-2, -6), 131.8, 131.3 (**C**H$_\delta$), 124.1, 122.5 (C$_\delta$-1, -4), 117.0 (C$_\gamma$-3, -5), 106.8 (**C**≡CSi), 92.5 (CH$_2$**C**≡C), 92.0 (C≡**C**Si), 82.4 (C$_\gamma$-1), 80.4 (CH$_2$-C≡**C**), 68.2 (OCH_2), 29.7–28.7 (7 signals), 26.0, 19.5 (CH_2), 18.7 (CH_3), 11.3 (CH); elemental analysis calcd (%) for $C_{48}H_{75}OISi$ (823.118): C 70.04, H 9.18; found: C 70.06, H 9.06.

Additional note: Although the accompanying products of this reaction, Ph_3PO and diisopropyl hydrazodicarboxylate, can be removed by two precipitations from a solution of the reaction product mixture in CH_2Cl_2 by mixing with ethanol, column chromatography is necessary to remove a product that is formed in small amounts and whose structure consists of the alkynol and (part of) the azo/hydrazo reagent. This side product has a comparatively small R_f value.

Ethyl 3,5-bis-{4-[2-(4-(25-(4-(2-triisopropylsilylethynyl)phenyl)pentacos-24-yn-1-yloxy)phenyl)ethinyl]phenyl}-4-hydroxybenzoate (7b): [$Pd(PPh_3)_2Cl_2$] (60 mg, 0.085 mmol) and CuI (33 mg, 0.17 mmol) were added to a solution of **6** (3.13 g, 8.54 mmol) and **5b** (15.50 g, 18.83 mmol) in piperidine (250 mL). The reaction mixture was stirred for 21 h at room temperature. It was cooled (ice bath) and poured into cold (ice bath) 5 N HCl (600 mL). The precipitate was filtered off, washed well with water, and dried (P_4O_{10}, vacuum). Flash chromatography [petroleum ether/CH_2Cl_2 3:1 *v*/*v* was used until the first fraction, the residual iodo compound, was eluted (R_f (**5b**) = 0.7. Then petroleum ether/CH_2Cl_2 1:1 *v*/*v* was used to elute the product **7b**; R_f (**7b**) = 0.57] gave **5b** (1.5 g, 10 %) as a colorless solid and **7b** (11.0 g, 73 %) as a slightly brown solid. M.p. 52.5–54.0 °C; ^{1}H NMR: $\delta =$ 7.99 (s, 2 H, H$_\alpha$), 7.61, 7.53 (AA′XX′, 4 H each, H$_\beta$), 7.46 (half of AA′XX′, 4 H, H$_\gamma$-2, -6), 7.36, 7.29 (AA′XX′, 4 H each, H$_\delta$), 6.86 (half of AA′XX′, 4 H, H$_\gamma$-3, -5), 5.76 (s, 1 H, OH), 4.36 (q, $J = 7.1$ Hz, 2 H, CO_2CH_2), 3.96 (t, $J =$ 6.6 Hz, 4 H, ArOC**H**$_2$), 2.38 (t, $J = 7.0$ Hz, 4 H, C**H**$_2$C≡C), 1.77 (m, 4 H, OCH$_2$C**H**$_2$), 1.58 (m, 4 H, C**H**$_2$CH$_2$C≡C), 1.38 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.5–1.2 (m, 76 H, CH_2), 1.10 (apparent s, 42 H, C**H**(C**H**$_3$)$_2$); ^{13}C NMR: $\delta = 166.1$ (CO_2), 159.4 (C$_\gamma$-4), 153.2 (C$_\alpha$-4), 135.9 (C$_\beta$-1), 133.1 (C$_\gamma$-2, -6), 132.0 (C$_\beta$-3, -5), 131.8 (C$_\delta$-2, -6 or C$_\delta$-3, -5), 131.6 (C$_\alpha$-2, -6), 131.3 (C$_\delta$-3, -5 or C$_\delta$-2, -6), 129.3 (C$_\beta$-2, -6), 128.3 (C$_\alpha$-3, -5), 124.1 (C$_\delta$-1 or C$_\delta$-4), 123.7 (C$_\beta$-4), 123.4 (C$_\alpha$-1), 122.5 (C$_\delta$-4 or C$_\delta$-1), 114.9 (C$_\gamma$-1), 114.6 (C$_\gamma$-3,-5), 106.8 (**C**≡CSi), 92.5 (CH$_2$**C**≡C), 92.0 (C≡**C**Si), 90.6 (C≡**C**Ar$_\gamma$), 87.6 (Ar$_\beta$**C**≡C), 80.4 (CH$_2$C≡**C**), 68.1 (ArO**C**H$_2$), 60.9 (CO_2CH_2), 29.7–28.7 (10 signals), 26.0, and 19.5 (CH_2), 18.6 (CH**C**H$_{32}$), 14.4 (CH_2CH_3), 11.3 (SiCH); elemental analysis calcd (%) for $C_{121}H_{166}O_5Si_2$ (1756.826): C 82.72, H 9.52; found: C 82.71, H 9.51.

Ethyl 3,5-bis-{4-[2-(4-(25-(4-ethynylphenyl)pentacos-24-yn-1-yloxy)phenyl)ethinyl]phenyl}-4-hydroxybenzoate (8b): 1 M nBu_4NF in THF (12.5 mL, 12.5 mmol) was added to a solution of **7b** (10.89 g, 6.20 mmol) in THF (110 mL) at room temperature. Immediately the solution showed a green fluorescence. After 2 h of stirring, 2 N HCl (13 mL) was added. The solution turned colorless and a colorless precipitate formed. After addition of ethanol (80 mL), the precipitate was isolated and washed well with water and finally with ethanol, to give **8b** (8.8 g, 99 %) as a beige solid. Thermal behavior determined by DSC (10 K min^{-1}) and polarizing microscopy upon

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first (second) heating scan: endothermic transition at 116 (112) and 123 (121) °C; with the microscope crystal ripening is observed at 116–118 °C. Above 122 °C **8b** forms an isotropic melt. ^{1}H NMR: $\delta = 7.98$ (s, 2H, H_α), 7.61, 7.51 (AA′XX′, 4H each, H_β), 7.46 (half of AA′XX′, 4H, H_γ-2, -6), 7.38, 7.31 (AA′XX′, 4H each, H_δ), 6.86 (half of AA′XX′, 4H, H_γ-3, -5), 5.77 (s, 1H, OH), 4.36 (q, $J = 7.1$ Hz, 2H, CO_2CH_2), 3.96 (t, $J = 6.5$ Hz, 4H, $ArOCH_2$), 3.10 (s, 2H, C≡C**H**), 2.38 (t, $J = 7.0$ Hz, 4H, $CH_2C{\equiv}C$), 1.77 (m, 4H, OCH_2CH_2), 1.56 (m, 4H, $CH_2CH_2C{\equiv}C$), 1.38 (t, $J = 7.1$ Hz, 3H, CH_3), 1.5–1.2 (m, 76H, CH_2); ^{13}C NMR: $\delta = 166.1$ (CO_2), 159.4 (C_γ-4), 153.2 (C_α-4), 135.9 (C_β-1), 133.1 (C_γ-2, -6), 132.0 (C_β-3, -5), 131.9 (C_δ-2, -6 or C_δ-3, -5), 131.6 (C_α-2, -6), 131.4 (C_δ-3, -5 or C_δ-2, -6), 129.3 (C_β-2, -6), 128.3 (C_α-3, -5), 124.7 (C_δ-1 or C_δ-4), 123.6, 123.4 (C_α-1, C_β-4), 121.1 (C_δ-4 or C_δ-1), 114.9 (C_γ-1), 114.6 (C_γ-3, -5), 92.8 ($CH_2C{\equiv}C$), 90.6 ($C{\equiv}CAr_\gamma$), 87.6 ($Ar_\beta C{\equiv}C$), 83.4 (**C**≡CH), 80.2 ($CH_2C{\equiv}C$), 78.3 (C≡**C**H), 68.1 ($ArOCH_2$), 60.9 (CO_2CH_2), 29.7–28.7 (10 signals), 26.0, and 19.5 (CH_2), 14.4 (CH_3); elemental analysis calcd (%) for $C_{103}H_{126}O_5$ (1444.136): C 85.67, H 8.79; found: C 85.31, H 8.95.

