Poly[2]catenanes and Cyclic Oligo[2]catenanes Containing Alternating Topological and Covalent Bonds: Synthesis and Characterization

Jean-Luc Weidmann,[a] Jean-Marc Kern,*[a] Jean-Pierre Sauvage,*[a] Dirk Muscat,[b] Susan Mullins,[b] Werner Köhler,[b, c] Christine Rosenauer,[b] Hans Joachim Räder,[b] Kai Martin,[b] and Yves Geerts*[b, d]

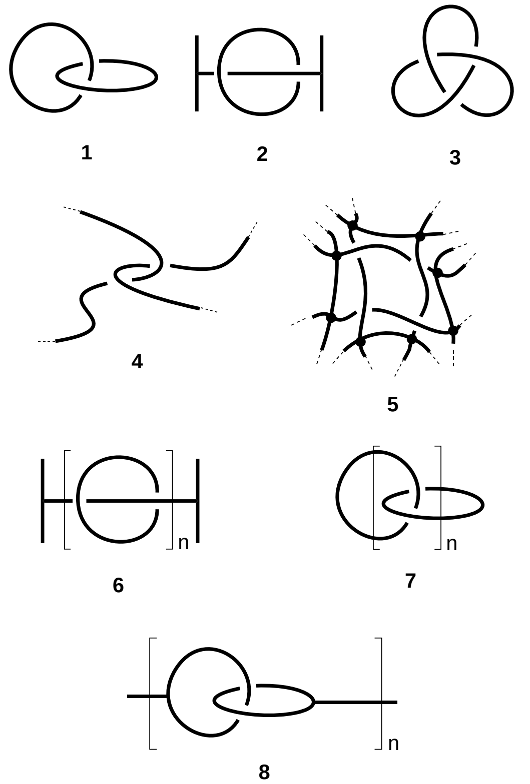
Abstract: Large bifunctionalized catenate and catenand, composed of macrocycles containing 45 atoms, have been synthesized and copolymerized with a terephthalic acid derivative to afford a cyclic oligo[2]catenand and a linear poly[2]catenate. Poly[2]catenand was obtained by demetalation of poly[2]catenate. The molecular weight distribution of these polymers, which are composed of alternating topological and covalent bonds, has been characterized by gel permeation chromatography (GPC) with universal calibration, viscometry, and MALDI-TOF mass spectrometry. We were able to synthesize a poly[2]catenate and a poly[2]catenand with a degree of polymerization (DP) equal to 8–9. In addition, an upper value of the Kuhn segment length of poly[2]catenand has been determined and is discussed in the light of its structure.

Keywords: catenanes · copper · polycondensations · structure elucidation · supramolecular chemistry

Introduction

In the course of the last fifteen years, intense research efforts have been devoted to the synthesis and characterization of topologically and structurally appealing molecules, such as catenanes **1**, rotaxanes **2**, and knots **3**[1] (Scheme 1). All these types of molecules contain defined topological or mechanical bonds between some of their subunits, without the involvement of covalent bonds.[2]

Conversely, entanglements that take place between polymer chains in the solid state and in concentrated solutions result from the statistical behavior of macromolecules and are not defined at the molecular level. Therefore, the schematic drawing of an entanglement **4**, shown in Scheme 1, certainly oversimplifies a complex reality since entanglements are



Scheme 1. Schematic drawings of topological bonds that occur in molecular and macromolecular systems: [2]catenane **1**, rotaxane **2**, trefoil molecular knot **3**, entanglement **4**, interpenetrating polymer network **5**, polyrotaxane **6**, polycatenane **7**, and poly[2]catenane **8**.

