The Effect of Ring Size on Catenane Synthesis

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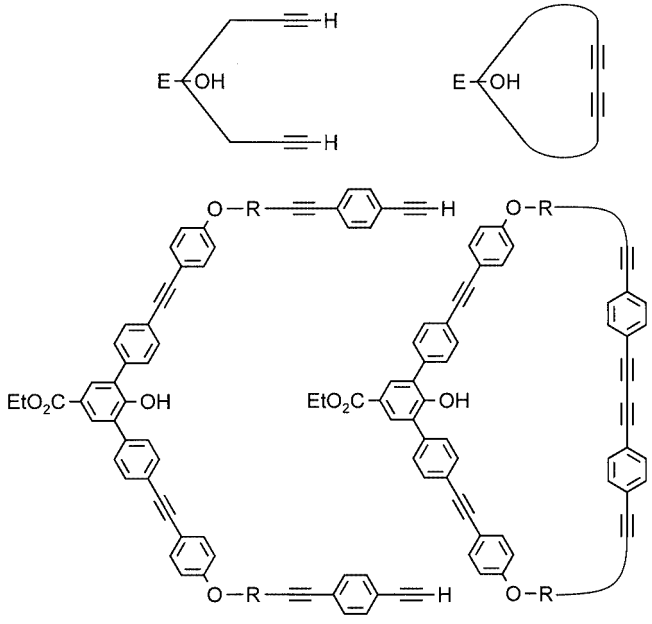
The synthesis of a [2]catenane with 87-membered rings was improved and extended to [2]catenanes with 63- and 147-membered rings. One of the key features is the carbonate linkage between phenols with tolane substituents in the 2- and 6-positions, which serves as a covalent template for the geometrical arrangement of a macrocycle and a ring precursor. Subsequent cyclization of the threaded ring precursor gives the precatenane as the main product, and this is converted into the catenane by carbonate hydrolysis. As well as the precatenane, its dumbbell shaped isomer is formed in the cyclization step. From the known conformation of the templating carbonate moiety and the strong dependence of the ratio of precatenane and dumbbell on the ring size, the dumbbell's origin is attributed to the conformational flexibility of the large rings and not to geometrical ambiguity of the carbonate moiety.

Introduction

The core of an efficient route to catenanes is the geometrical arrangement of the building blocks prior to ring-closure, in such a way that the two rings are entwined after their formation. In early work by Schill[1−3] and Lüttringhaus,[1,4] covalent bonds were used to arrange the building blocks. These procedures are very tedious. The routes developed later by Dietrich−Buchecker and Sauvage,[5−9] Stoddart,[10] Vögtle,[11−13] Hunter,[14] Leigh,[15,16] and Fujita[17] use directing, non-covalent forces such as complex formation, charge-transfer interaction, π-π-stacking, and hydrogen bonding for the geometrical organization of the building blocks and have found widespread use. Some time ago, we reported on a strategy based on a carbonate linkage between phenols with tolane substituents in the 2- and 6-positions as a covalent template to achieve an appropriate geometrical arrangement of a ring and a ring precursor.[18] This strategy proved to be very efficient for the synthesis of [2]catenane **9b**, starting from ring **1b** and ring precursor **5b(H)** (Scheme 1). After conversion of the ring **1b** into the chloroformate **2b**, the ring was threaded onto the ring precursor **5b(Na)** upon the formation of the carbonate linkage. The terminal alkyne moieties of product **6b** were then dimerized to afford precatenane **7b** as the main product. The last step was the selective hydrolysis of the carbonate linkage of **7b** to provide [2]catenane **9b**.



1-11	-R-
a	$-(CH_2)_{11}-$
b	$-(CH_2)_{23}-$
c	$-(CH_2)_{23}-C\equiv C-C_6H_3(O-(CH_2)_{23}-)-C\equiv C-$

The synthetic route was devised to allow for the formation of a chemically and geometrically widely variable family of catenanes. One pivotal question concerned how variable our strategy is in terms of ring size, because variability of the ring size is an important prerequisite for study of the

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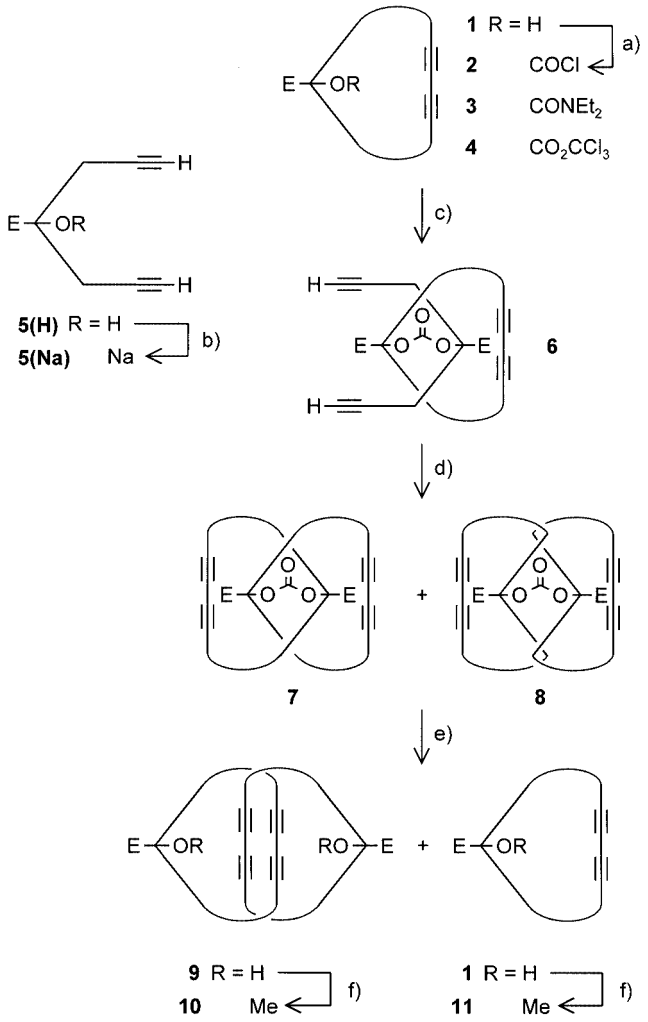


Scheme 1. a) Cl_2CO, iPr_2NEt, THF or CH_2Cl_2; b) NaH, THF; c) starting from **2**, +**5(Na)**, THF; d) CuCl, $CuCl_2$, pyridine, pseudo-high dilution; e) nBu_4NF, THF, room temperature or 50 °C; f) MeI, K_2CO_3, DMF, 35−38 °C. For the precise structures see the index

influence of the translational mobility of the rings on the material properties of catenanes and their polymers. This issue has not been addressed for the other routes mentioned above. With one exception,[19] only modest changes in ring size have been made and systematic studies are completely lacking.

A further important stimulus for us to vary the ring size of the catenanes was given by the dumbbell shaped compound **8b**, found as a by-product in the synthesis of precatenane **7b**. The dumbbell **8b** is a residual-topological isomer[20] of the precatenane **7b**. In the precatenane the two rings are entwined, while the rings of the dumbbell are not. Both compounds are the result of intramolecular alkyne dimerization, so the formation of **8b** could be a hint that the carbonate linkage is not an unambiguous template. We took this possibility very seriously, because structural unambiguity of a template is pivotal for efficient catenane synthesis.

Here we present the synthesis of [2]catenanes with substantially differing ring sizes, discuss improvements of our synthetic route, and elucidate the formation of the dumbbells.

Results and Discussion

Synthesis of the Catenanes 9a−c

The starting compounds for the synthesis of the catenanes **9** are the macrocycles **1**[24] and the cycle precursors **5(H)**.[24] In a first step, macrocycles **1** are converted into the corresponding chloroformates **2**. In our original procedure we used triphosgene and triethylamine for this reaction.[18] We later found that use of an excess of triethylamine resulted in the formation of carbamates **3**.[25] Most probably these are formed through an Arbusov-type reaction between the chloroformates **2** formed in situ and Et_3N. Such a reaction has been described, but only at higher temperatures.[26] An excess of amine would be desirable to compensate for losses due to hydrolysis of triphosgene and subsequent formation of triethylammonium hydrochloride. Furthermore, the large differences in the molecular masses of macrocycles **1** and of Et_3N makes a 1:1 dosage of **1** and Et_3N a challenge. In order to avoid carbamate formation and to allow working with an excess of amine, Et_3N was substituted by the sterically demanding diisopropylethylamine. Indeed, even in the presence of seven equivalents of iPr_2NEt, no carbamate was formed. Unexpectedly, there was also no more formation of carbonate **8**, which had been detected as a minor side product when triphosgene and Et_3N were used.[27] However, ^1H NMR spectroscopy revealed that we had still not found the ideal procedure: the chloroformate **2b** obtained through the reaction between macrocycle **1b**, triphosgene, and iPr_2NEt was contaminated with a small amount of carbonate **4b**.[28] Use of diphosgene in place of triphosgene did not prevent the formation of carbonate **4b**, so we finally switched to phosgene. Use of phosgene in combination with iPr_2NEt reproducibly gave the chloroformates **2** in a quantitative and clean reaction. Of course, working with the highly toxic gas phosgene needs a very well thought out experimental procedure. With the apparatus shown in the Supporting Information, safe handling and working with small amounts of phosgene was possible. For detection of any phosgene leakage we used filter paper that had been soaked with a mixture of diphenylamine and 4-dimethylaminobenzaldehyde.[29] When exposed to phosgene, it turns deep yellow.