Gigantocycle 9b: A mixture of $CuCl_2$ (1.20 g, 8.30 mmol) and CuCl (6.90 g, 69.7 mmol) was dried by gently heating (ca. 60 °C) it under a stream of argon. After cooling to room temperature, pyridine (1 L) was added. The suspension was heated to 50 °C for ca. 30 min to dissolve most of the copper salts. After cooling to room temperature, solution of **8b** (3.00 g, 2.07 mmol) in pyridine (300 mL) was added to the resulting suspension within 240 h using a syringe pump. It was necessary to gently heat the solution of **8b** to dissolve all of the starting material. Once in solution, **8b** stays dissolved for a sufficient time. After the addition was complete, the reaction mixture was stirred for additional 24 h. Most of the solvent was removed (50 °C bath temp., 10 mbar) and the residue was dissolved in CH_2Cl_2 and 2N HCl. The organic phase was washed with 2N HCl until the aqueous phase stayed acidic and the color of the organic phase had changed to yellow. The combined aqueous phases were extracted with CH_2Cl_2 and the combined organic phases were dried ($MgSO_4$). The solvent was removed in vacuo. Flash chromatography (petroleum ether/CH_2Cl_2 3:2 → 1:1 *v*/*v*) gave macrocycle **9b** (2.6 g, 87%) as a yellow solid.

The addition time can be significantly reduced. The addition of a solution of **8b** (1.40g, 0.97 mmol) in pyridine (200 mL) to a suspension of $CuCl_2$ (1.11 g, 8.23 mmol) and CuCl (6.44 g, 65.1 mmol) in pyridine (500 mL) within 56 h gave macrocycle **9b** (1.2 g, 83%). Thermal behavior determined by DSC (10 K min^{-1}) and polarizing microscopy upon first (second and third) heating scan: $T_{cr\text{-}cr} = 147$ (133) °C, $T_{cr\text{-}n} = 151$ (142) °C, $T_{n\text{-}i} = 161$ °C; ^{1}H NMR: $\delta = 7.99$ (s, 2H, H_α), 7.61, 7.52 (AA′XX′, 4H each, H_β), 7.46 (half of AA′XX′, 4H, H_γ-2, -6), 7.39, 7.30 (AA′XX′, 4H each, H_δ), 6.86 (half of AA′XX′, 4H, H_γ-3, -5), 5.72 (s, 1H, OH), 4.36 (q, $J = 7.1$ Hz, 2H, CO_2CH_2), 3.97 (t, $J = 6.5$ Hz, 4H, $ArOCH_2$), 2.38 (t, $J = 7.0$ Hz, 4H, $CH_2C{\equiv}C$), 1.77 (m, 4H, OCH_2CH_2), 1.57 (m, 4H, $CH_2CH_2C{\equiv}C$), 1.38 (t, $J = 7.1$ Hz, 3H, CH_3), 1.5–1.2 (m, 76H, CH_2); ^{13}C NMR: $\delta = 166.1$ (CO_2), 159.4 (C_γ-4), 153.2 (C_α-4), 135.9 (C_β-1), 133.1 (C_γ-2, -6), 132.3 (C_δ-2, -6 or C_δ-3, -5), 132.0 (C_β-3, -5), 131.6 (C_δ-3, -5 or C_δ-2, -6), 131.5 (C_α-2, -6), 129.3 (C_β-2, -6), 128.3 (C_α-3, -5), 125.2 (C_δ-1 or C_δ-4), 123.6, 123.4 (C_α-1, C_β-4), 120.6 (C_δ-4 or C_δ-1), 115.0 (C_γ-1), 114.7 (C_γ-3, -5), 93.6 ($CH_2C{\equiv}C$), 90.6 ($C{\equiv}CAr_\gamma$), 87.6 ($Ar_\beta C{\equiv}C$), 82.0 (**C**≡C-C≡**C**), 80.2 ($CH_2C{\equiv}C$), 75.2 (C≡**C**-C≡C), 68.1 ($ArOCH_2$), 61.0 (CO_2CH_2), 29.6–28.7 (9 signals), 25.9, and 19.5 (CH_2), 14.4 (CH_3); UV/Vis: λ (ε [10^6 cm^2 mol^{-1}]) = 265 (496), 281 (582), 297 (790), 312 (1020), 333 (919), 359 nm (4271 10^6 cm^2 mol^{-1}); emission ($\lambda_{excitation} = 310$ nm) $\lambda = 367$, 397 nm; elemental analysis calcd (%) for $C_{103}H_{124}O_5$ (1442.120): C 85.79, H 8.67; found: C 85.86, H 8.68.

Hydrogenated gigantocycle 28: Pd/C (10%; 3 mg, 3×10^{-4} mmol) was added to a solution of macrocycle **9b** (324 mg, 0.22 mmol) in THF (20 mL). Hydrogen was introduced from a balloon by means of a glass tube which dipped into the suspension. After 3 d at room temperature a second portion of Pd/C (10%; 3 mg, 3×10^{-4} mmol) was added and the reaction mixture was stirred for another 2 d under a layer of hydrogen. The catalyst was removed by filtration. The solvent was removed and the residue purified by chromatography (petroleum ether/CH_2Cl_2 1:1 → 1:2 *v*/*v*) to yield **28** (263 mg, 80%) as a colorless solid. Due to a proton signal at 5.5 ppm the reaction was believed to be incomplete after 3 d therefore more Pd/C was added. However, the intensity of this signal increased upon further reaction. To avoid this side reaction, a shorter reaction time is recommended. Thermal behavior determined by DSC (10 K min^{-1}) and polarizing microscopy upon first (second and third) heating scan: melting at 78 (79), crystallization at 80 (86), melting at 106 and 110 (107) °C; upon cooling: crystallization at 71 °C; ^{1}H NMR: $\delta = 7.97$ (s, 2H, H_α), 7.45, 7.25 (AA′XX′, 4H each, H_β), 7.06 (half of AA′XX′, 4H, H_γ-2, -6), 7.06 (apparent s, 8H, H_δ), 6.81 (half of AA′XX′, 4H, H_γ-3, -5), 5.78 (s, OH), 4.36 (q, $J = 7.1$ Hz, 2H, CO_2CH_2), 3.93 (t, $J = 6.6$ Hz, 4H, $ArOCH_2$), 2.93 (m, 8H, $Ar_\beta(CH_2)_2Ar_\gamma$), 2.61–2.52 (m, 8H, $CH_2Ar_\delta CH_2$), 1.76 (m, 4H, OCH_2CH_2), 1.38 (t, $J = 7.1$ Hz, 3H, CH_3), 1.7–1.2 (m, 92H, CH_2); ^{13}C NMR: $\delta = 166.4$ (CO_2), 157.5 (C_γ-4), 153.4 (C_α-4), 141.8, 140.1, 139.7, 134.1, 133.3 (C_β-1, C_β-4, C_γ-1, C_δ-1, C_δ-4), 131.3 (C_α-2, -6), 129.4, 129.20 (C_β-2, -6, C_γ-2, -6), 129.17 (C_β-3, -5), 128.6 (C_α-3, -5), 128.2 (CH_δ), 123.0 (C_α-1), 114.5 (C_γ-3, -5), 68.0 ($ArOCH_2$), 60.7 (CO_2CH_2), 37.8, 36.7, 35.5, 35.4, 31.5, 31.0 ($ArCH_2CH_2$), 29.6–29.3 (4 signals, CH_2), 26.0 (CH_2), 14.4 (CH_2CH_3); elemental analysis calcd (%) for $C_{103}H_{148}O_5$ (1466.312): C 84.37, H 10.17; found: C 84.41, H 10.29.