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[a] Dr. J.-M. Kern, Dr. J.-P. Sauvage, Dr. J.-L. Weidmann
Laboratoire de Chimie Organo-Minérale, UMR 7513 CNRS Faculté de Chimie, Université Louis Pasteur
4, rue Blaise Pascal, F-67000 Strasbourg (France)
Fax: (+33)3-88-41-61-30
E-mail: sauvage@chimie.u-strasbg.fr

[b] Dr. Y. Geerts,[+] Dr. D. Muscat, Dr. S. Mullins, Dr. W. Köhler,[++]
Dr. C. Rosenauer, Dr. H. J. Räder, Dr. K. Martin
Max-Planck-Institute for Polymer Research
Ackermannweg 10, D-55128 Mainz (Germany)

[+] Present address: Université Libre de Bruxelles, Laboratoire de Chimie Macromoléculaire, CP 206/1
Boulevard du Triomphe, B-1050 Bruxelles (Belgium)

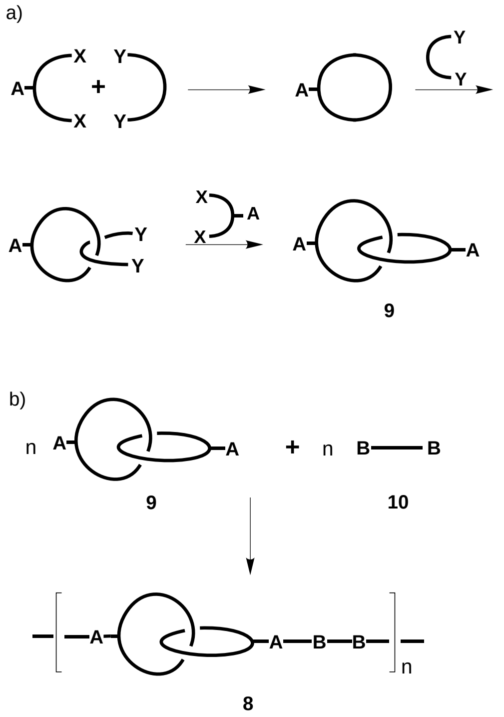
[++] Present address: Physikalisches Institut Universität Bayreuth
D-95440 Bayreuth (Germany)

nonlocalized and dynamic in nature. However, they play a central role in polymer physics and must be considered to govern the mechanical properties,[3a] the rheology,[3b] and the dynamics[4] of the polymers. A closely related example of a complex system that results from nondefined topological bonds is given by interpenetrating polymer networks **5** which are composed of two independent networks that are mechanically connected to each other by mutual interpenetration.[5]

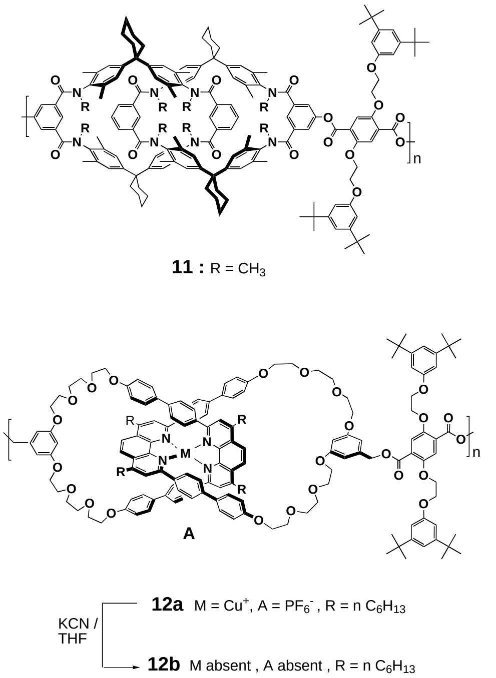
Only a limited number of macromolecular architectures contain defined topological bonds, namely, polyrotaxanes **6**,[6] polycatenanes **7**, and poly[2]catenanes **8**.[7] In the case of polyrotaxanes, the topological bonds occur between the polymer chain and the macrocycles. Consequently, the properties of polyrotaxanes, although strictly different from those of their individual components, deviate only partially from the main stream of polymer properties. In particular, the rupture of a single topological bond will not substantially affect the macromolecular structure of the polyrotaxane backbone. Polycatenanes **7** and poly[2]catenanes **8** are structurally different from polyrotaxanes **6** since they contain topological bonds in the main chain, and breaking one or several topological bonds will result in the degradation of the polymer. Clearly, the interest in polycatenanes and poly[2]-catenanes goes beyond their structures, since catenane units contain new elements of mobility which result from the free rotational and elongational motions of one macrocycle within the other. To date, there have been no reports of any polymers that contain such molecular knee-joints. Thus, the dynamics and viscoelastic properties of polycatenanes and poly[2]catenanes are anticipated to deviate strongly from those of more conventional polymer architectures. Specifically, it is anticipated that poly[2]catenanes will exhibit unusual viscoelastic properties, for example, a very large loss modulus, low activation energy for viscous flow, and rapid stress relaxation as a consequence of the presence of the mobility elements contained in the catenane units.

