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Published on Web 04/10/2003

Facile Access to Monodisperse Ultralarge Rings

Muhammad Raza Shah,[†,‡] Stefan Duda,[†] Beate Müller,[†] Adelheid Godt,*[,†] and Abdul Malik[‡]

Contribution from the Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany and the H. E. J. Research Institute of Chemistry, University of Karachi, Karachi-75270, Pakistan

Received January 13, 2003; E-mail: godt@mpip-mainz.mpg.de

Abstract: A facile access to monodisperse ultralarge rings counting 126, 174, and 294 ring atoms is described. It follows a reaction sequence that is well suited for the preparation of [2]catenanes but altered just in the sequence of the two steps cyclization and carbonate formation. The carbonate acts as a covalent template that is easily formed and later cleaved. The obtained monocyclic products are constitutional isomers of the catenanes.

Introduction

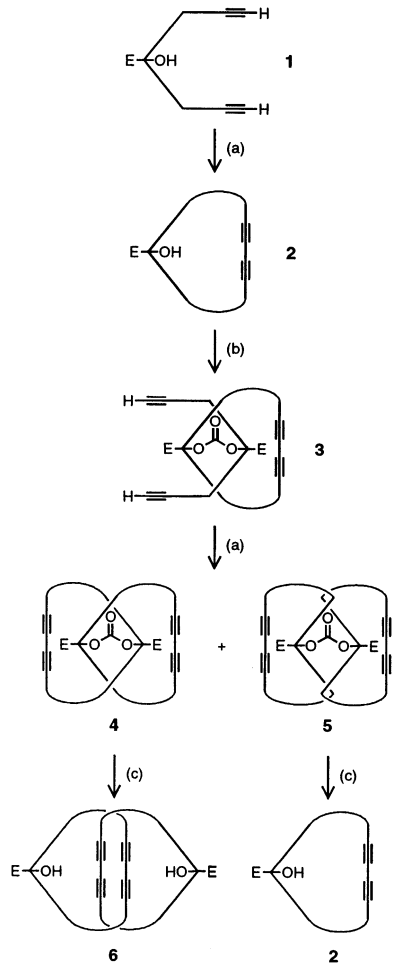
When devising a reaction sequence to form [2]catenanes, one of the most critical questions to answer is how to promote the entwinement of the rings to get reasonable yields. We have demonstrated a successful route to [2]catenanes that employs a carbonate group as a covalent template.[1]

The route (Scheme 1) comprises the following main steps: (1) cyclization of ring precursor **1** to obtain ring **2**, (2) threading of that ring onto a second ring precursor and their geometrical fixation through carbonate linkage, (3) formation of the second ring through oxidative alkyne dimerization under pseudohigh dilution, which gives a mixture of catenane precursor **4** and its topologically isomeric carbonate **5**, and (4) carbonate cleavage providing catenane **6** and ring **2** which were separated by standard column chromatography. We were curious what products would be obtained if we changed the step's sequence in the way that first the carbonate **7** is formed and then the formation of both rings in the same step is pursued (Scheme 2). This approach could again give the catenane precursor **4** accompanied by the isomeric carbonate **5**, but it might as well lead to the dimer precursor **8** or to a mixture of all of these three possible products of an intramolecular alkyne dimerization.

Results and Discussion

The carbonates **7a**−**c** were prepared starting from the ring precursors **1a**−**c** through a reaction with sodium hydride followed by the addition of triphosgene. Subsequent slow addition of a solution of the carbonates **7a**−**c** to a suspension of CuCl and $CuCl_2$ in pyridine gave in all cases dominantly products with a smaller hydrodynamic volume than the starting material **7a**−**c** as revealed by a comparison of the size exclusion chromatograms (SECs, Figure 1). This proves that most of the material underwent intramolecular alkyne dimerization which is in accordance with the formation of catenane precursor **4**, carbonate **5** and dimer precursor **8**. The former two are known

Scheme 1 [a]



[a] Key. (a) CuCl, $CuCl_2$, pyridine, room temperature; (b) 1) $COCl_2$, $^{i}Pr_2NEt$; 2) + mono sodium salt of **1**; (c) $^{n}Bu_4NF$, 50 °C. For precise structures see the index.

[†] Max-Planck-Institut für Polymerforschung.
[‡] H. E. J. Research Institute.

(1) (a) Ünsal, Ö.; Godt, A. *Chem. Eur. J.* **1999**, *5*, 1728. (b) Duda, S. PhD thesis, University Mainz, **2002**. (c) Godt, A., unpublished results.