Tridec-12-inyltrimethylsilyl ether (11): Lithium acetylide ethylenediamine complex (15.7 g, 171 mmol) was added portionwise at −30 °C to THF (50 mL). The suspension was cooled to −20 °C and 1,3-dimethyl-1,3-diazacyclohexan-2-on (125 mL) was added. At a temperature of −20 to −10 °C 11-bromoundecyltrimethylsilyl ether (**10**) (50.0 g, 155 mmol) was added dropwise. When the addition was complete, the cooling bath was removed and the reaction mixture stirred for 24 h at room temperature. To the cooled (ice bath) reaction mixture saturated aqueous NH_4Cl and water were added and the mixture extracted with diethyl ether. The combined organic phases were washed with water and dried ($MgSO_4$). Fractional distillation (90–105 °C, 10^{-2} mbar) using a Bösherz distillation column gave **11** (23.7 g, 57%) as a colorless liquid containing ca. 5% of tridec-12-yn-1-ol [determined by ^{1}H NMR spectroscopy; characteristic signal: $\delta = 3.58$ (t, $J = 6$ Hz, 2H, $HOCH_2$)]. The distillation fractions at lower temperature contained olefinic material, most probably $H_2C{=}CH(CH_2)_9OTMS$. ^{1}H NMR: $\delta = 3.46$ (t, $J = 6.7$ Hz, 2H, OCH_2), 2.06 (dt, $^3J = 6.9$ Hz, $^4J = 2.6$ Hz, 2H, $CH_2C{\equiv}C$), 1.81 (t, $J = 2.6$ Hz, 1H, C≡C**H**), 1.42 (m, 4H, OCH_2CH_2, $CH_2CH_2C{\equiv}C$), 1.4–1.1 (m, 14H, CH_2), 0.00 (s, 9H, $SiCH_3$); ^{13}C NMR: $\delta = 84.3$, 68.0 (C≡C), 62.5 (OCH_2), 32.7, 29.5–28.4 (7 signals), 25.7, 18.2 (CH_2), −0.6 ($SiCH_3$); elemental analysis calcd (%) for $C_{16}H_{32}OSi$ (268.517): C 71.56, H 12.01; found: C 71.13, H 11.90.

Additional note: Occasionally the amount of tridec-12-yn-1-ol was much larger. In these cases, the product was silylated in a manner analogous to the procedure given for the preparation of **10**. The use of tridec-12-yn-1-ol for coupling with **19a** results in a distinctly larger amount of by-products such as butadiynes (alkyne dimerization product) being produced. This is in contrast to the smooth reaction of **3** that yielded only traces of butadiyne as side product.

13-[4-(2-Triisopropylsilylethynyl)phenyl]tridec-12-yn-1-ol (4a): CuI (145 mg, 0.76 mmol) and $[PdCl_2(PPh_3)_2]$ (266 mg, 0.38 mmol) were added to a solution of **11** (10.19 g, 37.94 mmol) and **19a** (17.50 g, 45.53 mmol) in piperidine (133 mL). After stirring the reaction mixture for 2.5 h at room temperature, the solvent was removed in vacuo and the residue was dissolved in diethyl ether (100 mL). 2N HCl (100 mL) was added and the reaction mixture was stirred overnight. The organic phase was washed with 2N HCl. The combined aqueous phases were extracted with diethyl ether and the combined organic phases were dried (Na_2SO_4). The solvent was removed in vacuo. Flash chromatography (petroleum ether/CH_2Cl_2 1:1 *v*/*v*; $R_f = 0.12$) gave alkynol **4a** (14.5 g, 85%) as a yellow oil. ^{1}H NMR: $\delta = 7.36$, 7.28 (AA′XX′, 2H each, ArH), 3.56 (t, $J = 6.6$ Hz, 2H, CH_2OH), 2.56 (s, 1H, OH), 2.37 (t, $J = 7.0$ Hz, 2H, $CH_2C{\equiv}C$), 1.54 (m, 4H, CH_2CH_2OH, $CH_2CH_2C{\equiv}C$), 1.5–1.2 (m, 14H, CH_2), 1.10 (apparent s, 21H, $CH(CH_3)_2$); ^{13}C NMR: $\delta = 131.6$, 131.2 (CH_δ), 124.1, 122.4 (C_δ-4, C_δ-1), 106.8 (**C**≡CSi), 92.3 ($CH_2C{\equiv}C$), 91.8 (C≡**C**Si), 80.3 ($CH_2C{\equiv}C$), 62.6 ($HOCH_2$), 32.6, 29.5–28.6 (7 signals), 25.7,/19.4 (CH_2), 18.5 (CH_3), 11.2 (CH); elemental analysis calcd (%) for $C_{30}H_{48}OSi$ (452.799): C 79.58, H 10.68; found: C 79.59, H 10.60.

4-{13-[4-(2-Triisopropylsilylethynyl)phenyl]tridec-12-yn-1-yloxy}-1-iodobenzene (5a): Diisopropyl azodicarboxylate (15.9 mL, 80.7 mmol) was added to a solution of alkynol **4a** (27.62 g, 61.00 mmol), 4-iodophenol (17.76 g, 80.70 mmol), and PPh_3 (21.17 g, 80.70 mmol) in THF (400 mL). This is an exothermic reaction. After stirring the reaction mixture for 3 h at room temperature, the solvent was removed in vacuo. Flash chromatography (petroleum ether/CH_2Cl_2 1:1 *v*/*v*; $R_f = 0.89$) gave **5a** as a brown oil which slowly solidified. Recrystallization from ethanol (ca. 400 mL) gave **5a** (29.4 g, 73%) as a colorless solid. M.p. 39.1–39.9 °C; ^{1}H NMR: $\delta = 7.52$ (half of AA′XX′, 2H, H_γ-2, -6), 7.37, 7.30 (AA′XX′, 2H each, H_δ), 6.65 (half of AA′XX′, 2H, H_γ-3, -5), 3.88 (t, $J = 6.6$ Hz, 2H, OCH_2), 2.39 (t, $J = 7.0$ Hz,

2H, C$\mathbf{H}_2$C≡C), 1.74 (m, 2H, OCH$_2$C$\mathbf{H}_2$), 1.59 (m, 2H, C$\mathbf{H}_2$CH$_2$C≡C), 1.5–1.2 (m, 14H, CH$_2$), 1.12 (apparent s, 21H, C$\mathbf{H}$(C$\mathbf{H}_3$)$_2$); ^{13}C NMR: δ = 159.0 (C_γ-4), 138.1 (C_γ-2, -6), 131.8, 131.3 (CH$_\delta$), 124.1, 122.5 (C_δ-1, -4), 117.0 (C_γ-3, -5), 106.8 (**C**≡CSi), 92.5 (CH$_2$**C**≡C), 92.0 (C≡**C**Si), 82.4 (C_γ-1), 80.4 (CH$_2$C≡**C**), 68.1 (OCH$_2$), 29.5–28.7 (7 signals), 26.0, 19.5 (CH$_2$), 18.6 (CH$_3$), 11.3 (CH); elemental analysis calcd (%) for $C_{36}H_{51}IOSi$ (654.794): C 66.04, H 7.85; found: C 66.113, H 7.88.