Threading of the ring is the next step. For that purpose the ring precursors **5(H)** were deprotonated with sodium hydride. Reaction of the resulting sodium phenolates **5(Na)** with the chloroformates **2** gave the carbonates **6** (63−87%).[30] In the previously published synthetic procedure for catenane **9b**,[18] we had used a ring precursor with trimethylsilyl groups as protecting groups for the terminal alkyne moieties instead of **5b(H)**. As we experienced later, though, use of trimethylsilyl and even triethylsilyl as alkyne protecting groups resulted in ring precursors slightly contaminated by species with chains of double length. Monodisperse compounds could only be obtained through

use of the triisopropylsilyl group,[24] which is usually removed by treatment with nBu$_4$NF. However, nBu$_4$NF will not only remove the triisopropylsilyl groups but also cleave the carbonate linkage,[18] so the alkyne moieties have to be deprotected prior to carbonate formation. Luckily, no alkyne protecting groups are needed during the threading, at least as long as approximately one equivalent of NaH is used, thus avoiding competition between sodium phenolate and sodium acetylide for the chloroformate. Sodium acetylide will be formed in the presence of excess sodium hydride. Not only does the modified procedure present the option of working with monodisperse cycle precursors, but it also saves one synthetic step, the removal of protecting groups, at a very late stage of the catenane synthesis.

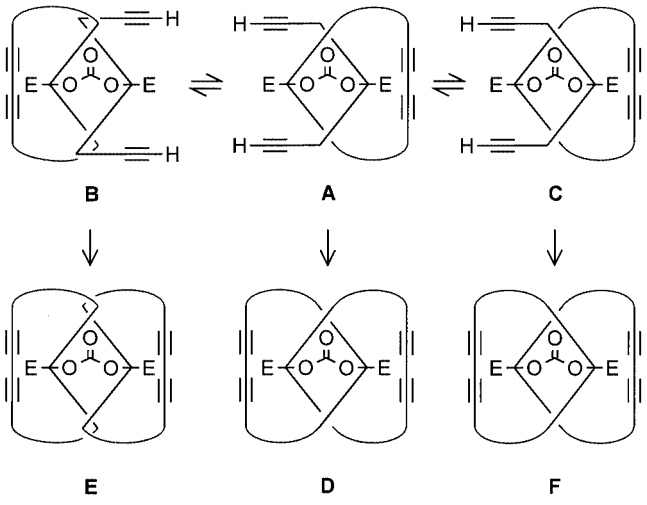
The carbonates **6** were slowly added to suspensions of CuCl and $CuCl_2$ in pyridine.[31] Under these pseudo-high dilution conditions, the intramolecular alkyne dimerization was strongly preferred over the intermolecular reaction, as revealed by size exclusion chromatography (SEC) and the isolated yields of 74−88%. Cyclization is accompanied by a decrease in the hydrodynamic volume of the molecule and thus by an increase in elution time from a SEC column. Intramolecular cyclization, however, gives not only the precatenanes **7** but also the dumbbells **8**. These two products have elution times too similar to be separable and thus distinguishable by SEC.[32] Unambiguous proof that mixtures of **7** and **8** had indeed been obtained came from NMR spectroscopy. The ^{1}H NMR spectra in all cases indicate the presence of two compounds, which must have closely related structures because of their very similar NMR spectroscopic data. The data for the minor compounds are identical with those from the dumbbells **8a**−**c**, which were prepared separately from the sodium salt of **1** and triphosgene or through the reaction between the sodium salt of **1** and **2**. Chromatography of the crude product from the alkyne dimerization served only to remove the oligomers. No attempt was made to separate precatenanes **7** from the corresponding dumbbells **8**. Treatment of these mixtures with nBu$_4$NF in THF gave mixtures of catenanes **9** and macrocycles **1**, the latter originating from the cleavage of the carbonate linkage of the dumbbells **8**. That the macrocycles **1** are products of the carbonate cleavage step is taken as additional evidence of the dumbbells **8** as by-products in the cyclization step. The two products **9** and **1** can easily be separated by standard column chromatography on silica gel, as was shown for the isolation of **9a** and **9b**. Equally well, it is possible first to perform a methylation of the phenolic hydroxyl group and then to separate the catenanes **10** from the macrocycles **11**. The latter procedure was carried out for the preparation of **10b** and **10c**.

As in the case of catenane **9b**, the structures of the two new catenanes **9a** and **10c** were established by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The NMR spectra of the catenanes **9** and **10** are very similar to those of the corresponding macrocycles **1** and **11**, respectively,[33] which proves the structural integrity of the catenanes. The mass spectra of the catenanes confirmed the correct masses. The field desorption mass spectrum of **9a** shows signals at m/z = 2210.9, 1105.3, 736.6, and 552.7; these data correspond well to the calculated figures for the singly up to quadruply charged catenane (M^+: 2210.9, M^{2+}: 1105.5, M^{3+}: 737.0, M^{4+}: 552.7). The MALDI-TOF spectrum (dithranol, KO_2CCF_3) of catenane **10c** shows a signal at m/z = 4818.9 and a very weak signal at 4780, which correspond to the calculated figures for [M + K^+] (4818.6) and for M^+ (4779.5).[34]

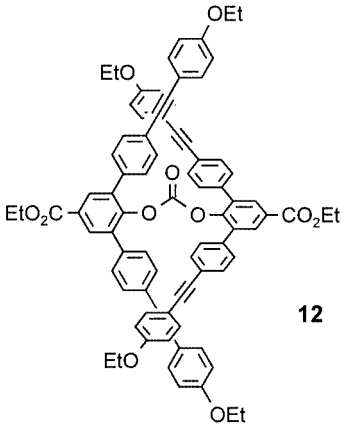
The Origin of the Dumbbells 8a−c

As described above, the cyclization of **6a**−**c** gave the precatenanes **7a**−**c** accompanied by the dumbbells **8a**−**c**. The formation of the latter compounds challenged the use of carbonate as a covalent template. Compounds **6** are assumed to adopt a conformation similar to that known for carbonate **12** and structurally closely related carbonates,[36] since the NMR spectroscopic data for **12** and those for the corresponding parts of compounds **6** are nearly identical. The two angular moieties of **12** that are linked through the carbonate group intersect in such a way that the tolane substituents point towards the corners of a distorted tetrahedron with the carbonate group sitting in the middle of the tetrahedron. This situation is illustrated as conformer **A** in Scheme 2. Cyclization of **A** gives precatenane **D**. The additional formation of dumbbells **8** may point to an equilibrium between the conformers **A** and **C**. In **C**, the two angular blocks are oriented approximately parallel to each other and so ring and ring precursor are no longer entwined. Cyclization of **C** would give **F**, which may be one of the conformers of dumbbells **8**. However, the assumption of an equilibrium between the conformers **A** and **C** is in contradiction with the results of our ^{1}H NMR spectroscopic investigation on the conformation and dynamics of model carbonate **12** and related carbonates in THF.[36] This study revealed that, put simply, the angular moieties rotate around the carbonyl group with the O−C_{aryl} bonds as the axes of rotation and with the rotation of the two angular moieties being coupled because the tolane substituents are too long to allow them to pass each other. No hint of an equilibrium between conformers corresponding to **A** and **C** was found. An alternative explanation for the formation of **8** is an equilibrium between conformers **A** and **B**.[37] If **A** converts into **B**, the angular moiety folds back into the ring and so the ring precursor unthreads. Such a conformational change should be easily possible as a consequence of the long, flexible alkyl chains as well as the ether linkage between the aliphatic chain and the angular, shape-persistent moiety. Upon cyclization of **B** the dumbbell **E** is formed, which, as conformer **F**, is one of the conceivable conformers of compounds **8**.[39] With increasing ring size, the energies of the two conformers **A** and **B** and so the probabilities of the formation of **7** and **8** should become more and more similar.[40] Indeed, the ratios of (**7a**−**c**):(**8a**−**c**) were found to be 6:1, 2.7:1, and 1.6:1 for the rings with 63, 87, and 147 ring atoms, respectively.[41] This result clearly supports the conformational equilibrium between **A** and **B** as the origin of the dumbbells. This finding points to a fundamental limitation in the use of geometrical preorganization, such as is

achieved with the carbonate for catenane synthesis, when working with huge, rather flexible rings. Preorganization similar to that achieved by the carbonate linkage was obtained by Sauvage[5−9] with a Cu^{I}-phenanthroline complex and more recently by Leigh[42] with a Zn^{2+}-2,6-diiminopyridine complex.[43] In these cases enlargement of the ring will also give rise to dumbbell-shaped side products with the additional feature that the ratio of precatenane and dumbbell will be influenced by the fairly easy ligand exchange.



Scheme 2. For the precise structures see the index



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Conclusion

The synthesis of [2]catenanes through the use of a carbonate linkage as a covalent template has been improved so that monodisperse ring precursors can be used, the number of steps is reduced, and the procedure for the formation of the chloroformates, which are important synthetic intermediates, is easy and reproducible. It has been shown that the strategy is applicable to the synthesis of catenanes of very different ring sizes, ranging from 63- to 147-membered rings. The formation of dumbbells **8** as by-products in the formation of precatenanes **7** is attributed to the conformational flexibility of the macrocycles. Dumbbell formation is also to be expected when other templates are used. It is therefore a general limitation for the efficiency of catenane synthesis, especially if large ring sizes are aimed at. Nevertheless, even for the 147-membered ring the precatenane was still the major product.

Experimental Section

General: All reactions were carried out under inert atmosphere in dried Schlenk flasks. NaH is extremely hygroscopic, so the dispersion of NaH was stored and handled strictly under argon. Small amounts were weighed by filling a shortened, dry NMR tube of known weight under argon with the solid dispersion and determining the mass increase. The dispersion did not stick to the glass, so quantitative transfer into the reaction vessel was possible. The amounts of **1** and **2** were calculated on the basis of the determined amount of NaH.