10.1021/ja034147c CCC: $25.00

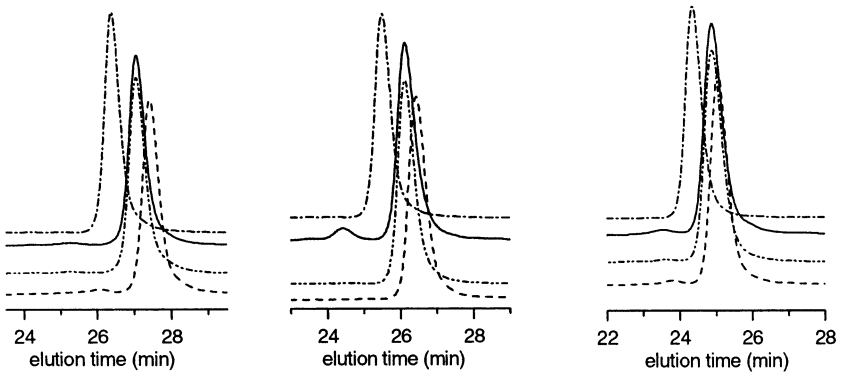
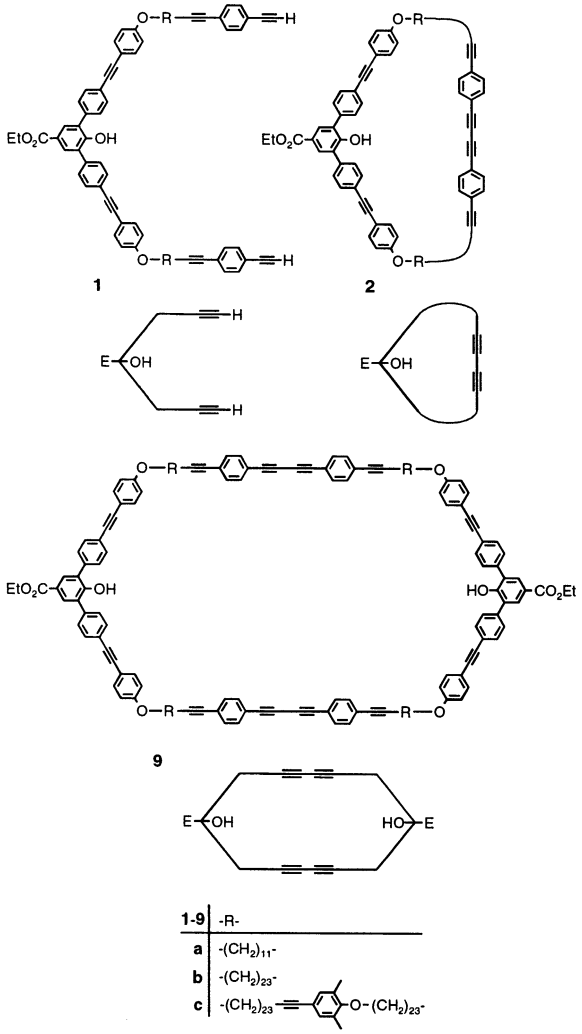
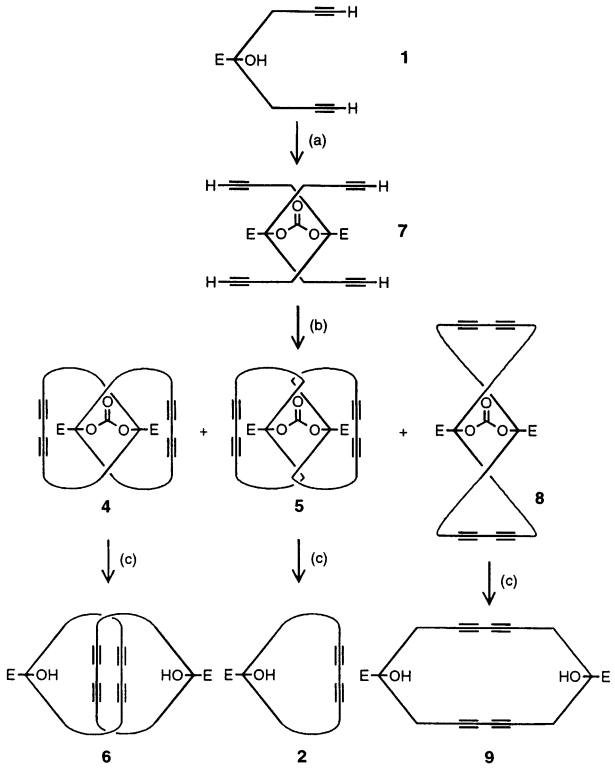


Figure 1. Comparative size exclusion chromatograms of the starting material carbonate **7** (-•-•), the crude product that was obtained through reaction of **7** with CuCl, $CuCl_2$ in pyridine (—), the product of cyclization after column chromatography (-••-••), and the mixture of catenane precursor **4** and isomeric carbonate **5** (- - -) obtained through the route depicted in Scheme 1. Chromatograms from left to right correspond to compounds with increasing ring size, e.g., **7a** (left), **7b** (middel), **7c** (right).



Scheme 2 [a]



[a] Key. (a) 1) NaH, 2) $CO(OCCl_3)_2$; (b) CuCl, $CuCl_2$, pyridine; (c) $^nBu_4NF$, 50 °C. For precise structures see the index.

from our previous work.[1] They were indeed found in the reaction mixture, but as side products only, identified through the corresponding signals of small intensity in the ^1H NMR spectra. The main compound in comparison exhibited slightly different shifts of the ^1H NMR signals and a different elution time upon size exclusion chromatography (Figure 1).

Therefore, we conclude that dimer precursor **8** was the main product. The NMR signals as well as the elution times from SEC of the different isomers are so similar that the isomers' ratio cannot be determined. Since the three isomeric compounds **4b**, **5b** and **8b** and **4c**, **5c** and **8c** showed very similar R_F values on silica gel using petroleum ether/CH_2Cl_2 as solvent no separation was attempted and only residual copper salts and material of higher molecular mass formed through intermolecular alkyne dimerization were removed chromatographically. Also the three isomers **4a**, **5a** and **8a** were not separated, although comparative TLC indicated that separation is possible. Treatment of the mixtures consisting of **4**, **5**, and **8** with $^nBu_4NF$ in THF for selective cleavage of the carbonate group without ester hydrolysis[1] gave mixtures of catenane **6**, ring **2** and, as the major product, dimer **9**. The dimers **9a** (74%), **9b** (65%), and **9c** (48%) were isolated through chromatography. In a second experiment, dimer **9b** (49%) was isolated by crystallization due to its remarkably low solubility in dichloromethane. The smaller dimer **9a** is also not very well soluble in dichloromethane or chloroform whereas the largest dimer **9c** is well

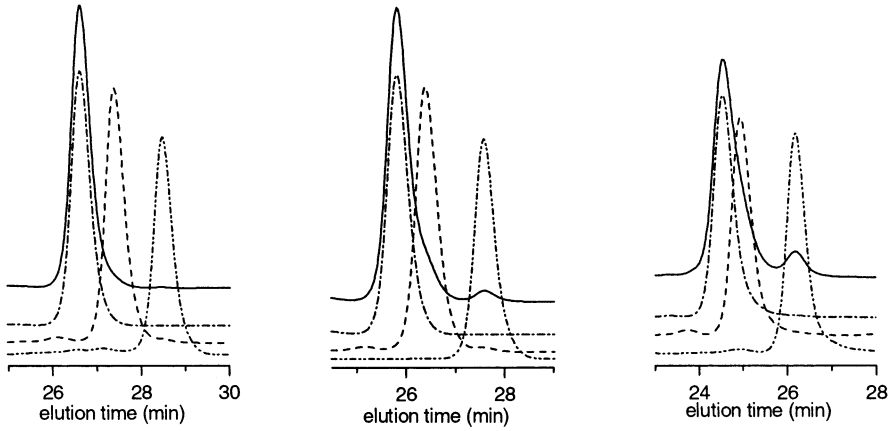


Figure 2. Comparative size exclusion chromatograms of the crude product obtained through the reaction of the mixture consisting of **4**, **5**, and **8** with $^{n}Bu_4NF$ that leads to carbonate cleavage (—), isolated dimer **9** (-•-•), ring **2** (-••-••), and catenane **6** (- - --).[2b] Chromatograms from left to right correspond to compounds with increasing ring size, e.g., **9a** (left), **9b** (middel), **9c** (right).