Ethyl 3,5-bis-{4-[2-(4-(13-(4-(2-triisopropylsilylethynyl)phenyl)tridec-12-yn-1-yloxy)phenyl)ethinyl]phenyl}-4-hydroxybenzoate (7a): CuI (30 mg, 0.16 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (57 mg, 0.08 mmol) were added to a degassed solution of terphenylene **6** (3.00 g, 8.19 mmol) and iodo compound **5a** (11.79 g, 18.01 mmol) in piperidine (150 mL). After stirring the reaction mixture for 3 h at room temperature the piperidine was removed in vacuo and the residue was dissolved in CH_2Cl_2 and 2N HCl. The organic phase was washed with 2N HCl and the combined aqueous phases were extracted with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4). The solvent was removed in vacuo. Flash chromatography (petroleum ether/CH_2Cl_2 1:1 *v*/*v*; R_f (**5a**) = 0.92, R_f (**7a**) = 0.70) gave **7a** (9.7 g, 83%) as a highly viscous, slightly brown oil. ^{1}H NMR: δ = 7.99 (s, 2H, H$_\alpha$), 7.62, 7.53 (AA′XX′, 4H each, H$_\beta$), 7.47 (half of AA′XX′, 4H, H$_\gamma$-2, -6), 7.38, 7.31 (AA′XX′, 4H each, H$_\delta$), 6.87 (half of AA′XX′, 4H, H$_\gamma$-3, -5), 5.82 (s, 1H, OH), 4.37 (q, J = 7.1 Hz, 2H, CO$_2$CH$_2$), 3.95 (t, J = 6.5 Hz, 4H, ArOC$\mathbf{H}_2$), 2.4 (t, J = 7.0 Hz, 4H, C$\mathbf{H}_2$C≡C), 1.78 (m, 4H, OCH$_2$C$\mathbf{H}_2$), 1.57 (m, 4H, C≡CCH$_2$C$\mathbf{H}_2$), 1.5–1.2 (m, 28H, CH$_2$), 1.12 (apparent s, 42H, C$\mathbf{H}$(C$\mathbf{H}_3$)$_2$); ^{13}C NMR: δ = 166.1 (CO$_2$), 159.4 (C_γ-4), 153.2 (C_α-4), 135.9 (C_β-1), 133.1 (C_γ-2, -6), 131.9 (C_β-3, -5), 131.8 (C_δ-2, -6 or C_δ-3, -5), 131.5 (C_α-2, -6), 131.3 (C_δ-3, -5 or C_δ-2, -6), 129.2 (C_β-2, -6), 128.3 (C_α-3, -5), 124.1 (C_δ-1 or C_δ-4), 123.6 (C_β-4), 123.3 (C_α-1), 122.5 (C_δ-4 or C_δ-1), 114.9 (C_γ-1), 114.6 (C_γ-3,-5), 106.8 (**C**≡CSi), 92.5 (CH$_2$**C**≡C), 92.0 (C≡**C**Si), 90.6 (C≡**C**Ar$_\gamma$), 87.6 (Ar$_\beta$**C**≡C), 80.4 (CH$_2$C≡**C**), 68.1 (ArO**C**H$_2$), 60.9 (CO$_2$**C**H$_2$), 29.5–28.7 (7 signals, CH$_2$), 26.0 (**C**H$_2$CH$_2$C≡C), 19.5 (**C**H$_2$C≡C), 18.6 (CH**C**H$_3$), 14.4 (CH$_3$), 11.3 (SiCH); elemental analysis calcd (%) for $C_{97}H_{118}O_5Si_2$ (1420.167): C 82.04, H 8.37; found: C 81.99, H 8.29.

Ethyl 3,5-bis-{4-[2-(4-(13-(4-ethynylphenyl)tridec-12-yn-1-yloxy)phenyl)-ethinyl]phenyl}-4-hydroxybenzoate (8a): 1M nBu$_4$NF in THF (17.3 mL, 17.3 mmol) was added to a solution of **7a** (11.18 g, 7.87 mmol) in THF (100 mL). After stirring for 2 h, 2N HCL (11.8 mL) was added. After the addition of ethanol (200 mL) **8a** (8.4 g, 96%) was obtained as a colorless solid. M.p. 132.0–133.7 °C; ^{1}H NMR: δ = 7.99 (s, 2H, H$_\alpha$), 7.61, 7.53 (AA′XX′, 4H each, H$_\beta$), 7.48 (half of AA′XX′, 4H, H$_\gamma$-2, -6), 7.40, 7.33 (AA′XX′, 4H each, H$_\delta$), 6.87 (half of AA′XX′, 4H, H$_\gamma$-3, -5), 5.85 (s, 1H, OH), 4.36 (q, J = 7.1 Hz, 2H, CO$_2$C$\mathbf{H}_2$), 3.94 (t, J = 6.5 Hz, 4H, ArOC$\mathbf{H}_2$), 3.13 (s, 2H, C≡C**H**), 2.40 (t, J = 7.0 Hz, 4H, C$\mathbf{H}_2$C≡C), 1.77 (m, 4H, OCH$_2$C$\mathbf{H}_2$), 1.60 (m, 4H, C$\mathbf{H}_2$CH$_2$C≡C), 1.38 (t, J = 7.1 Hz, 3H, CH$_3$), 1.5–1.2 (m, 28H, CH$_2$); ^{13}C NMR: δ = 166.0 (**C**O$_2$), 159.3 (C_γ-4), 153.2 (C_α-4), 135.9 (C_β-1), 133.0 (C_γ-2, -6), 131.9 (C_β-3, -5), 131.8 (C_δ-2, -6 or C_δ-3, -5), 131.5 (C_α-2, -6), 131.4 (C_δ-3, -5 or C_δ-2, -6), 129.2 (C_β-2, -6), 128.3 (C_α-3, -5), 124.7 (C_δ-1 or C_δ-4), 123.5, 123.3 (C_α-1, C_β-4), 121.0 (C_δ-4 or C_δ-1), 114.9 (C_γ-1), 114.5 (C_γ-3, -5), 92.7 (CH$_2$**C**≡C), 90.6 (C≡**C**Ar$_\gamma$), 87.6 (Ar$_\beta$**C**≡C), 83.3 (**C**≡CH), 80.2 (CH$_2$C≡**C**), 78.4 (C≡**C**H), 68.0 (ArO**C**H$_2$), 60.9 (CO$_2$**C**H$_2$), 29.5–28.6 (7 signals), 26.0, 19.4 (CH$_2$), 14.4 (CH$_3$); FD-MS: m/z (%): 1106.9 (100) $[M]^+$, 553.4 (66) $[M]^{2+}$. A correct elemental analysis was not obtained.