The starting materials **1** and **5(H)** were synthesized as described.[24] THF was dried over sodium/benzophenone. Diethyl ether used for the extraction of chloroformates **2** was distilled from sodium/benzophenone to remove the stabilizer. For flash chromatography silica gel was used. 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≡CH. This signal does not appear in the DEPT spectrum, as we have observed in a variety of compounds of the ArC≡CH and AlkC≡CH type.[44] NMR spectroscopic data for the precursors were also used for signal assignment.[24] The subscripts α, β, γ, δ, and ε refer to the aromatic rings. The hydroxybenzoate moiety is referred to as α. The benzene unit closest to the hydroxybenzoate moiety is referred to as β, the benzene unit connected with Ar_β by only one ethyne moiety is referred to as γ, the benzene unit connected with Ar_γ by the alkane chain is referred to as δ, and the remaining benzene unit is referred to as ε. For the numbering of the positions, ethyl 4-hydroxybenzoate is regarded as the substituted parent compound. Melting points were either determined under ambient atmosphere by use of a microscope with a heating table or in open capillaries. In cases of liquid crystallinity, the transition temperature into the liquid crystalline phase determined by DSC is reported.

Chloroformate 2a: Macrocycle **1a** (2.00 g, 1.81 mmol) and then *N*,*N*-diisopropylethylamine (0.45 mL, 2.57 mmol) were added to a solution of phosgene (0.25 mL, 3.62 mmol) in THF (20 mL).[45] Immediately a colorless solid precipitated. The reaction mixture was stirred for 3 h at room temperature. Diethyl ether and HCl (2 N) were added. The organic phase was washed with HCl (2 N). The combined aqueous phases were extracted with diethyl ether. The combined organic phases were dried ($MgSO_4$) and the solvent was removed in vacuo to give chloroformate **2a** (1.9 g, 89%) as a slightly yellow solid. M.p. 191.0−191.5 °C. ^1H NMR: δ = 8.14 (s, 2 H, H_α), 7.62 (half of AA′XX′, 4 H, H_β), 7.48 (half of AA′XX′, 4 H, H_γ-2,-6), 7.46 (half of AA′XX′, 4 H, H_β), 7.41 and 7.32 (AA′XX′, 4 H each, H_δ), 6.88 (half of AA′XX′, 4 H, H_γ-3,-5), 4.42 (q, *J* = 7.2 Hz, 2 H, CO_2CH_2), 4.01 (t, *J* = 6.3 Hz, 4 H, $ArOCH_2$), 2.39 (t, *J* = 7.0 Hz, 4 H, $CH_2C{\equiv}C$), 1.77 (m, 4 H, OCH_2CH_2), 1.59 (m, 4 H, $CH_2CH_2C{\equiv}C$), 1.41 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.5−1.2 (m, 28 H, CH_2). ^{13}C NMR: δ = 165.1 (CO_2), 159.3 (C_γ-4), 148.8, 148.2 (COCl, C_α-4), 135.2, 134.8 (C_β-1, C_α-3,-5), 133.1 (C_γ-2,-6), 132.2 (CH_δ), 131.7 (C_β-3,-5), 131.5 (CH_δ), 131.3 (C_α-2,-6), 130.2 (C_α-1),

128.9 (C_β-2,-6), 125.2 (C_δ-1 or C_δ-4), 124.1 (C_β-4), 120.6 (C_δ-4 or C_δ-1), 114.9 (C_γ-1), 114.8 (C_γ-3,-5), 93.6 ($CH_2C{\equiv}C$), 91.0 ($C{\equiv}CAr_\gamma$), 87.6 ($Ar_\beta C{\equiv}C$), 81.9 ($C{\equiv}C{-}C{\equiv}C$), 80.2 ($CH_2C{\equiv}C$), 75.2 ($C{\equiv}C{-}C{\equiv}C$), 67.8 ($ArOCH_2$), 61.5 (CO_2CH_2), 29.6−28.6 (8 signals), 25.6, 19.5 (CH_2), 14.3 (CH_3). $C_{80}H_{75}O_6Cl$ (1167.927): calcd. C 82.27, H 6.47; found C 82.21, H 6.51. FD-MS: *m*/*z* (%) = 1167.0 (100) [M^+] with ^{37}Cl-isotope peak at 1169.1, 583.5 (7) [M^{2+}].

Compound 6a: Cycle precursor **5a(H)** (1.52 g, 1.37 mmol) was added to a suspension of sodium hydride (60% suspension in mineral oil, 60 mg, 1.44 mmol) in THF (160 mL). Gas evolution was observed and the reaction mixture turned green-yellow. The chloroformate **2a** (1.60 g, 1.37 mmol) was then added. After the reaction mixture had been stirred for 19 h at room temperature, HCl (2 N) and diethyl ether were added. The organic phase was washed with HCl (2 N), 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. Flash chromatography [petroleum ether/CH_2Cl_2, 1:1 v/v to elute **1a** and **5a(H)** and then CH_2Cl_2 to elute **6a**] gave a mixture of **1a** and **5a(H)** (153 mg) as a slightly yellow solid and **6a** (2.7 g, 87%) as a slightly yellow solid.

Analytical Data of 6a: ^1H NMR: δ = 7.90, 7.85 (2 s, 2 H each, H_α), 7.60, 7.58 (two halves of two AA′XX′, 4 H each, H_γ-2,-6), 7.41−7.24 (m, 32 H, H_β, H_δ), 6.91, 6.90 (two halves of two AA′XX′, 4 H each, H_γ-3,-5), 4.33, 4.30 (2 q, *J* = 7.1 Hz, 4 H each, CO_2CH_2), 4.05 (t, *J* = 6.3 Hz, 4 H, $ArOCH_2$), 3.99 (t, *J* = 6.6 Hz, 4 H, $ArOCH_2$), 3.13 (s, 2 H, C≡CH), 2.39 (m, 8 H, $CH_2C{\equiv}C$), 1.79 (m, 8 H, OCH_2CH_2), 1.58 (m, 8 H, $CH_2CH_2C{\equiv}C$), 1.5−1.2 (m, 62 H, CH_2, CH_3). ^{13}C NMR: δ = 165.31, 165.26 (CO_2), 159.28, 159.20 (C_γ-4), 147.5 (CO_3), 147.2, 147.1 (C_α-4), 135.6, 135.5, 135.34, 135.28 (C_α-3,-5, C_β-1), 133.2 (C_γ-2,-6), 132.2, 131.9 (CH_δ), 131.6 (broad with shoulder at δ = 313.7 ppm, C_β-3,-5, C_α-2,-6), 131.5, 131.4 (CH_δ), 129.2, 129.1 (C_α-1), 128.6 (C_β-2,-6), 125.1 (C_δ-1 or C_δ-4 of ring), 124.7 (C_δ-1 or C_δ-4 of ring precursor), 123.22, 123.18 (C_β-4), 121.0 (C_δ-4 or C_δ-1 of ring precursor), 120.5 (C_δ-4 or C_δ-1 of ring), 115.29, 115.28 (C_γ-1), 114.9 (C_γ-3,-5 of ring), 114.6 (C_γ-3,-5 of ring precursor), 93.6 ($CH_2C{\equiv}C$ of ring), 92.7 ($CH_2C{\equiv}C$ of ring precursor), 90.8, 90.7 ($C{\equiv}CAr_\gamma$), 88.4, 88.3 ($Ar_\beta C{\equiv}C$), 83.3 ($C{\equiv}CH$), 81.9 ($C{\equiv}C{-}C{\equiv}C$), 80.2 ($CH_2C{\equiv}C$), 78.4 ($C{\equiv}CH$), 75.1 ($C{\equiv}C{-}C{\equiv}C$), 68.1, 67.8 ($ArOCH_2$), 61.2 (CO_2CH_2), 29.7−28.6 (13 signals), 26.0, 25.6, 19.5, 19.4 (CH_2), 14.3 (CH_3). $C_{159}H_{152}O_{11}$ (2238.954): calcd. C 85.30, H 6.84; found C 85.13, H 7.03. FD-MS: *m*/*z* (%) = 2238.7 (48) [M^+], 1119.8 (100) [M^{2+}], 746.5 (60) [M^{3+}].

Mixture of Precatenane 7a and Dumbbell 8a: Precatenane **7a** was prepared by the procedure given for the preparation of precatenane **7c**, starting from CuCl (6.44 g, 65.1 mmol) and $CuCl_2$ (1.11 g, 8.26 mmol) in pyridine (500 mL) and a solution of **6a** (1.00 g, 0.45 mmol) in pyridine (92 mL) that was added to the copper salts over 53 h. After completion of the addition, the reaction mixture was stirred for an additional 24 h. Workup as described for **7c**, followed by flash chromatography (CH_2Cl_2), gave a mixture of **7a** and **8a** in two fractions − first fraction (754 mg, 75%, **7a**:**8a** ≈ 16:1), second fraction (129 mg, 13%, **7a**:**8a** ≈ 2:1) − as slightly yellow solids. ^1H NMR: δ = 7.87 (broad s, 4 H, H_α), 7.60 (half of AA′XX′, 8 H, H_γ-2,-6), 7.33, 7.26 (AA′XX′ with underlying broad signals, 32 H, H_β, H_δ), 6.92 (half of AA′XX′, 8 H, H_γ-3,-5), 4.31 (q, *J* = 7.1 Hz, 4 H, CO_2CH_2), 4.05 (t, *J* = 6.2 Hz, 8 H, $ArOCH_2$), 2.37 (t, *J* = 7.0 Hz, 8 H, $CH_2C{\equiv}C$), 1.80 (m, 8 H, OCH_2CH_2), 1.6−1.2 (m, 70 H, CH_2, CH_3). ^{13}C NMR: δ = 165.3 (CO_2), 159.3 (C_γ-4), 147.4 (CO_3), 147.2 (C_α-4), 135.5 (C_α-3,-5, C_β-1), 133.2 (C_γ-2,-6), 132.2 (CH_δ), 131.6 (C_α-2,-6, C_β-3,-5), 131.5 (CH_δ), 129.2 (C_α-1), 128.6 (very broad, C_β-2,-6), 125.1 (C_δ-1 or C_δ-4), 123.2 (C_β-4), 120.6 (C_δ-1 or C_δ-4), 115.4 (C_γ-1), 114.9 (C_γ-3,-5), 93.6 ($CH_2C{\equiv}C$), 90.8 ($C{\equiv}CAr_\gamma$), 88.5 ($Ar_\beta C{\equiv}C$), 81.9 ($C{\equiv}C{-}C{\equiv}C$), 80.2 ($CH_2C{\equiv}C$), 75.1 ($C{\equiv}C{-}C{\equiv}C$), 67.9 ($ArOCH_2$), 61.2 (CO_2CH_2), 29.2−28.7 (7 signals), 25.7, 19.5 (CH_2), 14.3 (CH_3). Additional NMR signals of low intensity assigned to **8a**: ^1H NMR: δ = 7.85 (s, H_α), 7.56 (one signal of one half of AA′XX′, H_γ-2,-6), 7.40 (half of AA′XX′, H_β or H_δ), 6.84 (one signal of one half of AA′XX′, H_γ-3,-5). ^{13}C NMR: δ = 159.1 (C_γ-4), 135.45 (C_α-3,-5, C_β-1), 132.2 (CH_δ), 75.3 ($C{\equiv}C{-}C{\equiv}C$), 67.7 ($ArOCH_2$), 28.4, 28.2, 25.2 (CH_2). $C_{159}H_{150}O_{11}$ (2236.938): calcd. C 85.37, H 6.76; found C 84.91, H 6.69. FD-MS: *m*/*z* (%)= 2238.0 (55) [M^+], 1119.2 (100) [M^{2+}], 745.6 (20) [M^{3+}].