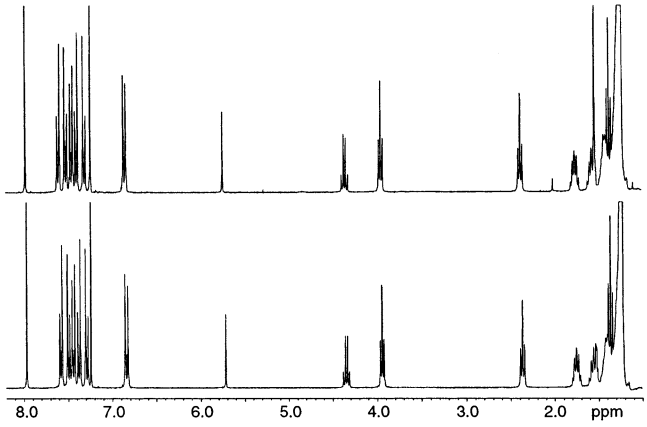


Figure 3. ^1H NMR spectrum ($CDCl_3$, room temperature, 300 MHz) of dimer **9b** (top) and catenane **6b** (bottom).

soluble in these solvents. Catenanes and rings were unambiguously identified through ^1H NMR spectroscopy, TLC and SEC (Figure 2).[2]

On the basis of our conclusion that dimer precursors **8** are the main products of the cyclization, carbonate cleavage must mainly yield the dimers **9**. NMR data and mass spectra (see data given in the Experimental Section) are in full agreement with this structure. As expected, the ^1H and ^{13}C NMR spectra of dimer, corresponding catenane, and corresponding ring look very much alike. As an example, the ^1H NMR spectra of dimer **9b** and catenane **6b** are presented in Figure 3.[4]

SEC as well as the different R_F values on silica gel and the different solubility offer unambiguous proof that albeit of the very similar NMR data and identical *m/z* values the main product is different from the known catenane **6**. There is independent support for the assigned structure of dimer **9a** coming from cyclization of **1a** on reaction with CuCl and $CuCl_2$ in pyridine.[3] While changing the dilution and the addition rate of **1a**, in one case besides the ring **2a** a substantial amount of higher mass species was formed. From this experiment, a compound was isolated that was identified through NMR spectroscopy and mass spectrometry as the cyclic dimer **9a**. This compound and the main product obtained from **7a** as described above show identical NMR spectra, SECs, and R_F values.

As mentioned above, the products **4**, **5**, and **8** of intramolecular alkyne dimerization had not been separated. Therefore, the ratio of these products is mirrored in the ratio of the products obtained after carbonate cleavage. Integration of the signals of the SECs[5] and taking into account the known ratio of catenane precursor **4** and isomeric carbonate **5**[6] gives the following approximate ratios of the dimer **9**, catenane **6** and ring **2**: for the medium sized rings, **9b**, **6b**, **2b**, a ratio of 1:1:14, and for the largest rings, **9c**, **6c**, **2c**, a ratio of 1:1:4. The corresponding ratio for the smallest rings, **9a**, **6a**, **2a** cannot be determined because of too small amounts of ring **2a** present in the mixture (Figure 2). Obviously, with increasing chain length, the portion of ring and of catenane increases, which means that the cyclization becomes less selective in respect to the isomers formed in the intramolecular reaction. Nevertheless, even with the longest chain used in this work the dimer precursor **8** was the definitely preferred product.

Through interchanging the two steps cyclization and carbonate formation, our strategy of catenane formation becomes a route to monodisperse ultralarge rings.[7,8] This is unique in comparison to the reported methods of catenane synthesis that employ other organization centers.[9] With the 2,9-diphenyl-1,10-phenanthroline-Cu(I) complex as the organization center, a [2]catenate (a [2]catenane-Cu(I) complex) is formed independently of the sequence of the reaction steps cyclization and complex forma-

(2) (a) For this comparison, the crude product of the carbonate cleavage as well as fractions isolated upon chromatography or recrystallisation were used. Catenanes and rings obtained through our former route (ref 1, 3) provided the data for comparison. (b) For comparison only *O*-methylated catenane **6c** was available. It shows the same retention time as the parent compound **6c**.

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(4) For a comparative plot of catenane **6b** and ring **2b** see ref 1a.

(5) UV detection at $\lambda = 254$ nm was used. Catenane **6b** and ring **2b** show identical UV−vis spectra. The extinction coefficient ϵ of catenane **6b** is double that of the ring **2b**. Accordingly, it is assumed that catenane **6b** and dimer **8b** show the same UV−vis spectra and have the same ϵ. The same is assumed to be true for the corresponding compounds with the smaller and larger rings.

(6) Compound **3** is assumed as an intermediate for the formation of **4** and **5** when starting from **7**. Therefore the ratio of **4** and **5** found as byproducts of the formation of **8** should be the same as found when **3** is used as the starting material to synthesize catenane **6**.

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tion.[12,13] Also, with a 2,6-di(benzylimino)pyridine-Zn(II) complex[14] and a 2,6-bis(benzimidazol-2-yl)pyridine-Fe(II) complex[15] that had been formed from the corresponding ring precursors and Zn and Fe salts, respectively, only [2]catenates were reported as the products. The exclusive formation of catenate in these cases is probably due to a perfect matching of dimensions such as the angles at the complex and the length of the chains that form the ring. This is suggested by the finding that using a terpyridine unit instead of the 2,9-diphenyl-1,10-phenanthroline, the Fe(II) complex of a cylic dimer was formed instead of a catenate.[16] Additionally, bridging a substituted 2,9-diphenyl-1,10-phenanthroline-Cu(I) complex with mono- and oligosaccharides Shinkai found the catenate or the Cu(I) complex of the cyclic dimer as the product, depending on the length of the bridges.[17] In our case, we neither had to change the angles at the organization center nor the chain length but only the sequence of two synthetic steps to obtain either catenane **6** or dimer **9**. This was found to be true for chains of very different length.