Gigantocycle 9a: A suspension of CuCl (8.94 g, 90.3 mmol) and $CuCl_2$ (1.46 g, 10.8 mmol) in pyridine (1.5 L) was prepared as described for the preparation of **9b**. To this suspension was added a solution of **8a** (1.00 g, 0.90 mmol) in pyridine (100 mL) at room temperature within 70 h by means of a syringe pump. When the addition was complete the reaction mixture was stirred for an additional 24 h. Workup as described for **9b** followed by flash chromatography (petroleum ether/CH_2Cl_2 1:1 *v*/*v*; R_f = 0.47) gave **9a** (813 mg, 82%). M.p. 201 °C; ^{1}H NMR: δ = 8.00 (s, 2H, H$_\alpha$), 7.61, 7.51 (AA′XX′, 4H each, H$_\beta$), 7.47 (half of AA′XX′, 4H, H$_\gamma$-2, -6), 7.39, 7.31 (AA′XX′, 4H each, H$_\delta$), 6.87 (half of AA′XX′, 4H, H$_\gamma$-3, -5), 5.72 (s, 1H, OH), 4.37 (q, J = 7.1 Hz, 2H, CO$_2$C$\mathbf{H}_2$), 4.01 (t, J = 6.3 Hz, 4H, ArOC$\mathbf{H}_2$), 2.38 (t, J = 7.0 Hz, 4H, C$\mathbf{H}_2$C≡C), 1.76 (m, 4H, OCH$_2$C$\mathbf{H}_2$), 1.58 (m, 4H, C$\mathbf{H}_2$CH$_2$C≡C), 1.38 (t, J = 7.1 Hz, 3H, CH$_3$), 1.50–1.20 (m, 28H, CH$_2$); ^{13}C NMR: δ = 166.2 (CO$_2$), 159.3 (C_γ-4), 153.3 (C_α-4), 135.8 (C_β-1), 133.1 (C_γ-2, -6), 132.2 (C_δ-2, -6 or C_δ-3, -5), 132.0 (C_β-3, -5), 131.5 (C_δ-3, -5 or C_δ-2, -6), 131.3 (C_α-2, -6), 129.3 (C_β-2, -6), 128.3 (C_α-3 -5), 125.2 (C_δ-1 or C_δ-4), 123.6, 123.3 (C_α-1, C_β-4), 120.6 (C_δ-4 or C_δ-1), 115.0 (C_γ-1), 114.8 (C_γ-3, -5), 93.6 (CH$_2$**C**≡C), 90.7 (C≡**C**Ar$_\gamma$), 87.7 (Ar$_\beta$**C**≡C), 82.0 (**C**≡C-C≡**C**), 80.2 (CH$_2$C≡**C**), 75.2 (C≡**C**-C≡C), 67.9 (ArO**C**H$_2$), 61.0 (CO$_2$**C**H$_2$), 29.2–28.6 (7 signals), 25.6, and 19.5 (CH$_2$), 14.4 (CH$_3$); elemental analysis calcd (%) for $C_{79}H_{76}O_5$ (1105.472): C 85.83, H 6.93; found: C 85.47, H 6.76; FD-MS: m/z (%): 2210.0 (24) $[2M]^+$, 1105.3 (100) $[M]^+$, 552.9 (8)$[M]^{2+}$.

3,5-Dimethyl-4-[25-[4-(2-triisopropylsilylethynyl)phenyl]pentacos-24-yn-1-yloxy}-1-iodobenzene (12): Following the procedure given for the preparation of **5b**, compound **12** was prepared, starting from **4b** (10.08 g, 16.2 mmol), 2,6-dimethyl-4-iodophenol (4.80 g, 19.3 mmol), PPh_3 (5.10 g, 19.4 mmol), and diisopropyl azodicarboxylate (3.84 mL, 19.5 mmol) in THF (175 mL). Flash chromatography (petroleum ether/CH_2Cl_2 1:1 *v*/*v*; R_f = 0.95) gave slightly impure **12** (13 g). This material was dissolved in CH_2Cl_2 (30 mL) and the solution was added to ethanol (200 mL). The resulting precipitate was isolated to give **12** (11.4 g, 82%) as a colorless solid. M.p. 46.2–46.8 °C; ^{1}H NMR: δ = 7.37, 7.30 (AA′XX′, 2H each, H$_\varepsilon$), 7.32 (s, 2H, H$_\delta$-2, -6), 3.70 (t, J = 6.6 Hz, 2H, OCH$_2$), 2.39 (t, J = 7.0 Hz, 2H, C$\mathbf{H}_2$C≡C), 2.21 (s, 6H, ArC$\mathbf{H}_3$), 1.77 (m, 2H, OCH$_2$C$\mathbf{H}_2$), 1.57 (m, 2H, C$\mathbf{H}_2$CH$_2$C≡C), 1.5–1.2 (m, 38H, CH$_2$), 1.12 (apparent s, 21H, C$\mathbf{H}$(C$\mathbf{H}_3$)$_2$); ^{13}C NMR δ = 156.1 (C_δ-4), 137.4 (C_δ-2, -6), 133.6 (C_δ-3, -5), 131.8, 131.3 (**C**H$_\varepsilon$), 124.1, 122.5 (C_ε-1, C_ε-4), 106.8 (**C**≡CSi), 92.5 (CH$_2$**C**≡C), 92.0 (C≡**C**Si), 87.3 (C_δ-1), 80.3 (CH$_2$C≡**C**), 72.5 (OCH$_2$), 30.3–28.7 (8 signals), 26.1, 19.5 (CH$_2$), 18.6 (CH**C**H$_3$), 15.9 (Ar**C**H$_3$), 11.3 (Si**C**H); elemental analysis calcd (%) for $C_{50}H_{79}OISi$ (851.172): C 70.56, H 9.36; found: C 70.56, H 9.41.

25-{3,5-Dimethyl-4-[25-(4-(2-triisopropylsilylethynyl)phenyl)pentacos-24-yn-1-yloxy]-1-iodophenyl}pentacos-24-yn-1-ol (13): [Pd(PPh$_3$)$_2$Cl$_2$] (17 mg, 0.02 mmol) and CuI (9 mg, 0.05 mmol) were added to a solution of iodo compound **12** (2.22 g, 2.60 mmol) and alkynol **3** (0.86 g, 2.36 mmol) in piperidine (40 mL) at room temperature. After stirring the reaction mixture at 50 °C for 19 h, the reaction mixture was cooled (ice bath) and poured into cold (ice bath) 5N HCl (200 mL). The brown colored precipitate was filtered off, washed with water and dried (P_4O_{10}, vacuum). Flash chromatography (petroleum ether/CH_2Cl_2 1:2 *v*/*v*; R_f (**12**) = 0.96, R_f (**13**) = 0.51) gave **13** (1.75 g, 68%) as a brownish solid. M.p. 76.5–77.0 °C; ^{1}H NMR: δ = 7.37, 7.30 (AA′XX′, 2H each, H$_\varepsilon$), 7.04 (s, 2H, H$_\delta$-2, -6), 3.71 (t, J = 6.6 Hz, 2H, ArOC$\mathbf{H}_2$), 3.63 (t, J = 6.6 Hz, 2H, HOC$\mathbf{H}_2$), 2.39, 2.35 (2 t, J = 7.0 Hz, 2H each, C$\mathbf{H}_2$C≡C), 2.21 (s, 6H, ArC$\mathbf{H}_3$), 1.77 (m, 2H, ArOCH$_2$C$\mathbf{H}_2$), 1.57 (m, 6H, C$\mathbf{H}_2$CH$_2$C≡C, HOCH$_2$C$\mathbf{H}_2$), 1.5–1.2 (m, 76H, CH$_2$), 1.11 (apparent s, 21H, C$\mathbf{H}$(C$\mathbf{H}_3$)$_2$); ^{13}C NMR δ = 155.8 (C_δ-4), 131.9 (CH$_\delta$), 131.8, 131.3 (CH$_\varepsilon$), 130.9 (C_δ-3,-5), 124.1, 122.5 (C_ε-1, C_ε-4), 119.0 (C_δ-1), 106.8(**C**≡CSi), 92.5 (CH$_2$**C**≡CAr$_\varepsilon$), 92.0 (C≡**C**Si), 89.0 (CH$_2$**C**≡CAr$_\delta$), 80.33, 80.32 (CH$_2$C≡**C**), 72.4 (ArO**C**H$_2$), 63.1 (HOCH$_2$), 32.8–28.7 (12 signals), 26.1, 25.7, 19.5, 19.4 (CH$_2$), 18.6 (CH**C**H$_3$), 16.1 (Ar**C**H$_3$), 11.3 (Si**C**H); elemental analysis calcd (%) for $C_{75}H_{126}O_2Si$ (1087.917): C 82.80, H 11.67; found: C 82.64, H 11.73.