Catenane 9a and Ring 1a: A mixture of **7a** and **8a** (547 mg, 0.24 mmol; **7a**:**8a** ≈ 16:1) was dissolved in THF (12 mL), and nBu_4NF in THF (1 M, 1.23 mL, 1.23 mmol) was added. After the reaction mixture had been stirred for 18 h at room temperature,[46] it was worked up with CH_2Cl_2 and water. The combined organic phases were washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Flash chromatography (petroleum ether/CH_2Cl_2, 1:2) gave **1a** (37 mg; 7%) as a pale yellow solid and slightly impure **9a** (423 mg, 78%). Flash chromatography (CH_2Cl_2) of the latter fraction gave catenane **9a** (376 mg, 70%) as a pale yellow solid.

Analytical Data of 9a: M.p. 180 °C. ^1H NMR: δ = 7.98 (s, 4 H, H_α), 7.56, 7.47 (AA′XX′, 8 H each, H_β), 7.44 (half of AA′XX′, 8 H, H_γ-2,-6), 7.36, 7.27 (AA′XX′, 8 H each, H_δ), 6.84 (half of AA′XX′, 8 H, H_γ-3,-5), 5.71 (s, 2 H, OH), 4.34 (q, *J* = 7.2 Hz, 4 H, CO_2CH_2), 3.97 (t, *J* = 6.3 Hz, 8 H, $ArOCH_2$), 2.36 (t, *J* = 7.0 Hz, 8 H, $CH_2C{\equiv}C$), 1.74 (m, 8 H, OCH_2CH_2), 1.56 (m, 8 H, $CH_2CH_2C{\equiv}C$), 1.36 (t, *J* = 7.2 Hz, 6 H, CH_3), 1.5−1.2 (m, 56 H, CH_2). ^{13}C NMR: δ = 166.1 (CO_2), 159.3 (C_γ-4), 153.4 (C_α-4), 135.8 (C_β-1), 133.1 (C_γ-2,-6), 132.2 (CH_δ), 131.9 (C_β-3,-5), 131.5 (CH_δ), 131.2 (C_α-2,-6), 129.3 (C_β-2,-6), 128.3 (C_α-3,-5), 125.1 (C_δ-1 or C_δ-4), 123.5, 123.2 (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 ($CH_2C{\equiv}C$), 90.7 ($C{\equiv}CAr_\gamma$), 87.8 ($Ar_\beta C{\equiv}C$), 82.0 ($C{\equiv}C{-}C{\equiv}C$), 80.2 ($CH_2C{\equiv}C$), 75.2 ($C{\equiv}C{-}C{\equiv}C$), 67.9 ($ArOCH_2$), 60.9 (CO_2CH_2), 29.3−28.7 (5 signals), 25.8, 19.5 (CH_2), 14.4 (CH_3). $C_{158}H_{152}O_{10}$ (2210.944): FD-MS: *m*/*z* (%) = 2210.9 (15) [M^+], 1106.3 (100) [M^{2+}], 736.6 (5) [M^{3+}], 552.7 (5) [M^{4+}].

Dumbbell 8a: Ring **1a** (0.14 g, 0.13 mmol) was added to a suspension of sodium hydride (60% suspension in mineral oil, 5.0 mg, 0.13 mmol) in THF (50 mL). Gas evolution was observed and the reaction mixture turned yellow-green. Chloroformate **2a** (0.15 g, 0.13 mmol) was then added. After the reaction mixture had been stirred overnight at room temperature, CH_2Cl_2 and HCl (2 N) were added. The organic phase was washed with HCl (2 N), and the combined aqueous phases were extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), and the solvent was removed in vacuo. Flash chromatography (petroleum ether/CH_2Cl_2, 1:1 v/v to elute starting material, then CH_2Cl_2 to elute the product) gave ring **1a** (29 mg, 10%) as a pale yellow solid and dumbbell **8a** (219 mg, 77%) as a pale yellow solid. M.p. 120 °C. ^1H NMR: δ = 7.84 (s, 4 H, H_α), 7.56 (half of AA′XX′, 8 H, H_γ-2,-6), 7.38 (half of AA′XX′, 8 H, H_β or H_δ), 7.32 (half of AA′XX′, 8 H, H_β or H_δ), 7.23 (two halves of two AA′XX′, 16 H, H_β, H_δ), 6.87 (half of AA′XX′, 8 H, H_γ-3,-5), 4.30 (q, *J* = 7.1 Hz, 4 H, CO_2CH_2), 4.06 (t, *J* = 6.1 Hz, 8 H, $ArOCH_2$), 2.33 (t, *J* = 7.3 Hz, 8 H, $CH_2C{\equiv}C$), 1.77 (m, 8 H, OCH_2CH_2), 1.6−1.4 (m, 16 H, CH_2), 1.4−1.2 (m, 48 H, CH_2), 1.30 (t, *J* = 7.0 Hz, 6 H, CH_3). ^{13}C NMR: δ = 165.3 (CO_2), 159.1 (C_γ-4), 147.8 (CO_3), 147.2 (C_α-4), 135.5, 135.4 (C_α-3,-5, C_β-1), 133.2 (C_γ-2,-6), 132.2 (CH_δ), 131.7 (C_β-3,-5), 131.6 (C_α-

2,-6), 131.5 (CH_δ), 129.2 (C_α-1), 128.6 (C_β-2,-6), 125.1 (C_δ-1 or C_δ-4), 123.2 (C_β-4), 120.5 (C_δ-4 or C_δ-1), 115.4 (C_γ-1), 114.9 (C_γ-3,-5), 93.6 ($CH_2C\equiv C$), 90.8 ($C\equiv CAr_\gamma$), 88.5 ($Ar_\beta C\equiv C$), 81.9 ($C\equiv C-C\equiv C$), 80.1 ($CH_2C\equiv C$), 75.3 ($C\equiv C-C\equiv C$), 67.7 ($ArOCH_2$), 61.2 (CO_2CH_2), 29.1−28.2 (8 signals, CH_2), 25.2 ($CH_2CH_2C\equiv C$), 19.6 ($CH_2C\equiv C$), 14.3 (CH_3). $C_{159}H_{150}O_{11}$ (2236.938): calcd. C 85.37, H 6.76; found C 85.20, H 6.81.

Chloroformate 2b:[47] Macrocycle **1b** (924 mg, 0.64 mmol) and then *N*,*N*-diisopropylethylamine (0.25 mL, 1.4 mmol) were added to a solution of phosgene (0.35 mL, 5.1 mmol) in CH_2Cl_2 (10 mL).[45] Upon addition of the amine, **1b** went completely into solution. According to ^{1}H NMR of a small sample, the reaction was incomplete after 3 h at room temperature, so more *N*,*N*-diisopropylethylamine (0.3 mL, 1.7 mmol) was added. Three hours later, the reaction mixture was cooled with an ice bath, and diethyl ether (20 mL) and HCl (2 N) were added. To dissolve the precipitate, CH_2Cl_2 (10 mL) and diethyl ether (16 mL) were added. The organic phase was washed several times with HCl (2 N), then with brine, and finally dried ($MgSO_4$). The solvent was removed in vacuo to give chloroformate **2b** (923 mg, 96%) as a colorless solid. ^{1}H NMR: δ = 8.11 (s, 2 H, H_α), 7.60 (half of AA′XX′, 4 H, H_β), 7.46 (half of AA′XX′, 4 H, H_γ-2,-6), 7.45 (half of AA′XX′, 4 H, H_β), 7.39 and 7.30 (AA′XX′, 4 H each, H_δ), 6.86 (half of AA′XX′, 4 H, H_γ-3,-5), 4.41 (q, J = 7.1 Hz, 2 H, CO_2CH_2), 3.97 (t, J = 6.5 Hz, 4 H, $ArOCH_2$), 2.38 (t, J = 7.0 Hz, 4 H, $CH_2C\equiv C$), 1.77 (m, 4 H, OCH_2CH_2), 1.58 (m, 4 H, $CH_2CH_2C\equiv C$), 1.40 (t, J = 7.1 Hz, 3 H, CH_3), 1.5−1.2 (m, 76 H, CH_2).