Conclusion

The predominant formation of dimer precursors **8** over catenane precursor **4** and carbonate **5** starting from **7** presents a facile route to a group of compounds, monodisperse ultralarge rings[7,8] with functional groups, that are otherwise difficult to obtain. It shows that our strategy of catenane formation is even more versatile and can easily be switched to a synthesis of the constitutionally isomeric dimer by simply interchanging the two steps cyclization and carbonate formation. The carbonate linkage that is used as a covalent template is formed and cleaved cleanly and so easily that this method appears as attractive as methods using noncovalent templates for ring formation.[11,18,19] As demonstrated with the isolation of 126-, 174- and 294-membered rings, the ring size can be greatly varied. Such ultralarge rings are of interest because they are macromolecules with a special topology.[20−22] Because of their functionalities the rings are attractive building blocks not only for catenanes with huge rings but also for special macromolecular architectures such as ring-coil polymers.[23] Furthermore, this easy accessibility of both the catenane **6** and its constitutional isomer, the dimer **9**, will allow comparative studies to unravel how the unique topology of catenanes influences the materials properties of [2]catenanes and poly[2]catenanes.

Experimental Section

General. All reactions were carried out under inert atmosphere in dried Schlenk flasks. The ring precursors **1** were synthesized as described.[3] THF was dried over sodium/benzophenone. For flash chromatography silica gel was used. TLC was carried out on silica gel coated aluminum foils (Merck aluminum foils $60F_{254}$). 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, as we have observed in a variety of compounds of the type ArC≡**C**H and AlkC≡**C**H.[24] Additionally, NMR data of precursors and representative model compounds[3,25] were used for signal assignment. 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. If not otherwise mentioned, the melting points were determined under ambient atmosphere using a microscope with a heating table. Size exclusion chromatograms were recorded at room temperature using polystyrene columns, THF as the mobile phase, and UV-detection.

Carbonate 7a.[26] To a suspension of NaH (60% dispersion in mineral oil, 37.7 mg, 0.943 mmol) in THF (17 mL) was added ring precursor **1a** (1.0438 g, 0.9425 mmol) as a solid. After the gas evolution had ceased, solid triphosgene (46.6 mg, 0.157 mmol) was added to the reddish clear solution. Slowly, the reaction mixture became turbid and the color faded. After 18 h at room temperature, 2N HCl (2 mL), water and diethyl ether were added successively. The aqueous phase was extracted with diethyl ether and the combined organic phases were washed with brine and dried ($MgSO_4$). Flash chromatography (petroleum ether/CH_2Cl_2 1:2 to elute residual ring precursor **1a** and some

(9) The Hunter−Vögtle−Leigh route (ref 10) to [2]catenanes made from aromatic amides and aromatic acid chlorides gives besides the catenane its monocyclic constitutional isomer. The geometrical organisation of the building blocks is achieved in-situ and the self-assembled structures are in equilibrium with the constituents. Therefore the way on which this isomer is formed is unknown. This excludes a comparison with our and the other discussed methods. The same argument holds for the result of Vance (ref 11).

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(26) In these experiments stoechiometry is essential because of: (a) terminal, unprotected alkynes; (b) six phenols of rather high molecular mass per triphosgene. While triphosgene is sufficiently inert towards hydrolysis to allow its handling under air for a short time, NaH is extremely hygroscopic. Therefore, the dispersion of NaH was stored and strictly handled 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. Therefore, quantitative transfer into the reaction vessel was possible. The amount of the residual components was calculated based on the determined amount of NaH.

residual chloroformate of **1a** that is an in situ formed intermediate; then 1:4 to elute the product) gave carbonate **7a** (889 mg, 84%) as a pale yellow solid. mp determined with DSC: 52.0 °C; ^{1}H NMR: δ = 7.86 (s, 4 H, H_α), 7.57 (half of AA′XX′, 8 H, H_γ-2,−6), 7.38 and 7.32 (AA′XX′, 8 H each, H_δ), 7.38 and 7.29 (broadened AA′XX′, 8 H each, H_β), 6.89 (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, ArOC**H**$_2$), 3.12 (s, 4 H, C≡CH), 2.39 (t, J = 7.0 Hz, 8 H, CH_2C≡C), 1.80 (m, 8 H, OCH_2C**H**$_2$), 1.59 (m, 8 H, C**H**$_2$$CH_2$C≡C), 1.5−1.2 (m, 62 H, CH_2, CH_3); ^{13}C NMR: δ = 165.3 (CO_2), 159.3 (C_γ-4), 147.6 (CO_3), 147.1 (C_α-4), 135.6, 135.3 (C_α-3,−5, C_β-1), 133.2 (C_γ-2,−6), 131.9 (CH_δ), 131.72 (C_α-2,−6), 131.66 (slightly broadened, C_β-3,−5), 131.4 (CH_δ), 129.2 (C_α-1), 128.6 (slightly broadened, C_β-2,−6), 124.7 (C_δ-1 or C_δ-4), 123.3, (C_β-4), 121.0, (C_δ-4 or C_δ-1), 115.3 (C_γ-1), 114.6 (C_γ-3,−5), 92.8 (CH_2**C**≡C), 90.7 (C≡**C**Ar$_\gamma$), 88.2 (Ar$_\beta$**C**≡C), 83.4 (**C**≡CH), 80.2 (CH_2C≡**C**), 78.4 (C≡**C**H), 68.1 (ArO**C**H$_2$), 61.3 (CO_2**C**H$_2$), 29.5−28.6 (7 signals), 26.0 and 19.5 (CH_2), 14.3 (CH_3); elemental analysis (%) calcd for $C_{159}H_{154}O_{11}$ (2240.970): C 85.22, H 6.93; found C 85.09, H 7.08.