4-{25-[3,5-Dimethyl-4-(25-(4-(2-triisopropylsilylethynyl)phenyl)pentacos-24-yn-1-yloxy)phenyl]pentacos-24-yn-1-yloxy}-1-iodobenzene (14): Following the procedure given for the preparation of **5b**, compound **14** was obtained starting from **13** (7.18 g, 6.60 mmol), 4-iodophenol (1.75 g, 7.95 mmol), PPh_3 (2.10 g, 8.01 mmol), and diisopropyl azodicarboxylate (1.58 mL, 8.02 mmol) in THF (300 mL). Flash chromatography (petroleum ether/CH_2Cl_2 1:2 *v*/*v*; R_f = 0.97) gave slightly impure **14**. This product was dissolved in warm CH_2Cl_2 (30 mL) and the solution was added to ethanol (250 mL) to precipitate **14** (6.6 g, 78%) as a colorless solid. M.p. 63.9–64.7 °C; ^{1}H NMR: δ = 7.53 (half of AA′XX′, 2H, H$_\gamma$-2, -6), 7.37, 7.30 (AA′XX′, 2H each, H$_\varepsilon$), 7.05 (s, 2H, ArH$_\delta$), 6.66 (half of AA′XX′, 2H, H$_\gamma$-3, -5), 3.89 (t, J = 6.6 Hz, 2H, Ar$_\gamma$OC$\mathbf{H}_2$), 3.71 (t, J = 6.6 Hz, 2H, Ar$_\delta$OC$\mathbf{H}_2$), 2.39, 2.36 (2t, J = 7.0 Hz, 2H each, C$\mathbf{H}_2$C≡C), 2.21 (s, 6H, ArC$\mathbf{H}_3$), 1.75 (m, 4H, OCH$_2$C$\mathbf{H}_2$), 1.56 (m, 4H, C$\mathbf{H}_2$CH$_2$C≡C), 1.5–1.2 (m, 76H, CH$_2$), 1.12 (apparent s, 21H, C$\mathbf{H}$(C$\mathbf{H}_3$)$_2$); ^{13}C NMR δ = 159.0 (C_γ-4), 155.8 (C_δ-4), 138.1 (C_γ-2, -6), 132.0 (CH$_\delta$), 131.8, 131.3 (CH$_\varepsilon$), 130.9 (C_δ-3, -5), 124.1, 122.5 (C_ε-1, -4), 119.1 (C_δ-1), 117.0 (C_γ-3, -5), 106.8 (**C**≡CSi), 92.5 (CH$_2$**C**≡CAr$_\varepsilon$), 92.0 (C≡**C**Si), 89.0 (CH$_2$**C**≡CAr$_\delta$), 82.4 (C_γ-1), 80.4, 80.3 (CH$_2$C≡**C**), 72.4 (Ar$_\delta$OCH$_2$), 68.1 (Ar$_\gamma$OCH$_2$), 30.4–28.7 (12 signals), 26.1, 26.0, 19.5, and 19.4 (CH$_2$), 18.7 (CH**C**H$_3$), 16.1 (Ar**C**H$_3$), 11.3 (Si**C**H); elemental analysis calcd (%) for $C_{81}H_{129}O_2ISi$ (1289.912): C 75.42, H 10.08; found: C 75.49, H 10.05.

Ethyl 3,5-bis-{4-[25-(3,5-dimethyl-4-(25-(4-(2-triisopropylsilylethynyl)phenyl)pentacos-24-yn-1-yloxy)phenyl)pentacos-24-yn-1-yloxy]phenyl}-4-hydroxybenzoate (15): [Pd(PPh$_3$)$_2$Cl$_2$] (37 mg, 0.05 mmol) and CuI (20 mg, 0.11 mmol) were added to a solution of terphenylene **6** (0.833 g, 2.27 mmol) and iodo compound **14** (6.45 g, 5.00 mmol) in piperidine (120 mL). The

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reaction mixture was stirred for 19 h at room temperature. It was cooled (ice bath) and poured into cold (ice bath) 5 N HCl (600 mL). The precipitate was filtered off, washed with water, and dried (P_4O_{10}, vaccum). Flash chromatography [Petroleum ether/CH_2Cl_2 2:1 *v*/*v* was used until the first fraction, residual iodo compound **14**, was eluted (R_f (**14**) = 0.87, then petroleum ether/CH_2Cl_2 1:1 *v*/*v* was used to elute the product **15**; R_f (**15**) = 0.63.] gave **15** (4.7 g, 76%) as a brownish solid. M.p. 66.2–66.8 °C; ^{1}H NMR: δ = 8.01 (s, 2H, H_α), 7.63, 7.55 (AA′XX′, 4H each, H_β), 7.48 (half of AA′XX′, 4H, H_γ-2, -6), 7.38, 7.31 (AA′XX′, 4H each, CH_ε), 7.06 (s, 4H, ArH_δ), 6.88 (half of AA′XX′, 4H, H_γ-3, -5), 5.82 (brs, 1H, O**H**), 4.38 (q, J = 7.1 Hz, 2H, CO_2CH_2), 3.96 (t, J = 6.6 Hz, 4H, $Ar_\gamma OCH_2$), 3.72 (t, J = 6.6 Hz, 4H, $Ar_\delta OCH_2$), 2.40, 2.37 (2t, J = 7.0 Hz, 4H each, $CH_2C{\equiv}C$), 2.22 (s, 12H, $ArCH_3$), 1.78 (m, 8H, OCH_2CH_2), 1.59 (m, 8H, $CH_2CH_2C{\equiv}C$), 1.39 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.5–1.2 (m, 152H, CH_2), 1.13(apparent s, 21H, $CH(CH_3)_2$); ^{13}C NMR: δ = 166.1 (**C**O_2), 159.4 (C_γ-4), 155.8 (C_δ-4), 153.2 (C_α-4), 135.9 (C_β-1), 133.1 (C_γ-2, -6), 131.9 (C_β-3, -5, CH_δ), 131.8 (CH_ε), 131.5 (C_α-2, -6), 131.3 (CH_ε), 130.9 (C_δ-3, -5), 129.2 (C_β-2, -6), 128.3 (C_α-3, -5), 124.1 (C_ε-1 or C_ε-4), 123.6 (C_β-4), 123.3 (C_α-1), 122.5 (C_ε-4 or C_ε-1), 119.1 (C_δ-1), 115.0 (C_γ-1), 114.5 (C_γ-3, -5), 106.8 (**C**≡CSi), 92.5 (CH_2**C**≡CAr_ε), 92.0 (C≡**C**Si), 90.6 (C≡**C**Ar_γ), 89.0 ($CH_2C{\equiv}CAr_\delta$), 87.6 (Ar_β**C**≡C), 80.4, 80.3 ($CH_2C{\equiv}$**C**), 72.4 ($Ar_\delta OCH_2$), 68.1 ($Ar_\gamma OCH_2$), 60.9 (CO_2CH_2), 30.4–28.7 (12 signals), 26.1, 26.0, 19.5, 19.4 (CH_2), 18.6 ($CHCH_3$), 16.1 ($ArCH_3$), 14.4 (CH_2CH_3), 11.3 (Si**C**H); elemental analysis calcd (%) for $C_{187}H_{274}O_7Si_2$ (2690.414): C 83.48, H 10.27; found: C 83.28, H 10.33.