Compound 6b: Cycle precursor **5b(H)** (396.8 mg, 0.27 mmol) was added to a suspension of sodium hydride (60% suspension in mineral oil, 11.1 mg, 0.28 mmol) in THF (10 mL). Gas evolution was observed and the reaction mixture turned green-yellow. Chloroformate **2b** (413.4 mg, 0.27 mmol) was then added. After the reaction mixture had been stirred overnight at room temperature, HCl (2 N) was added. The organic phase was washed with HCl (2 N) and brine, 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. Flash chromatography (petroleum ether/CH_2Cl_2, 1:1 v/v) gave **6b** (558 mg, 70%) as a slightly yellow solid. For analytical data see.[18]

Mixture of Precatenane 7b and Dumbbell 8b: Precatenane **7b** was prepared by the procedure given for the preparation of precatenane **7c**, starting from a solution of **6b** (978 mg, 0.34 mmol) in pyridine (97 mL), which was added to the suspension of CuCl and $CuCl_2$ in pyridine (identical to that described) over 39 h. After completion of the addition, the reaction mixture was stirred for an additional 53 h. Workup as described for **7c** followed by flash chromatography (petroleum ether/CH_2Cl_2, 1:1.5 v/v) gave as the first fraction **1b** (11 mg) and as the second fraction a mixture (ca. 2.7:1) of **7b** and **8b** (770 mg, 79%) as a colorless solid. Another experiment with use of an identical copper suspension and addition of the solution of **6b** (1.31 g, 0.45 mmol) in pyridine (178 mL) over 71 h gave a mixture (ca. 2.7:1) of **7b** and **8b** (1.06 g, 82%). For analytical data see ref.[18]

Catenane 10b and Ring 11b: nBu$_4$NF in THF (1 M, 2.5 mL, 2.5 mmol) was added to a solution of a mixture (ca. 2.7:1) of **7b** and **8b** (741 mg, 0.25 mmol) in THF (11 mL). The solution immediately became fluorescent green. After the reaction mixture had been stirred for 18 h at 50 °C, it was cooled with an ice bath, and HCl (2 N, 1.5 mL) was added, whereupon the solution became pale yellow and a precipitate formed. After addition of ethanol (15 mL) and cooling with liquid N_2, the precipitate was isolated, washed with HCl (2 N), water, and finally with ethanol, and dried to give a mixture of catenane **9b** and ring **1b** (737 mg, 100%) as a beige-colored solid.[48] This mixture (737 mg, 0.51 mmol of OH groups) was dissolved in THF (7 mL) and DMF (7 mL), and K_2CO_3 (154 mg, 1.11 mmol) and methyl iodide (0.4 mL, 6 mmol) were added. The suspension was kept at 50 °C for 14 h. After cooling with an ice bath, HCl (5 N) was added cautiously (gas evolution!). The separating oil was dissolved in diethyl ether. The aqueous phase was extracted with diethyl ether and the combined organic phases were washed successively with HCl (5 N), water, saturated aqueous Na_2SO_3, and water, and dried ($MgSO_4$). The solvent was removed under reduced pressure. Flash chromatography (petroleum ether/CH_2Cl_2, 1.5:1 → 1:1.4 v/v) gave as the first fraction **11b** (148 mg, 20% over two steps) as a colorless solid and as the second fraction catenane **10b** (475 mg, 64% over two steps) as a colorless solid. The products were freeze-dried using benzene.

Analytical Data for Ring 11b: $T_{c\rightarrow n}$ = 132 °C. ^{1}H NMR: δ = 8.03 (s, 2 H, H_α), 7.58 (apparent s, 8 H, H_β), 7.46 (half of AA′XX′, 4 H, H_γ-2,-6), 7.39 and 7.30 (AA′XX′, 4 H each, H_δ), 6.86 (half of AA′XX′, 4 H, H_γ-3,-5), 4.38 (q, J = 7.1 Hz, 2 H, CO_2CH_2), 3.97 (t, J = 6.5 Hz, 4 H, $ArOCH_2$), 3.18 (s, 3 H, OCH_3), 2.38 (t, J = 7.0 Hz, 4 H, $CH_2C\equiv C$), 1.77 (m, 4 H, OCH_2CH_2), 1.57 (m, 4 H, $CH_2CH_2C\equiv C$), 1.38 (t, J = 7.1 Hz, 3 H, CH_2CH_3), 1.5−1.2 (m, 76 H, CH_2). ^{13}C NMR: δ = 166.0 (CO_2), 159.3 (C_γ-4), 158.8 (C_α-4), 137.2, 135.2 (C_α-3,-5, C_β-1), 133.1 (C_γ-2,-6), 132.3 (CH_δ), 131.5 (C_α-2,-6), 131.6 (CH_δ), 131.4 (C_β-3,-5), 129.2 (C_β-2,-6), 126.5 (C_α-1), 125.2 (C_δ-1 or C_δ-4), 123.0 (C_β-4), 120.6 (C_δ-4 or C_δ-1), 115.1 (C_γ-1), 114.7 (C_γ-3,-5), 93.6 ($CH_2C\equiv C$), 90.3 ($C\equiv CAr_\gamma$), 87.9 ($Ar_\beta C\equiv C$), 82.0 ($C\equiv C-C\equiv C$), 80.2 ($CH_2C\equiv C$), 75.2 ($C\equiv C-C\equiv C$), 68.0 ($ArOCH_2$), 61.1 (CO_2CH_2), 60.6 (OCH_3), 29.6−28.7 (9 signals), 25.9, and 19.5 (CH_2), 14.4 (CH_2CH_3). $C_{104}H_{126}O_5$ (1456.147): calcd. C 85.78, H 8.72; found C 85.77, H 8.77.

Analytical Data for Catenane 10b: $T_{c\rightarrow n}$ = 111 °C. ^{1}H NMR: δ = 8.03 (s, 4 H, H_α), 7.57 (apparent s, 16 H, H_β), 7.45 (half of AA′XX′, 8 H, H_γ-2,-6), 7.38 and 7.29 (AA′XX′, 8 H each, H_δ), 6.84 (half of AA′XX′, 8 H, H_γ-3,-5), 4.38 (q, J = 7.1 Hz, 4 H, CO_2CH_2), 3.95 (t, J = 6.5 Hz, 8 H, $ArOCH_2$), 3.16 (s, 6 H, OCH_3), 2.37 (t, J = 7.0 Hz, 8 H, $CH_2C\equiv C$), 1.76 (m, 8 H, OCH_2CH_2), 1.56 (m, 8 H, $CH_2CH_2C\equiv C$), 1.38 (t, J = 7.1 Hz, 6 H, CH_2CH_3), 1.5−1.2 (m, 152 H, CH_2). ^{13}C NMR: δ = 166.0 (CO_2), 159.3 (C_γ-4), 158.8 (C_α-4), 137.2 and 135.2 (C_α-3,-5, C_β-1), 133.0 (C_γ-2,-6), 132.2 (CH_δ), 131.6 (C_α-2,-6), 131.5 (CH_δ), 131.4 (C_β-3,-5), 129.2 (C_β-2,-6), 126.5 (C_α-1), 125.2 (C_δ-1 or C_δ-4), 123.0 (C_β-4), 120.6 (C_δ-4 or C_δ-1), 115.0 (C_γ-1), 114.6 (C_γ-3,-5), 93.6 ($CH_2C\equiv C$), 90.3 ($C\equiv CAr_\gamma$), 87.9 ($Ar_\beta C\equiv C$), 82.0 ($C\equiv C-C\equiv C$), 80.2 ($CH_2C\equiv C$), 75.2 ($C\equiv C-C\equiv C$), 68.0 ($ArOCH_2$), 61.1 (CO_2CH_2), 60.6 (OCH_3), 29.7−28.7 (9 signals), 25.9, and 19.6 (CH_2), 14.4 (CH_2CH_3). $C_{208}H_{252}O_{10}$ (2912.294): calcd. C 85.78, H 8.72; found C 85.74, H 8.74.

Chloroformate 2c:[47] Macrocycle **1c** (879 mg, 0.370 mmol) was added to a solution of phosgene (0.3 mL, 4.3 mmol) in CH_2Cl_2 (12 mL), followed by *N*,*N*-diisopropylethylamine (0.2 mL, 1.1 mmol).[45] Upon addition of the amine, **1c** went completely into solution. According to ^{1}H NMR of a small sample the reaction was incomplete after 3 h at room temperature, so more *N*,*N*-diisopropylethylamine (0.3 mL, 1.7 mmol) was added. Three hours later, the reaction mixture was cooled with an ice bath and diethyl ether and HCl (2 N) were added. The organic phase was washed several times with HCl (2 N), then with brine, and finally dried ($MgSO_4$). The solvent was removed in vacuo to give chloroformate **2c** (879 mg, 97%) as an off-white solid containing traces of a product

formed from diisopropylethylamine showing characteristic signals at 4.30 and 3.45−3.25 ppm. This by-product can be removed by extensive washing of the organic phase with HCl (2 N). However, the material was used as obtained without further purification for the next step to obtain **6c**. ^{1}H NMR: δ = 8.11 (s, 2 H, H_α), 7.60 (half of AA′XX′, 4 H, H_β), 7.46 (half of AA′XX′, 4 H, H_γ-2,-6), 7.45 (half of AA′XX′, 4 H, H_β), 7.40 and 7.31 (AA′XX′, 4 H each, H_ε), 7.03 (s, 4 H, H_δ), 6.86 (half of AA′XX′, 4 H, H_γ-3,-5), 4.41 (q, *J* = 7.1 Hz, 2 H, CO_2CH_2), 3.96 (t, *J* = 6.5 Hz, 4 H, $Ar_\gamma OCH_2$), 3.70 (t, *J* = 6.6 Hz, 4 H, $Ar_\delta OCH_2$), 2.39 and 2.34 (2 t, *J* = 6.8 Hz, 4 H each, $CH_2C{\equiv}C$), 2.20 (s, 12 H, $ArCH_3$), 1.76 (m, 8 H, OCH_2CH_2), 1.55 (m, 8 H, $CH_2CH_2C{\equiv}C$), 1.39 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 1.5−1.2 (m, 152 H, CH_2). $C_{170}H_{231}O_8Cl$ (2438.163). FD-MS: *m*/*z* = 2439.8 (M^+, 100%; accompanied by the isotope peak at 2441.5, not baseline separated), 1220.6 (M^{2+}, 40%), 813.7 (M^{3+}, 26%).