Carbonate 7b.[26] As described for carbonate **7a**, carbonate **7b** (918 mg, 87%) was obtained starting from NaH (60% dispersion in mineral oil, 28.8 mg, 0.720 mmol) in THF (17 mL), ring precursor **1b** (1.0398 g, 0.7200 mmol), and triphosgene (35.7 mg, 0.120 mmol). For extraction a mixture of diethyl ether, CH_2Cl_2 and THF was used because of the product's low solubility in diethyl ether. In contrast to carbonate **7a**, carbonate **7b** was eluted with petroleum ether/CH_2Cl_2 1:3. mp: 64.8−66.1 °C; ^{1}H NMR: δ = 7.87 (s, 4 H, H_α), 7.57 (half of AA′XX′, 8 H, H_γ-2,−6), 7.38 and 7.32 (AA′XX′, 8 H each, H_δ), 7.38 and 7.29 (broadened AA′XX′, 8 H each, H_β), 6.89 (half of AA′XX′, 8 H, H_γ-3,−5), 4.33 (q, J = 7.1 Hz, 4 H, CO_2CH_2), 3.98 (t, J = 6.6 Hz, 8 H, ArOC**H**$_2$), 3.12 (s, 4 H, C≡CH), 2.39 (t, J = 7.0 Hz, 8 H, CH_2C≡C), 1.80 (m, 8 H, OCH_2C**H**$_2$), 1.59 (m, 8 H, C**H**$_2$$CH_2$C≡C), 1.31 (t, J = 7.1 Hz, 6 H, CH_3), 1.5−1.2 (m, 152 H, CH_2); ^{13}C NMR: δ = 165.3 (CO_2), 159.3 (C_γ-4), 147.6 (CO_3), 147.1 (C_α-4), 135.6, 135.3 (C_α-3,−5, C_β-1), 133.2 (C_γ-2,−6), 131.9 (CH_δ), 131.72 (C_α-2,−6), 131.66 (slightly broadened, C_β-3,−5), 131.4 (CH_δ), 129.2 (C_α-1), 128.6 (slightly broadened, C_β-2,−6), 124.7 (C_δ-1 or C_δ-4), 123.3 (C_β-4), 121.0, (C_δ-4 or C_δ-1), 115.3 (C_γ-1), 114.6 (C_γ-3,−5), 92.8 (CH_2**C**≡C), 90.8 (C≡**C**Ar$_\gamma$), 88.3 (Ar$_\beta$**C**≡C), 83.4 (**C**≡CH), 80.1 (CH_2C≡**C**), 78.4 (C≡**C**H), 68.1 (ArO**C**H$_2$), 61.3 (CO_2**C**H$_2$), 29.7−28.6 (8 signals), 26.1 and 19.5 (CH_2), 14.3 (CH_3); elemental analysis (%) calcd for $C_{207}H_{250}O_{11}$ (2914.266): C 85.31, H 8.65; found C 85.31, H 8.63.

Carbonate 7c.[26] To a suspension of NaH (60% dispersion in mineral oil, 6.0 mg, 0.150 mmol) in THF (7 mL) was added ring precursor **1c** (351.9 mg, 0.148 mmol) as a solid. The turbid intensively yellow mixture was heated slightly to give a nearly clear solution. At room temperature, solid triphosgene (7.3 mg, 0.025 mmol) was added upon which the color disappeared abruptly. Because after 5 h only a trace of carbonate (ca. 7%, determined by ^{1}H NMR spectroscopy of a small sample) had been formed, DMAP (47 mg, 0.38 mmol) was added. Immediately, a colorless solid precipitated. One hour later, TLC (petroleum ether/CH_2Cl_2 1:1) revealed a nearly quantitative conversion. Therefore, to the reaction mixture, 5 N HCl (2 mL) and then water were added. The newly formed colorless precipitate was isolated, washed with 5N HCl, water, and finally with ethanol. Flash chromatography (petroleum ether/CH_2Cl_2 3:2 to elute residual ring precursor **1c**, then 1:1 → 1:1.2 to elute the product) gave carbonate **7c** (277 mg, 78%) as a colorless solid. mp determined with DSC: 57.4 °C; ^{1}H NMR: δ = 7.86 (s, 4 H, H_α), 7.56 (half of AA′XX′, 8 H, H_γ-2,−6), 7.38 and 7.31 (AA′XX′, 8 H each, H_ϵ), 7.38 and 7.28 (AA′XX′, 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_2C**H**$_2$), 3.98 (t, J = 6.5 Hz, 8 H, Ar$_\gamma$OC**H**$_2$), 3.70 (t, J = 6.6 Hz, 8 H, Ar$_\delta$OC**H**$_2$), 3.11 (s, 4 H, C≡CH), 2.38 and 2.34 (2 t, J = 7.0 Hz, 8 H each, CH_2C≡C), 2.20 (s, 24 H, ArC**H**$_3$), 1.78 (m, 16 H, OCH_2C**H**$_2$), 1.55 (m, 16 H, C**H**$_2$$CH_2$C≡C), 1.31 (t, J = 7.2 Hz, 6 H, CH_2C**H**$_3$), 1.5−1.2 (m, 304 H, CH_2); ^{13}C NMR: δ = 165.3 (CO_2), 159.3 (C_γ-4), 155.8 (C_δ-4), 147.6 (CO_3), 147.1 (C_α-4), 135.6, 135.3 (C_α-3,−5, C_β-1), 133.2 (C_γ-2,−6), 131.94, 131.89 (CH_ϵ, CH_δ), 131.73 (C_α-2,−6), 131.67 (broadened, C_β-3,−5), 131.4 (CH_ϵ), 130.9 (C_δ-3,−5) 129.2 (C_α-1), 128.6 (broadened, C_β-2,−6) 124.7 (C_ϵ-1 or C_ϵ-4), 123.3 (C_β-4), 121.0 (C_ϵ-4 or C_ϵ-1), 119.0 (C_δ-1), 115.3 (C_γ-1), 114.6 (C_γ-3,−5), 92.8 (CH_2**C**≡CAr$_\epsilon$), 90.7 (C≡**C**Ar$_\gamma$), 89.0 (CH_2**C**≡CAr$_\delta$), 88.2 (Ar$_\beta$**C**≡C), 83.4 (**C**≡CH), 80.3 and 80.1 (CH_2C≡**C**), 78.3 (C≡**C**H), 72.4 (Ar$_\delta$O**C**H$_2$), 68.1 (Ar$_\gamma$O**C**H$_2$), 61.3 (CO_2**C**H$_2$), 30.4−28.6 (13 signals), 26.1, 26.0, 19.5, and 19.4 (CH_2), 16.1 (Ar**C**H$_3$), 14.3 (CH_2**C**H$_3$); elemental analysis (%) calcd for $C_{339}H_{466}O_{15}$ (4781.442): C 85.16, H 9.82; found C 85.30, H 9.85.