Ethyl 3,5-bis-{4-[25-(3,5-dimethyl-4-(25-(4-(ethynylphenyl)pentacos-24-yn-1-yloxy)-phenyl)pentacos-24-yn-1-yloxy]phenyl}-4-hydroxybenzoate (16): Following the procedure given for the preparation of **8b**, ring precursor **16** (3.7 g, 95%) was obtained as a very pale beige colored solid from treatment of **15** (4.45 g, 1.65 mmol) in THF (60 mL) with 1 M nBu$_4$NF in THF (3.3 mL, 3.3 mmol) and workup with 2 N HCl (5 mL) and ethanol (120 mL). M.p. 100 °C; ^{1}H NMR: δ = 8.00 (s, 2H, H_α), 7.62, 7.54 (AA′XX′, 4H each, H_β), 7.47 (half of AA′XX′, 4H, H_γ-2, -6), 7.39, 7.32 (AA′XX′, 4H each, CH_ε), 7.05 (s, 4H, ArH_δ), 6.87 (half of AA′XX′, 4H, H_γ-3, -5), 5.77 (s, 1H, O**H**), 4.38 (q, J = 7.1 Hz, 2H, CO_2CH_2), 3.97 (t, J = 6.6 Hz, 4H, $Ar_\gamma OCH_2$), 3.71 (t, J = 6.6 Hz, 4H, $Ar_\delta OCH_2$), 3.12 (s, 2H, C≡CH), 2.39, 2.36 (2t, J = 7.0 Hz, 4H each, $CH_2C{\equiv}C$), 2.21 (s, 12H, $ArCH_3$), 1.78 (m, 8H, OCH_2CH_2), 1.57 (m, 8H, $CH_2CH_2C{\equiv}C$), 1.39 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.5–1.2 (m, 152H, CH_2); ^{13}C NMR: δ = 166.1 (**C**O_2), 159.4 (C_γ-4), 155.8 (C_δ-4), 153.2 (C_α-4), 135.9 (C_β-1), 133.1 (C_γ-2, -6), 132.0 (C_β-3, -5, CH_δ), 131.9 (CH_ε), 131.6 (C_α-2,-6), 131.4 (CH_ε), 130.9 (C_δ-3, -5), 129.3 (C_β-2, -6), 128.3 (C_α-3, -5), 124.7 (C_ε-1 or C_ε-4), 123.7 (C_β-4), 123.4 (C_α-1), 121.1 (C_ε-4 or C_ε-1), 119.1 (C_δ-1), 115.0 (C_γ-1), 114.6 (C_γ-3, -5), 92.8 (CH_2**C**≡CAr_ε), 90.6 (C≡**C**Ar_γ), 89.0 (CH_2**C**≡CAr_δ), 87.6 (Ar_β**C**≡C), 83.4 (**C**≡CH), 80.4, 80.2 ($CH_2C{\equiv}$**C**), 78.4 (C≡**C**H), 72.4 ($Ar_\delta OCH_2$), 68.1 ($Ar_\gamma OCH_2$), 60.9 (CO_2CH_2), 30.4–28.7 (11 signals), 26.1, 26.0, 19.5, 19.4 (CH_2), 16.1 ($ArCH_3$), 14.4 (CH_2CH_3); elemental analysis calcd (%) for $C_{169}H_{234}O_7$ (2377.724): C 85.37, H 9.92; found: C 85.26, H 9.92.

Gigantocycle 17: A suspension of CuCl (5.00 g, 50.5 mmol) and $CuCl_2$ (678 mg, 5.00 mmol) in pyridine (500 mL) was prepared as described for the preparation of **9b**. To this suspension, a solution of ring precursor **16** (1.20 g, 0.50 mmol) in 1,2-dichlorobenzene (120 mL) was added within 62.4 h by means of a syringe pump. It was necessary to gently heat the solution of **16** to dissolve all of the starting material. Once in solution, **16** stays dissolved for at least 20 h. After the addition was complete, the reaction mixture was stirred for additional 3 d. Workup as described for **9b** gave a solution of **16** in 1,2-dichlorobenzene. Most of the 1,2-dichlorobenzene was distilled off (50 °C bath temp, 0.05 mbar) and the residue was dissolved in CH_2Cl_2 (30 mL). This solution was added dropwise to ethanol (130 mL). The colorless precipitate was isolated and washed with ethanol. Flash chromatography (petroleum ether/CH_2Cl_2 1:1 *v*/*v*; R_f = 0.37) gave **16** (961 mg, 80%) as a pale yellow solid. Thermal characterization: see text; ^{1}H NMR δ = 8.00 (s, 2H, H_α), 7.62, 7.54 (AA′XX′, 4H each, H_β), 7.47 (half of AA′XX′, 4H, H_γ-2, -6), 7.41, 7.32 (AA′XX′, 4H each, CH_ε), 7.05 (s, 4H, ArH_δ), 6.87 (half of AA′XX′, 4H, H_γ-3, -5), 5.75 (s, 1H, O**H**), 4.38 (q, J = 7.1 Hz, 2H, CO_2CH_2), 3.97 (t, J = 6.5 Hz, 4H, $Ar_\gamma OCH_2$), 3.71 (t, J = 6.6 Hz, 4H, $Ar_\delta OCH_2$), 3.12 (s, 2H,C≡CH), 2.40, 2.36 (2t, J = 7.0 Hz, 4H each, $CH_2C{\equiv}C$), 2.21 (s, 12H, $ArCH_3$), 1.76 (m, 8H, OCH_2CH_2), 1.56 (m, 8H, $CH_2CH_2C{\equiv}C$), 1.39 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.5–1.2 (m, 152H, CH_2); ^{13}C NMR: δ = 166.1 (**C**O_2), 159.4 (C_γ-4), 155.8 (C_δ-4), 153.2 (C_α-4), 135.9 (C_β-1), 133.1 (C_γ-2, -6), 132.3 (CH_ε), 132.0 (C_β-3, -5, CH_δ), 131.6 (C_α-2, -6), 131.4 (CH_ε), 130.9 (C_δ-3, -5), 129.3 (C_β-2, -6), 128.3 (C_α-3, -5), 125.2 (C_ε-1 or C_ε-4), 123.6 (C_β-4), 123.4 (C_α-1), 120.6 (C_ε-4 or C_ε-1), 119.1 (C_δ-1), 115.0 (C_γ-1), 114.6 (C_γ-3, -5), 93.6 ($CH_2C{\equiv}CAr_\varepsilon$), 90.6 (C≡**C**$Ar_\gamma$), 89.0 ($CH_2C{\equiv}CAr_\delta$), 87.6 ($Ar_\beta$**C**≡C), 82.0 (**C**≡C-C≡**C**), 80.4, 80.3 ($CH_2C{\equiv}$**C**), 75.2 (C≡**C-C**≡C), 72.4 ($Ar_\delta OCH_2$), 68.1 ($Ar_\gamma OCH_2$), 60.9 (CO_2CH_2), 30.4–28.6 (7 signals), 26.1, 26.0, 19.5, 19.4 (CH_2), 16.1 ($ArCH_3$), 14.4 (CH_2CH_3); elemental analysis calcd (%) for $C_{169}H_{232}O_7$ (2375.708): C 85.44, H 9.84; found: C 85.29, H 9.82.