Compound 6c: Cycle precursor **5c(H)** (712.2 mg, 0.299 mmol) was added to a suspension of sodium hydride (60% suspension in mineral oil, 12.1 mg, 0.30 mmol) in THF (17 mL). The yellow suspension was slightly heated to give a clear solution. Chloroformate **2c** (730.5 mg, 0.299 mmol) was then added, followed by addition of THF (1.5 mL) to wash down the chloroformate that had become stuck on the flask's wall. The solution slowly became turbid and the color faded. After 22 h at room temperature, HCl (2 N) and diethyl ether were added. The organic phase was washed with brine and dried ($MgSO_4$), and the solvent was removed under reduced pressure. Flash chromatography (petroleum ether/CH_2Cl_2, 1:1 → 1:1.2 v/v) gave **6c** (815 mg, 57%). The solvent was changed as soon as the carbonate was detected at the outlet of the column. As a first fraction, **5c(H)** and **1c** were eluted. To remove residual solvent, the product was freeze-dried using benzene. The low yield is probably due to loss of material during several experiments to find the best conditions for chromatographic isolation of **6c**. ^{1}H NMR: δ = 7.863, 7.858 (s, 2 H each, H_α), 7.56 (half of AA′XX′, 8 H, H_γ-2,-6), 7.41−7.26 (m, 32 H, H_β, H_ε), 7.03 (s, 8 H, H_δ), 6.88 (half of AA′XX′, 8 H, H_γ-3,-5), 4.31 (q, *J* = 7.1 Hz, 4 H, CO_2CH_2), 3.981, 3.975 (2 t, *J* = 6.5 Hz, 4 H each, $Ar_\gamma OCH_2$), 3.700, 3.695 (2 t, *J* = 6.6 Hz, 4 H each, $Ar_\delta OCH_2$), 3.11 (s, 2 H, C≡CH), 2.38 and 2.36 (2 t, *J* = 6.8 Hz, 8 H each, $CH_2C{\equiv}C$), 2.200, 2.198, 2.196 (s, together 24 H, $ArCH_3$), 1.77 (m, 16 H, OCH_2CH_2), 1.55 (m, 16 H, $CH_2CH_2C{\equiv}C$), 1.31 (t, *J* = 7.1 Hz, 6 H, CH_2CH_3), 1.5−1.2 (m, 304 H, CH_2). ^{13}C NMR: δ = 165.3 (CO_2), 159.3 (C_γ-4), 155.8 (C_δ-4), 147.6 (CO_3), 147.2 (C_α-4), 135.6, 135.4 (C_β-1, C_α-3,-5), 133.2 (C_γ-2,-6), 132.2 (CH_ε of ring), 131.94, 131.89 (CH_ε of ring precursor, CH_δ), 131.7 (broad, C_β-3,-5, C_α-2,-6), 131.5 (CH_ε or ring), 131.4 (CH_ε or ring precursor), 130.9 (C_δ-3,-5), 129.2 (C_α-1), 128.6 (C_β-2,-6), 125.2 (C_ε-1 or C_ε-4 of ring), 124.7 (C_ε-1 or C_ε-4 of ring precursor), 123.3 (C_β-4), 121.0 (C_ε-4 or C_ε-1 of ring precursor), 120.6 (C_ε-4 or C_ε-1 of ring), 119.1 (C_δ-1), 115.3 (C_γ-1), 114.66, 114.63 (C_γ-3,-5), 93.6 ($CH_2C{\equiv}CAr_\varepsilon$ of ring), 92.8 ($CH_2C{\equiv}CAr_\varepsilon$ of ring precursor), 90.8 ($C{\equiv}CAr_\gamma$), 89.0 ($CH_2C{\equiv}CAr_\delta$), 88.3, ($Ar_\beta C{\equiv}C$), 83.4 ($C{\equiv}CH$), 82.0 ($C{\equiv}C{-}C{\equiv}C$), 80.39, 80.36 and 80.3, 80.1 ($CH_2C{\equiv}C$), 78.3 ($C{\equiv}CH$), 75.2 ($C{\equiv}C{-}C{\equiv}C$), 72.4 ($Ar_\delta OCH_2$), 68.14, 68.11 ($Ar_\gamma OCH_2$), 61.3 (CO_2CH_2), 30.4−28.6 (17 signals), 26.12, 26.09, 26.01, 19.51, 19.47, and 19.37 (CH_2), 16.1 ($ArCH_3$), 14.3 (CH_2CH_3). $C_{339}H_{464}O_{15}$ (4777.426): calcd. C 85.19, H 9.79; found C 85.06, H 9.83.

Mixture of Precatenane 7c and Dumbbell 8c: CuCl (6.43 g, 65.0 mmol) and $CuCl_2$ (1.12 g, 8.3 mmol) were added to pyridine (1 L) and the resulting suspension was heated to 50 °C for 30 min to dissolve most of the copper salts. After the mixture had cooled to room temperature, a solution of **6c** (763 mg, 0.16 mmol) in pyridine (75 mL) was added by syringe pump over 30 h. After the reaction mixture had been stirred for an additional 90 h, pyridine was removed (45 °C bath temperature, 10 mbar) and the residue was suspended in CH_2Cl_2. The suspension was cooled with a dry ice − acetone bath and sufficient cold HCl (5 N) was added to dissolve all of the copper salts. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were washed with HCl (2 N) and dried ($MgSO_4$). The solvent was removed under reduced pressure. Flash chromatography (petroleum ether/CH_2Cl_2, 1:1 v/v) gave a mixture (ca. 2:1) of **7c** and **8c** (627 mg, 82%) as a pale yellow solid. The material was freeze-dried from benzene to remove residual solvent. ^{1}H NMR: δ = 7.86 (broadened s, 4 H, H_α of **7c**), 7.85 (s, 4 H, H_α of **8c**), 7.57, 7.56 (two halves of two AA′XX′, 8 H, H_γ-2,-6), 7.402, 7.396 (two halves of two AA′XX′, 8 H, H_ε), 7.313, 7.307 (two halves of two AA′XX′, 8 H, H_ε), 7.37 and 7.28 (broadened, 8 H each, H_β), [The overall integration of signals between 7.42 and 7.25 gives the correct value. Distribution of signal intensity has been made in accordance to the proposed structure.], 7.03 (s, 8 H, H_δ), 6.89, 6.88 (two halves of two AA′XX′, 8 H, H_γ-3,-5), 4.31 (q, *J* = 7.1 Hz, 4 H, CO_2CH_2), 3.98 (t, *J* = 6.5 Hz, 8 H, $Ar_\gamma OCH_2$), 3.70 (t, *J* = 6.6 Hz, 8 H, $Ar_\delta OCH_2$), 2.39 and 2.34 (2 t, *J* = 6.8 Hz, 8 H each, $CH_2C{\equiv}C$), 2.20 (s, 24 H, $ArCH_3$), 1.78 (m, 16 H, OCH_2CH_2), 1.55 (m, 16 H, $CH_2CH_2C{\equiv}C$), 1.31 (t, *J* = 7.1 Hz, 6 H, CH_2CH_3), 1.5−1.2 (m, 304 H, CH_2). ^{13}C NMR: δ = 165.3 (CO_2), 159.3 (C_γ-4), 155.8 (C_δ-4), 147.5 (CO_3), 147.2 (C_α-4), 135.6, 135.4 (C_β-1, C_α-3,-5), 133.2 (C_γ-2,-6), 132.2 (CH_ε), 131.9 (CH_δ), 131.67 (broadened, with shoulder at δ = 131.70 ppm, C_β-3,-5, C_α-2,-6), 131.5 (CH_ε), 130.9 (C_δ-3,-5), 129.2 (C_α-1), 128.6 (broad, C_β-2,-6), 125.2 (C_ε-1 or C_ε-4), 123.3 (broad, C_β-4), 120.6 (C_ε-4 or C_ε-1), 119.1 (C_δ-1), 115.3 (C_γ-1), 114.7 (C_γ-3,-5), 93.6 ($CH_2C{\equiv}CAr_\varepsilon$), 90.8 ($C{\equiv}CAr_\gamma$), 89.0 ($CH_2C{\equiv}CAr_\delta$), 88.3 ($Ar_\beta C{\equiv}C$), 82.0 ($C{\equiv}C{-}C{\equiv}C$), 80.4 and 80.3 ($CH_2C{\equiv}C$), 75.2 ($C{\equiv}C{-}C{\equiv}C$), 72.4 ($Ar_\delta OCH_2$), 68.1 ($Ar_\gamma OCH_2$), 61.3 ($CO_2CH_2$), 30.4−28.6 (12 signals), 26.1, 26.02, 25.99, 19.5, and 19.4 (CH_2), 16.1 ($ArCH_3$), 14.3 (CH_2CH_3). $C_{339}H_{462}O_{15}$ (4777.410): calcd. C 85.23, H 9.75; found C 85.08, H 10.00.