Cyclization of Carbonate 7a. A suspension of CuCl (6.44 g, 65.1 mmol) and $CuCl_2$ (1.11 g, 8.26 mmol) in pyridine[27] was stirred at 50 °C for 30 min to dissolve most of the copper salts. After the solution had reached room temperature, a solution of carbonate **7a** (600 mg, 0.27 mmol) in pyridine (113 mL) was added over 63 h using a syringe pump. After the reaction mixture was stirred for an additional 24 h, pyridine was removed (45 °C bath temperature, 10 mbar) and the residue was suspended in CH_2Cl_2. The suspension was cooled (ice bath) and cold 5N HCl was added. The aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with 2−5N HCl and dried ($MgSO_4$). The solvent was removed under reduced pressure. Flash chromatography (petroleum ether/CH_2Cl_2 1/4 v/v; R_f = 0.73) gave a mixture of **8a**, **4a**, and **5a** (525 mg, 88%) as a slightly yellow solid. ^{1}H NMR (Only the signals of **8a** are listed.): δ = 7.87 (s, 4 H, H_α), 7.56 (half of AA′XX′, 8 H, H_γ-2,−6), 7.39 and 7.30 (AA′XX′, 8 H each, H_δ), beneath the latter mentioned AA′XX′ system broadened signals of H_β (16 H) appear, 6.90 (half of AA′XX′, 8 H, H_γ-3,−5), 4.31 (q, J = 7.1 Hz, 4 H, CO_2CH_2), 3.99 (t, J = 6.5 Hz, 8 H, ArOC**H**$_2$), 2.41 (t, J = 6.3 Hz, 8 H, CH_2C≡C), 1.77 (m, 8 H, OCH_2C**H**$_2$), 1.57 (m, 8 H, C**H**$_2$$CH_2$C≡C), 1.5−1.2 (m, 62 H, CH_2, CH_3); ^{13}C NMR: δ = 165.3 (CO_2), 159.3 (C_γ-4), 147.1 (C_α-4), 147.0 (CO_3), 135.7, 135.2 (broad) (C_α-3,−5, C_β-1), 133.1 (C_γ-2,−6), 132.2 (CH_δ), 131.7 (C_α-2,−6), 131.6 (broad, C_β-3,−5), 131.5 (CH_δ), 129.1 (C_α-1), 128.7 (broad, C_β-2,−6), 125.2 (C_δ-1 or C_δ-4), 123.2 (C_β-4), 120.6 (C_δ-4 or C_δ-1), 115.2 (C_γ-1), 114.7 (C_γ-3,−5), 93.6 (CH_2**C**≡C), 90.7 (C≡**C**Ar$_\gamma$), 88.2 (Ar$_\beta$**C**≡C), 82.1 (**C**≡C−C≡**C**), 80.7 (CH_2C≡**C**), 75.2 (C≡**C**−**C**≡C), 68.0 (ArO**C**H$_2$), 61.3 (CO_2**C**H$_2$), 29.4−28.0 (7 signals), 25.9, and 19.4 (CH_2), 14.3 (CH_3); $C_{159}H_{150}O_{11}$ (2236.938): FD-MS: m/z = 2235.6 (100%, M^+), 1492.0 (17%), 1118.0 (75%, M^{2+}).

Cyclization of Carbonate 7b. A suspension of CuCl (6.44 g, 65.1 mmol) and $CuCl_2$ (1.11 g, 8.26 mmol) in pyridine[27] was stirred at 50 °C for 30 min to dissolve most of the copper salts. After the solution had reached room temperature, a solution of carbonate **7b** (220 mg, 0.08 mmol) in 1,2-dichlorobenzene (32 mL) was added over 18 h using a syringe pump. The reaction mixture was stirred for additional 26 h. Workup as described for the preparation of dimer precursor **8a** gave a solution of the products 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 (5 mL). This solution was added dropwise to ethanol (80 mL) and the very fine, colorless precipitate was isolated. Chromatography (chromatotron plate with silica gel, petroleum ether/CH_2Cl_2 1:1 v/v) gave a mixture of **8b**, **4b**, and **5b** (178 mg, 81%) as a colorless solid. ^{1}H NMR (Only signals of main product **8b** are listed.): δ = 7.86 (s, 4 H, H_α), 7.56 (half of AA′XX′, 8 H, H_γ-2,−6), 7.40 (half of AA′XX′, 8 H, H_δ), 7.37 (half of AA′XX′, broadened, 8 H, H_β), 7.31 (half of AA′XX′, 8 H, H_δ), 7.28 (half of AA′XX′, broadened, 8 H, H_β), 6.88 (half of AA′XX′, 8 H, H_γ-3,−5), 4.31 (q, J = 7.2 Hz, 4 H, CO_2CH_2), 3.97 (t, J = 6.5 Hz, 8 H, ArOC**H**$_2$), 2.40 (t, J = 6.6 Hz, 8 H, CH_2C≡C), 1.79 (m, 8 H, OCH_2C**H**$_2$), 1.56 (m, 8 H, C**H**$_2$$CH_2$C≡C), 1.30 (t, J = 7.2 Hz, 6 H, CH_3), 1.5−1.2

(27) In analogy to O'Krongly, D.; Denmeade, S. R.; Chiang, M. Y.; Breslow, R. *J. Am. Chem. Soc.* **1985**, *107*, 5544. Rigorous exclusion of oxygen turned out to slow the reaction. Therefore, solvents were not degassed. The same finding was reported by Dietrich-Buchecker, C. O.; Khemiss, A.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1986**, 1376.

(m, 152 H, CH_2). ^{13}C NMR: δ = 165.3 (CO_2), 159.3 (C_γ-4), 147.5 (CO_3), 147.1 (C_α-4), 135.6, 135.4 (C_α-3,−5, C_β-1), 133.2 (C_γ-2,−6), 132.3 (CH_δ), 131.67 (with shoulder at 131.72 ppm, broad, C_β-3,−5 and C_α-2,−6), 131.5 (CH_δ), 129.2 (C_α-1), 128.6 (broad, C_β-2,−6), 125.2 (C_δ-1 or C_δ-4), 123.2 (C_β-4), 120.6 (C_δ-4 or C_δ-1), 115.3 (C_γ-1), 114.7 (C_γ-3,−5), 93.6 (CH_2**C**≡CAr_δ), 90.8 (C≡**C**Ar_γ), 88.3 (Ar_β**C**≡C), 82.0 (**C**≡C−C≡**C**), 80.4 (CH_2C≡**C**), 75.2 (C≡**C**−**C**≡C), 68.1 (ArO**C**H_2), 61.3 (CO_2**C**H_2), 29.6−28.3 (8 signals), 26.0, and 19.4 (CH_2), 14.3 (CH_3); $C_{207}H_{246}O_{11}$ (2910.234): FD-MS: *m*/*z* = 2912.5 (9%, M^+), 1455.7 (100%, M^{2+}), 970.5 (6%, M^{3+}), 727.5 (3%, M^{4+}).