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[12] A. Godt, Ö. Ünsal, M. Roos, *J. Org. Chem.* **2000**, *65*, 2837. For purification of **6**, the column chromatography after the desilylation step can be substituted by dissolving the crude product in methylene chloride (ca. 35 mL, 12 g starting material) and dropping this solution into petroleum ether (ca. 600 mL) to precipitate the product as a colorless solid (83–87%).

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[14] See also: S. Poulain, N. Noiret, C. Nugier-Chauvin, H. Patin, *Lieb. Ann./Recueil* **1997**, 35; C. Cai, A. Vasella, *Helv. Chim. Acta* **1995**, *78*, 732.

[15] For example: A. Sharma, S. Chattopadhyay, *J. Org. Chem.* **1998**, *63*, 6128; K. Mori, H. Tomioka, *Lieb. Ann. Chem.* **1992**, 1011; P. Dussault, I. Q. Lee, *J. Org. Chem.* **1995**, *60*, 218.

[16] DMSO has been described as a suitable solvent for the reaction of ethynyllithium with bromoalkanes: W. N. Smith, O. F. Beumel, Jr., *Synthesis* **1974**, 441. However, we found that by-products due to the formation of the dimsyl anion were formed.

[17] This side product was obtained as the residue upon distillation of the crude product. The formation can be avoided using trimethylsilyl-ethynyllithium instead of ethynyllithium. The product TMSO-$(CH_2)_{11}$-C≡C-TMS is obtained in ca. 80% yield. After removal of the TMS groups, HO-$(CH_2)_{11}$-C≡C-H can be used as alkynol **3** for the coupling with **19**, albeit a distinct amount of HO-$(CH_2)_{11}$-C≡C−C≡C-$(CH_2)_{11}$-OH will be also formed.

[18] Procedure based on S. R. Abrams, *Can. J. Chem.* **1984**, *62*, 1333; S. R. Abrams, A. C. Shaw, M. Taddei, I. Fleming, *Org. Syn.* **1987**, *66*, 127.

[19] Estimated from ^{1}H NMR spectra using the signal of the CH_2O group (δ = 3.62) of **3** and that of the CH_3 group (δ = 0.86) of the by-product.

[20] S. R. Macaulay, *J. Org. Chem.* **1980**, *45*, 734; S. R. Macaulay, *Can. J. Chem.* **1980**, *58*, 2567.

[21] The reaction of NaH with diaminopropane at 75 °C gave a brown turbid solution with silvery balls, probably metallic sodium. The latter

may explain the reduction of the triple bond. However, it remains a mystery how sodium could be formed, and what happened to the hydroxyl functionality. None of these observations have been mentioned in the numerous papers that we know of reporting on this method of alkyne isomerization.

[22] J. C. Lindhoudt, G. L. van Mourik, H. J. J. Pabon, *Tetrahedron Lett.* **1976**, 2565; C. A. Brown, A. Yamashita, *J. Chem. Soc. Chem. Commun.* **1976**, 659; C. A. Brown, A. Yamashita, *J. Am. Chem. Soc.* **1975**, *97*, 891.

[23] H. Hommes, L. Brandsma, *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 160.

[24] $\delta = 5.08$ (quint., $J = 6.8$ Hz,), 4.63 (m with 5 lines in the intensity of ca. 1:2:2:2:1 with a spacing of ca. 3.2 Hz), 1.77 (t, $J = 2.4$ Hz). The approximate relative intensity of these signals is 4:7:7. The concrete structural formula of this enyne is not yet known to us.

[25] O. Mitsunobu, *Synthesis* **1981**, 1.

[26] Independently of the concise protecting group, the coupling products **18** were accompanied by the disubstitution product 1,4-bis(trialkylsilylethynyl)benzene as can be clearly seen from ^{1}H NMR spectra [δ(ArH) = 7.38 in $CDCl_3$]. For identification, bis(trimethylsilylethynyl)benzene was isolated as the second fraction of a column chromatography (SiO_2/petroleum ether) of the crude product of the coupling reaction with trimethylsilylethyne. However, separation of 1,4-bis(trialkylsilylethynyl)benzene from **18** or **19** is not necessary. This by-product was easily removed from the coupling products **4a**, **b** as a common chromatographic fraction with the excessive **19**.

[27] a) The existence of by-product **20b** in samples of **18b** was proven indirectly as described below through the proof of 4-iodo-4′-(trimethylsilylethynyl)tolane (**21b**) as a contaminant in **19b** because the ^{1}H NMR signals of **20b** are covered by those of **18b**. Attempts to prove **20b** as a by-product through mass spectrometry (FD-MS and EI-MS) failed. The ^{1}H NMR spectrum of compound **19b** shows a somewhat broad singlet of low intensity at 7.43 ppm, see ref. [27c]. The intensity of this singlet relative to the signals of the main compound **19b** varied from batch to batch. This singlet also appeared in the spectra of the products of the following synthetic steps, namely **4a**, **b(TMS)** and **5a**, **b(TMS)**, (that is **4a**, **b** and **5a**, **b** with a TMS instead of a TIPS protecting group). In the ^{1}H NMR spectra of the products **7a**, **b(TMS)** and **8a**, **b** (the latter derived from **7a**, **b(TMS)**) this signal appears very close to the signals of the main compound and can therefore only been seen when it is of sufficient intensity. No other additional signals of these by-products could be detected in the NMR spectra. Therefore, and because of the fact that the by-product present in a sample of **19b** reacted with the alkynols **3** or **11** giving again a product which differs from the main product **4a(TMS)** or **4b(TMS)** only by the singlet at 7.43 ppm, the minor component in a sample of **19b** must be structurally similar to **19b**. An explanation that fits all of our data is that **19b** contained **21b**. This compound could have formed only from the corresponding bromo compound **20b**, which consequently must be assumed to be a side product of the coupling reaction of 1-bromo-4-iodobenzene with trimethylsilylethyne. The formation of **20b** means that (4-bromophenyl)ethyne was formed in situ and reacted with **18b** to give **20b**. However, (4-bromophenyl)ethyne was never detected by ^{1}H NMR spectroscopy in the crude or purified samples of **18b**. This may be due to rapid oxidative dimerization upon workup as discussed in ref. 44; b) FD-MS spectra of **5(TMS) – 7(TMS)** and of **8** and **9** derived from **7(TMS)** reveal signals of $[M+100]^+$; c) the broadened singlet at 7.43 ppm is attributed to the four protons at the benzene ring carrying two ethyne substituents. This is in agreement with the data of ref. [28] and a comparison with a sample of pure **20b** which was obtained through Pd/Cu-catalyzed coupling of 4-bromophenylethyne with 1-iodo-4-(trimethylsilylethynyl)benzene.

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[29] P. Siemens, R. C. Livingston, F. Diederich, *Angew. Chem.* **2000**, *112*, 2740; *Angew. Chem. Int. Ed.* **2000**, *39*, 2632.

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