Mixture of Catenane 9c and Ring 1c: nBu_4NF in THF (1 M, 1.15 mL, 1.15 mmol) was added to a solution of a mixture (ca. 2:1) of **7c** and **8c** (540 mg, 0.113 mmol) in THF (6 mL). The solution immediately became fluorescent green. After the reaction mixture had been stirred for 15 h at 50 °C, it was cooled with an ice bath and HCl (2 N, 2 mL) was added, whereupon the solution became pale yellow and a precipitate formed. After addition of ethanol (20 mL), the precipitate was isolated, washed with HCl (2 N) and finally with ethanol, and dried to give a mixture (ca. 1:1 mol ratio) of **9c** and **1c** (525 mg, 98%) as a beige-colored solid. The ^{1}H NMR signals are assigned to **9c** and **1c** according to the signal intensity and in agreement with the known data of ring **1c**.[24] ^{1}H NMR spectroscopic data of **9c**: δ = 7.98 (s, 4 H, H_α), 7.60, 7.52 (AA′XX′, 8 H each, H_β), 7.455 (half of AA′XX′, 8 H, H_γ-2,-6), 7.398 and 7.310 (AA′XX′, 8 H each, H_ε), 7.03 (s, 8 H, H_δ), 6.85 (half of AA′XX′, 8 H, H_γ-3,-5), 5.76 (s, 2 H, OH), 4.361 (q, *J* = 7.1 Hz, 4 H, CO_2CH_2), 3.95 (t, *J* = 6.5 Hz, 8 H, $Ar_\gamma OCH_2$), 3.69 (t, *J* = 6.6 Hz, 8 H, $Ar_\delta OCH_2$), 2.39 and 2.34 (2 t, *J* = 6.8 Hz, 8 H each, $CH_2C{\equiv}C$), 2.20 (s, 24 H, $ArCH_3$), 1.76 (m, 16 H, OCH_2CH_2), 1.56 (m, 16 H, $CH_2CH_2C{\equiv}C$), 1.37 (t, *J* = 7.1 Hz, 6 H, CH_2CH_3), 1.5−1.2 (m, 304 H, CH_2).

Catenane 10c and Ring 11c:[49] K_2CO_3 (58 mg, 0.42 mmol) and methyl iodide (0.12 mL, 1.9 mmol) were added to a solution of a mixture (ca. 1:1) of **9c** and **1c** (515 mg, 0.22 mmol of OH groups) in THF (5 mL) and DMF (4 mL). The suspension was kept at 45−48 °C for 13 h. After cooling with an ice bath, HCl (5 N) was

added cautiously (gas evolution!). After addition of water, the precipitate was isolated, washed successively with HCl (5 N), water, and ethanol, and dried. Flash chromatography (petroleum ether/CH_2Cl_2, 10:7.5 → 1:1 v/v) gave as the first fraction ring **11c** (161 mg, 31%) as a colorless solid and as the second fraction catenane **10c** (320 mg, 62%) as a colorless solid. The products were freeze-dried using benzene.

Analytical Data of Ring 11c: $T_{c\rightarrow SmA}$ = 73.4 °C. ^{1}H NMR: δ = 8.03 (s, 2 H, H_α), 7.58 (apparent s, 8 H, H_β), 7.47 (half of AA′XX′, 4 H, H_γ-2,-6), 7.40 and 7.31 (AA′XX′, 4 H each, H_ε), 7.04 (s, 4 H, H_δ), 6.86 (half of AA′XX′, 4 H, H_γ-3,-5), 4.38 (q, *J* = 7.1 Hz, 2 H, CO_2CH_2), 3.96 (t, *J* = 6.5 Hz, 4 H, $Ar_\gamma OCH_2$), 3.70 (t, *J* = 6.6 Hz, 4 H, $Ar_\delta OCH_2$), 3.19 (s, 3 H, OCH_3), 2.39 and 2.35 (2 t, *J* = 6.8 Hz, 4 H each, $CH_2C{\equiv}C$), 2.20 (s, 12 H, $ArCH_3$), 1.75 (m, 8 H, OCH_2CH_2), 1.55 (m, 8 H, $CH_2CH_2C{\equiv}C$), 1.38 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 1.5−1.2 (m, 152 H, CH_2). ^{13}C NMR: δ = 166.0 (CO_2), 159.3 (C_γ-4), 158.8 (C_α-4), 155.8 (C_δ-4), 137.2, 135.2 (C_β-1, C_α-3,-5), 133.1 (C_γ-2,-6), 132.3 (CH_ε), 132.0 (CH_δ), 131.7 (C_α-2,-6), 131.5 (CH_ε), 131.4 (C_β-3,-5), 130.9 (C_δ-3,-5), 129.2 (C_β-2,-6), 126.5 (C_α-1), 125.2 (C_ε-1 or C_ε-4), 123.0 (C_β-4), 120.6 (C_ε-4 or C_ε-1), 119.0 (C_δ-1), 115.0 (C_γ-1), 114.6 (C_γ-3,-5), 93.6 ($CH_2C{\equiv}CAr_\varepsilon$), 90.3 ($C{\equiv}CAr_\gamma$), 89.0 ($CH_2C{\equiv}CAr_\delta$), 87.8 ($Ar_\beta C{\equiv}C$), 82.0 ($C{\equiv}C-C{\equiv}C$), 80.4 and 80.3 ($CH_2C{\equiv}C$), 75.2 ($C{\equiv}C-C{\equiv}C$), 72.4 ($Ar_\delta OCH_2$), 68.1 ($Ar_\gamma OCH_2$), 61.1 ($CO_2CH_2$), 60.6 ($OCH_3$), 30.4−28.6 (10 signals), 26.1, 26.0, 19.5, and 19.4 (CH_2), 16.1 ($ArCH_3$), 14.4 (CH_2CH_3). $C_{170}H_{234}O_7$ (2389.735): calcd. C 85.44, H 9.87; found C 85.45, H 10.07. FD-MS: *m*/*z* (%) = 2390.2 (100) [M^+], 1196.7 (86%) [M^{2+}], 796.6 (24) [M^{3+}].

Analytical Data of Catenane 10c: $T_{c\rightarrow SmA}$ = 70.6 °C. ^{1}H NMR: δ = 8.03 (s, 4 H, H_α), 7.57 (apparent s, 16 H, H_β), 7.45 (half of AA′XX′, 8 H, H_γ-2,-6), 7.40 and 7.31 (AA′XX′, 8 H each, H_ε), 7.03 (s, 8 H, H_δ), 6.85 (half of AA′XX′, 8 H, H_γ-3,-5), 4.38 (q, *J* = 7.1 Hz, 4 H, CO_2CH_2), 3.95 (t, *J* = 6.5 Hz, 8 H, $Ar_\gamma OCH_2$), 3.69 (t, *J* = 6.6 Hz, 8 H, $Ar_\delta OCH_2$), 3.19 (s, 6 H, OCH_3), 2.38 and 2.34 (2 t, *J* = 6.8 Hz, 8 H each, $CH_2C{\equiv}C$), 2.19 (s, 24 H, $ArCH_3$), 1.75 (m, 16 H, OCH_2CH_2), 1.54 (m, 16 H, $CH_2CH_2C{\equiv}C$), 1.38 (t, *J* = 7.1 Hz, 6 H, CH_2CH_3), 1.5−1.2 (m, 304 H, CH_2). ^{13}C NMR: δ = 166.0 (CO_2), 159.3 (C_γ-4), 158.8 (C_α-4), 155.8 (C_δ-4), 137.2, 135.2 (C_β-1, C_α-3,-5), 133.1 (C_γ-2,-6), 132.2 (CH_ε), 131.9 (CH_δ), 131.7 (C_α-2,-6), 131.5 (CH_ε), 131.4 (C_β-3,-5), 130.9 (C_δ-3,-5), 129.2 (C_β-2,-6), 126.5 (C_α-1), 125.2 (C_ε-1 or C_ε-4), 123.0 (C_β-4), 120.6 (C_ε-4 or C_ε-1), 119.0 (C_δ-1), 115.0 (C_γ-1), 114.6 (C_γ-3,-5), 93.6 ($CH_2C{\equiv}CAr_\varepsilon$), 90.3 ($C{\equiv}CAr_\gamma$), 89.0 ($CH_2C{\equiv}CAr_\delta$), 87.8 ($Ar_\beta C{\equiv}C$), 82.0 ($C{\equiv}C-C{\equiv}C$), 80.4 and 80.2 ($CH_2C{\equiv}C$), 75.2 ($C{\equiv}C-C{\equiv}C$), 72.4 ($Ar_\delta OCH_2$), 68.1 ($Ar_\gamma OCH_2$), 61.1 ($CO_2CH_2$), 60.6 ($OCH_3$), 30.4−28.6 (10 signals), 26.1, 26.0, 19.5, and 19.4 (CH_2), 16.1 ($ArCH_3$), 14.4 (CH_2CH_3). $C_{340}H_{468}O_{14}$ (4779.470): calcd. C 85.44, H 9.87; found C 85.80, H 10.20. MALDI-TOF (dithranol, KO_2CCF_3): *m*/*z* = 4818.9 [M + K^+], 4780 (very low intensity) [M^+].