Cyclization of Carbonate 7c. A suspension of CuCl (6.44 g, 65.1 mmol) and $CuCl_2$ (1.11 g, 8.26 mmol) in pyridine[27] was stirred at 50 °C for 30 min to dissolve most of the copper salts. After the solution had reached room temperature, a solution of carbonate **7c** (200 mg, 0.04 mmol) in 1,2-dichlorobenzene (18 mL) was added over 10 h using a syringe pump. The reaction mixture was stirred for additional 28 h. Workup as described for the preparation of dimer precursor **8b** followed by chromatography (chromatotron plate with silica gel, petroleum ether/CH_2Cl_2 1:1 v/v) gave a mixture of **8c**, **4c**, and **5c** (164 mg, 82%) as a colorless solid. ^1H NMR (Only signals of main product **8c** are listed.): 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), 7.37 and 7.28 (AA′XX′, 8 H each, H_β), 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), 3.97 (t, *J* = 6.5 Hz, 8 H, Ar_γOC**H**$_2$), 3.70 (t, *J* = 6.6 Hz, 8 H, Ar_δOC**H**$_2$), 2.39 and 2.34 (2 t, *J* = 6.8 Hz, 8 H each, CH_2C≡C), 2.20 (s, 24 H, ArC**H**$_3$), 1.77 (m, 16 H, OCH_2C**H**$_2$), 1.55 (m, 16 H, C**H**$_2CH_2C$≡C), 1.30 (t, *J* = 7.0 Hz, 6 H, CH_2C**H**$_3$), 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), 135.5, 135.3 (C_β-1, C_α-3,−5), 133.2 (C_γ-2,−6), 132.2 (CH_ϵ), 131.9 (CH_δ), 131.66 (broadened, with shoulder at 131.71 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), 119.0 (C_δ-1), 115.3 (C_γ-1), 114.6 (C_γ-3,−5), 93.6 (CH_2**C**≡CAr_ϵ), 90.8 (C≡**C**Ar_γ), 89.0 (CH_2**C**≡CAr_δ), 88.3 (Ar_β**C**≡C), 81.9 (**C**≡C−C≡**C**), 80.4 and 80.3 (CH_2C≡**C**), 75.2 (C≡**C**-**C**≡C), 72.4 (Ar_δO**C**H_2), 68.1 (Ar_γO**C**H_2), 61.3 (CO_2**C**H_2), 30.3−28.5 (16 signals), 26.07, 26.05, 26.01, 19.5, and 19.4 (CH_2), 16.1 (Ar**C**H_3), 14.3 (CH_2**C**H_3); $C_{339}H_{462}O_{15}$ (4777.410): MALDI-TOF (dithranol, KO_2CCF_3): *m*/*z* = 4778 (6%, M^+), 4816 (30%), $[M+K]^+$), 4885.3 (6%, $[M+Ag]^+$).

Dimer 9a. To the mixture of **8a**, **4a**, and **5a** (476 mg, 0.21 mmol) dissolved in THF (5 mL) was added 1M ^{n}Bu$_4$NF in THF (2.2 mL, 2.2 mmol). After stirring, the reaction mixture at 50 °C for 18 h, 2N HCl (1.3 mL) and ethanol (50 mL) were added successively. The precipitate (450 mg) was isolated, washed with ethanol and dried. Flash chromatography (petroleum ether/CH_2Cl_2 1/2 v/v) of a part of this mixture (381 mg) gave as a first fraction (11 mg) ring **2a** and dimer **9a**, as a second fraction dimer **9a** (100 mg) and as a third fraction catenane **6a** and dimer **9a** (47 mg). Due to the low solubility, a part of the dimer stayed at the top of the column. Therefore, the silica gel was extracted with warm $CHCl_3$ after having eluted ring **2a** and catenane **6a**. This extraction gave additional dimer **9a** (192 mg) as an off-white solid. The whole yield of dimer sums up to 292 mg (74%; This yield was calculated taking into account that only 85% of the crude material was separated by chromatography.) mp: 280 °C (decomposition). ^1H NMR: δ = 7.98 (s, 4 H, H_α), 7.60 and 7.52 (AA′XX′, 8 H each, H_β), 7.46 (half of AA′XX′, 8 H, H_γ-2,−6), 7.40 and 7.31 (AA′XX′, 8 H each, H_δ), 6.86 (half of AA′XX′, 8 H, H_γ-3,−5), 5.74 (s, 2H, OH), 4.36 (q, *J* = 7.1 Hz, 4 H, CO_2CH_2), 3.95 (t, *J* = 6.5 Hz, 8 H, ArOC**H**$_2$), 2.39 (t, *J* = 6.9 Hz, 8 H, CH_2C≡C), 1.76 (m, 8 H, OCH_2C**H**$_2$), 1.57 (m, 8 H, C**H**$_2CH_2C$≡C), 1.37 (t, *J* = 7.1 Hz, 6 H, CH_3), 1.5−1.2 (m, 56 H, CH_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), 132.3 (CH_δ), 132.0 (C_β-3,−5), 131.5 (CH_δ and 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), 114.9 (C_γ-1), 114.6 (C_γ-3,−5), 93.6 (CH_2**C**≡C), 90.6 (C≡**C**Ar_γ), 87.6 (Ar_β**C**≡C), 82.0 (**C**≡C−C≡**C**), 80.3 (CH_2C≡**C**), 75.2 (C≡**C**−**C**≡C), 68.1 (ArO**C**H_2), 60.9 (CO_2**C**H_2), 29.4−28.5 (7 signals), 25.9, and 19.5 (CH_2), 14.4 (CH_3); elemental analysis (%) calcd for $C_{158}H_{152}O_{10}$ (2210.944): C 85.83, H 6.93; found C 85.98, H 6.94; FD-MS: *m*/*z* = 2209.1 (100%, M^+), 1106.8 (83%, M^{2+}), 736.5 (22%, M^{3+}).