Dumbbell 8c: Macrocycle **1c** (146.5 mg, 0.062 mmol) was added to a suspension of sodium hydride (60% suspension in mineral oil, 3.4 mg, 0.09 mmol) in THF (3 mL). After the gas evolution had ceased, chloroformate **2c** (150.5 mg, 0.062 mmol) was added, followed by addition of THF (1 mL) to wash down the chloroformate that had become stuck on the flask's wall. The solution slowly became turbid. After 22 h of stirring at room temperature, the reaction mixture was cooled with an ice bath. HCl (2 N) and then water was added. The yellow precipitate was isolated, and washed with water and finally with ethanol. Flash chromatography (petroleum ether/CH_2Cl_2, 1.5:1 v/v to elute starting compounds, then petroleum ether/CH_2Cl_2, 1:1 → 1:1.2 v/v to elute the product) gave **8c** (237 mg, 80%) as a pale yellow solid. $T_{c\rightarrow lc}$ = 70.8 °C. ^{1}H NMR: δ = 7.86 (s, 4 H, H_α), 7.56 (half of AA′XX′, 8 H, H_γ-2,-6), 7.40 and 7.31 (AA′XX′, 8 H each, H_ε), 7.38 and 7.28 (slightly broadened, 8 H each, H_β), 7.04 (s, 8 H, H_δ), 6.88 (half of AA′XX′, 8 H, H_γ-3,-5), 4.31 (q, *J* = 7.1 Hz, 4 H, CO_2CH_2), 3.98 (t, *J* = 6.5 Hz, 8 H, $Ar_\gamma OCH_2$), 3.70 (t, *J* = 6.6 Hz, 8 H, $Ar_\delta OCH_2$), 2.39 and 2.35 (2 t, *J* = 6.8 Hz, 8 H each, $CH_2C{\equiv}C$), 2.20 (s, 24 H, $ArCH_3$), 1.78 (m, 16 H, OCH_2CH_2), 1.55 (m, 16 H, $CH_2CH_2C{\equiv}C$), 1.31 (t, *J* = 7.1 Hz, 6 H, CH_2CH_3), 1.5−1.2 (m, 304 H, CH_2). ^{13}C NMR: δ = 165.3 (CO_2), 159.3 (C_γ-4), 155.8 (C_δ-4), 147.6 (CO_3), 147.1 (C_α-4), 135.2, 135.3 (C_β-1, C_α-3,-5), 133.2 (C_γ-2,-6), 132.2 (CH_ε), 131.9 (CH_δ), 131.65 (broadened, with shoulder at δ = 131.70 ppm, C_β-3,-5, C_α-2,-6), 131.5 (CH_ε), 130.9 (C_δ-3,-5), 129.2 (C_α-1), 128.6 (C_β-2,-6), 125.2 (C_ε-1 or C_ε-4), 123.3 (C_β-4), 120.6 (C_ε-4 or C_ε-1), 119.0 (C_δ-1), 115.3 (C_γ-1), 114.6 (C_γ-3,-5), 93.6 ($CH_2C{\equiv}CAr_\varepsilon$), 90.8 ($C{\equiv}CAr_\gamma$), 89.0 ($CH_2C{\equiv}CAr_\delta$), 88.2 ($Ar_\beta C{\equiv}C$), 81.9 ($C{\equiv}C-C{\equiv}C$), 80.4 and 80.2 ($CH_2C{\equiv}C$), 75.2 ($C{\equiv}C-C{\equiv}C$), 72.4 ($Ar_\delta OCH_2$), 68.1 ($Ar_\gamma OCH_2$), 61.2 ($CO_2CH_2$), 30.3−28.6 (10 signals), 26.1, 26.0, 19.5, and 19.3 (CH_2), 16.1 ($ArCH_3$), 14.3 (CH_2CH_3). $C_{339}H_{462}O_{15}$ (4777.410): calcd. C 85.23, H 9.75; found C 85.27, H 9.80.

The Supporting Information (see footnote on the first page of this article) shows the apparatus for working with phosgene and the ^{1}H NMR spectra of compounds **1a**, **2b**, **2c**, **9a**, **10c**, and **11c**.

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[20] By application of the simple rule of arbitrary deformation for finding out whether two compounds are topological isomers (for a definition of topological isomerism see refs.[22,23]), the tether (i.e., the carbonate linkage) between the two rings of **7**

and **8** can collapse to a point common to both rings. This converts **7** into **8** and vice versa. Therefore, within the strict definition of topology, **7** and **8** are topologically identical. However, the real molecules **7** and **8** cannot be converted into each other without bond breaking and this is strictly forbidden in topology. Because of this dilemma the term "residual topology" was recently suggested in ref.[21]

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[25] For identification of carbamate **3b** in a mixture with chloroformate **2b** and carbonate **8b**, ^{1}H NMR spectroscopy and mass spectrometry were used. Diagnostic ^{1}H NMR signals of **3b**: δ = 8.06 (s, 2 H, H_α), 3.08, 3.01 (2 q, 2 H each, CH_2CH_3), 0.88, 0.77 (2 t, 3 H each, CH_2CH_3); FD-MS: *m*/*z* (%) = 1542.4 (62) [M^+], 770.4 (29) [M^{2+}]. Corresponding ^{1}H NMR signals and FD-MS signals were found for products obtained from the reaction of cycle precursor **5a(H)** with triphosgene and excess of Et_3N.

[26] R. E. Stenseth, R. M. Schisla, J. W. Baker, *J. Chem. Eng. Data* **1964**, *9*, 390.

[27] Dumbbells **8** can easily be detected by ^{1}H NMR spectroscopy because of the distinct signal shift for H_α (e.g., δ = 7.86, 7.99, and 8.11 for H_α of **8c**, **1c**, and **2c**, respectively). The data for the corresponding compounds with smaller rings are nearly the same.

[28] A maximum of 5% is estimated from the ^{1}H NMR spectra. A more precise figure cannot be obtained because of the very similar shifts of the signals. The identification of **4b** is based on ^{1}H NMR spectroscopy and mass spectrometry on mixtures of **4b** and **2b** as obtained from the reaction. Diagnostic ^{1}H NMR signals: δ = 8.12 (hardly resolved from H_α of **2b**), 7.58 (part of the signal of H_β); FD-MS: *m*/*z* (%) = 1605.5 (6) [M^+]; The 100% peak at *m*/*z* = 1504.7 corresponds to M^+ of **2b**. Corresponding ^{1}H NMR signals and FD-MS signals were found for products from experiments with ring precursor **5a(H)** and a model compound for **5(H)** bearing two methoxy groups instead of the long alkoxy substituents.

[29] Merck Index, 10th edition, **1983**, 1058.

[30] A by-product of unknown structure was formed in about a third of our twenty threading experiments. Diagnostic ^{1}H NMR signals are two broadened singlets at δ = 8.08 and 8.07 ppm and a triplet at δ = 2.93 ppm. This compound was eluted from silica gel only upon increasing the polarity of the solvent.

[31] Depending on the source of the pyridine, substantial carbonate cleavage occurred. We used pyridine as supplied commercially. Recent experiments have shown that pyridine distilled off from the reaction mixture can be reused for this cyclization without causing carbonate cleavage after it has been heated at reflux over CaH_2 and finally distilled.

[32] The SEC traces of the mixtures of precatenanes **7** and dumbbells **8** as obtained after column chromatography can be found in ref.[35]

[33] Compare NMR spectroscopic data given here and in ref.[24] and see NMR spectra in the Supporting Information. For a comparison of the ^{1}H NMR spectra of **9b** with **1b** see ref.[18] The shift differences of corresponding signals decrease with increasing ring size. All ^{1}H NMR signals of catenane **9a** and ring **1a** differ by 0.02−0.05 ppm. Differences of 0.01−0.03 ppm and 0.01−0.02 ppm are found between the ^{1}H NMR spectroscopic data of **9b** and **1b** and of **10c** and **11c**, respectively.

[34] The cyclic dimer (see ref.[35]) as an alternative structure for the isolated compounds was excluded for **9a**, **9c**, and **10c** by a combination of SECs, mass spectrometry, and NMR spectroscopy, as described for **9b** in ref.[18]

[35] M. R. Shah, S. Duda, B. Müller, A. Godt, A. Malik, *J. Am. Chem. Soc.* **2003**, *125*, 5408.

[36] A. Godt, Ö. Ünsal, V. Enkelmann, *Chem. Eur. J.* **2000**, *6*, 3522.

[37] A related result was reported by Isele et al. (refs.[4,38]). In this case the size of the threaded ring was kept constant and the length of the threading ring precursor was varied.

[38] G. L. Isele, B. M. Vuano, *Justus Liebigs Ann. Chem.* **1976**, 1903.

[39] The formation of some catenane due to entanglement of the long chains is possible, but only with a very low probability.

[40] The activation energy for the oxidative alkyne dimerization is assumed to be the same for the conformers **A**, **B**, and **C**.

[41] Precatenane and dumbbell have very similar, but nevertheless distinctly different NMR spectra. For the determination of the ratio, the signals of the aromatic protons (H_α) of the benzoate rings were used. The H_α signals can unambiguously be assigned to **7** and **8** because the H_α signal of **7** is broadened and the H_α signal of **8** has the usual width. Because the H_α signal of **7** is broadened and the shift difference between H_α signals of **7** and **8** is small ($\Delta\delta$ = 0.01 or 0.02) the integration is not very precise. Nevertheless, the figures are sufficiently accurate clearly to show the trend that, the larger the rings, the more dumbbell is formed.

[42] D. A. Leigh, P. J. Lusby, S. J. Teat, A. J. Wilson, J. K. Y. Wong, *Angew. Chem. Int. Ed.* **2001**, *40*, 1538.

[43] In other strategies (see refs.[10−17]), the species with geometrically arranged catenane subunits are formed in situ and reversibly. The formation of non-entwined rings as side products of catenane formation is therefore not necessarily due to conformational changes as discussed here.

[44] H. Kukula, S. Veit, A. Godt, *Eur. J. Org. Chem.* **1999**, 277.

[45] Treatment of macrocycle **1** with phosgene and *i*Pr_2NEt can be performed in THF or in CH_2Cl_2. The latter is probably the better solvent for this reaction, because no hydrolysis of the chloroformate was found upon aqueous workup, whereas the crude products of experiments performed in THF occasionally contained starting material **1**. The disadvantage of CH_2Cl_2 is its tendency to form emulsions with water. However emulsions can be avoided through addition of diethyl ether. This makes the extractive workup straightforward. To avoid hydrolysis of **2** when THF is used, either the THF must be removed or the reaction mixture must be diluted with a large amount of diethyl ether before water is added.

[46] The carbonate cleavage is very slow at room temperature, so cleavage at 50 °C, as described for the preparation of **9b**, and **9c**, is recommended.

[47] No correct elemental analysis was obtained. ^{1}H NMR spectra of the crude products are shown in the Supporting Information.

[48] As described in ref.[18] **9b** and **1b** can be separated by chromatography.

[49] All compounds containing the longest chains, including the synthetic precursors of ring **1c**, are contaminated with a trace of an unknown impurity. ^{1}H NMR spectra show an additional singlet of very low intensity at δ = 2.24 ppm, next to the signal of $Ar_\delta CH_3$ (see NMR spectra of **2c**, **10c**, and **11c** in the Supporting Information). We assume a structural defect associated with the dimethylphenol moiety.

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