Dimer 9b. As described for the preparation of dimer **9a**, a mixture (257 mg) of dimer **9b**, catenane **6b** and ring **2b** was obtained starting from a mixture of **8b**, **4b**, and **5b** (279 mg, 0.1 mmol) in THF (4.4 mL) and 1 M ^{n}Bu$_4$NF (1 mL) in THF. Flash chromatography (petroleum ether/CH_2Cl_2 1:1 → 1:2 v/v) of a part of this mixture (224 mg) gave as a first fraction (11 mg) ring **2b**, as a second fraction dimer **9b** (52 mg) and as a third fraction catenane **6b** and dimer **9b** (51 mg). Due to the low solubility a part of the dimer stayed at the top of the column. Therefore, the silica gel was extracted with warm $CHCl_3$ after having eluted ring **2b** and catenane **6b**. This extraction gave additional dimer **9b** (105 mg) as an off-white solid. The whole yield of dimer **9b** sums up to 157 mg (65%; This yield was calculated taking into account that only 87% of the crude material was separated by chromatography.) In another experiment starting from a mixture (120 mg) of **8b**, **4b**, and **5b** the dimer **9b** (58 mg, 49%) was isolated by recrystallization from CH_2Cl_2 (3 mL, the material was not completely dissolved). mp determined with DSC: 202 °C; ^1H NMR: δ = 7.98 (s, 4 H, H_α), 7.61 and 7.52 (AA′XX′, 8 H each, 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_δ), 6.85 (half of AA′XX′, 8 H, H_γ-3,−5), 5.75 (s, 2 H, OH), 4.36 (q, *J* = 7.1 Hz, 4 H, CO_2CH_2), 3.95 (t, *J* = 6.5 Hz, 8 H, ArOC**H**$_2$), 2.38 (t, *J* = 7.0 Hz, 8 H, C**H**$_2$C≡C), 1.77 (m, 8 H, OCH_2C**H**$_2$), 1.57 (m, 8 H, C**H**$_2CH_2C$≡C), 1.37 (t, *J* = 7.1 Hz, 6 H, C**H**$_3$), 1.5−1.2 (m, 152 H, C**H**$_2$); ^{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), 132.3 (CH_δ), 132.0 (C_β-3,−5), 131.5 (CH_δ and 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), 114.9 (C_γ-1), 114.6 (C_γ-3,−5), 93.6 (CH_2**C**≡C), 90.6 (C≡**C**Ar_γ), 87.6 (Ar_β**C**≡C), 82.0 (**C**≡C−C≡**C**), 80.3 (CH_2C≡**C**), 75.2 (C≡**C**-**C**≡C), 68.1 (ArO**C**H_2), 60.9 (CO_2**C**H_2), 29.6−28.6 (9 signals), 26.0, and 19.5 (CH_2), 14.4 (CH_3); elemental analysis (%) calcd for $C_{206}H_{248}O_{10}$ (2884.240): C 85.79, H 8.67; found C 85.72, H 8.68; MALDI-TOF (dithranol, KO_2CCF_3): *m*/*z* = 2884 (13%, M^+), 2923 (60%, $[M+K]^+$), 2961 (15%, $[M+2K]^+$).

Dimer 9c. As described for the preparation of dimer **9a**, a mixture of dimer **9c**, catenane **6c**, and ring **2c** was obtained starting from a mixture of **8c**, **4c**, and **5c** (125 mg, 0.03 mmol) in THF (2 mL) and 1 M *n*-Bu$_4$NF (0.6 mL) in THF. Twofold chromatography (chromatotron plate with silica gel, petroleum ether/CH_2Cl_2 4:1 → 2:1 v/v) gave as a first fraction (8 mg) ring **2c**, as a second fraction dimer **9c** (60 mg, 48%) and as a third fraction a mixture of catenane **6c** and dimer **9c** (17 mg). The material showed decomposition after being dissolved in $CDCl_3$ and recovered by removing the solvent in vacuo under mild heating (40 °C). The ^1H NMR spectrum suggests a specific but still unknown reaction at the dimethylphenolic moiety. The same behavior was found with the corresponding ring **2c**. mp determined with DSC: 110.8 °C; ^1H NMR: δ = 7.98 (s, 4 H, H_α), 7.61 and 7.52 (AA′XX′, 8 H each, H_β), 7.46 (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), 6.86 (half of AA′XX′, 8 H, H_γ-3,−5), 5.75 (s, 2 H, OH), 4.36 (q, *J* = 7.1 Hz, 4 H, CO_2CH_2), 3.95 (t, *J* = 6.5 Hz, 8 H, Ar_γOC**H**$_2$), 3.69 (t, *J* = 6.6 Hz, 8 H, Ar_δOC**H**$_2$), 2.38 and 2.34 (2 t, *J* = 6.9 Hz, 8 H each, CH_2C≡C), 2.20 (s, 24 H, ArC**H**$_3$), 1.77 (m, 16 H, OCH_2C**H**$_2$), 1.54 (m, 16 H, C**H**$_2CH_2C$≡C), 1.37 (t, *J* = 7.1 Hz, 6 H, CH_2C**H**$_3$), 1.5−1.2 (m, 304 H, CH_2); ^{13}C NMR: δ = 166.1 (**C**O_2), 159.3 (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), 131.9 (C_β-3,−5, CH_δ), 131.5 (C_α-2,−6, CH_ϵ), 130.9 (C_δ-3,−5), 129.2 (C_β-2,−6), 128.3

(C_α-3,−5), 125.2 (C_ϵ-1 or C_ϵ-4), 123.6 (C_β-4), 123.3 (C_α-1), 120.6 (C_ϵ-4 or C_ϵ-1), 119.0 (C_δ-1), 114.9 (C_γ-1), 114.6 (C_γ-3,−5), 93.6 (CH_2**C**≡CAr$_\epsilon$), 90.6 (C≡**C**Ar$_\gamma$), 89.0 (CH_2**C**≡CAr$_\delta$), 87.6 (Ar$_\beta$**C**≡C), 81.9 (**C**≡C−C≡**C**), 80.4 and 80.2 (CH_2C≡**C**), 75.2 (C≡**C**−**C**≡C), 72.4 (Ar$_\delta$O**C**H_2), 68.1 (Ar$_\gamma$O**C**H_2), 60.9 (CO_2**C**H_2), 30.4−28.6 (10 signals), 26.1, 26.0, 19.5, and 19.4 (CH_2), 16.1 (Ar**C**H_3), 14.4 (CH_2**C**H_3); $C_{338}H_{464}O_{14}$ (4751.416): MALDI-TOF (dithranol, KO_2CCF_3): *m*/*z* = 4752 (10%, M^+), 4791 46%, $[M+K]^+$), 4830 (19%, $[M+2K]^+$), 4869 (6%, $[M+3K]^+$).

Acknowledgment. We thank A. Beer and J. Thiel for assistance in the laboratory, S. Seywald for SEC measurements, and B. Ederer for support when writing the manuscript.

Supporting Information Available: H^1NMR spectrum of dimer **9c** (CDCl3, room temperature, 300 MHz). This material is available free of charge via the Internet at http://pubs.acs.org.

JA034147C