Several attempts towards the daunting synthetic challenge of high molecular weight polycatenanes have been made in the past.[1c, 7] However, the lack of efficient characterization methods, combined with nonselective synthetic strategies resulted in intractable and ill-characterized materials.[8] An outstanding forerunner of a real polycatenane is the olympiadane of Stoddart et al.; this is an oligocatenane of exact molecular weight and is composed of five repeat units.[9]

The synthesis of poly[2]catenanes **8** that contain alternating topological and covalent bonds does not encounter any conceptual difficulties since they can be made according to the general pathway presented in Scheme 2.[7] The synthesis involves the preformation of a difunctionalized catenane **9** and its subsequent copolymerization with a spacer **10**. Hitherto, only a limited number of poly[2]catenanes have appeared in the literature.[10–12]



Scheme 2. Synthetic strategy leading to poly[2]catenane **8**.



Scheme 3. Previously reported poly[2]catenane **11** and poly[2]catenate **12a** and poly[2]catenand **12b**.[10, 11] Poly[2]catenand **12b** is obtained by demetalation of **12a** (KCN, THF, room temperature).

Some of us have already reported the synthesis of the poly[2]catenate **12a** and the poly[2]catenand **12b**, (a catenate is a complex whose ligands consist of interlocking rings, whereas catenand is a free ligand) based on a highly mobile catenane that contains very large macrocycles of 45 atoms (Scheme 3).[11] More recently, some of us synthesized the poly[2]catenane **11** based on a highly rigid amide-type catenane that comprises macrocycles of only 32 atoms.[10] In the case of poly[2]catenane **11**, the relative motions of the macrocycles of the catenane units are frozen due to the presence of the methyl groups on the amide functions. Characteristically, poly[2]catenane **11** and poly[2]catenand **12b** represent two extreme situations where the mobility contained in the catenane units varies importantly. In

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particular, it is anticipated that the comparison of poly[2]catenane **11** with poly[2]catenand **12** will make evident the unusual viscoelastic properties expected from the presence of catenane units in the polymer backbone.

Here, we describe the detailed synthesis of poly[2]catenate **12a** and poly[2]catenand **12b** and the comprehensive investigation of their macromolecular characteristics. This work is intended to pave the way for the production of large amounts of well-characterized poly[2]catenanes for physical studies and represents the first step of a general research program, aimed at the fundamental study of the unusual viscoelastic properties and dynamics resulting from the introduction of topological bonds into a polymer main chain.

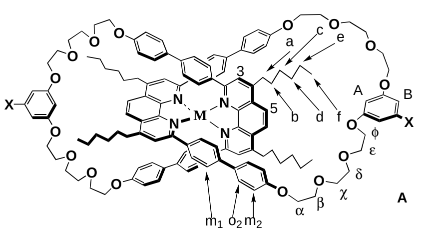
Results and Discussion

Design and synthesis of the polymer precursors: The three-dimensional template effect of copper(I) ions, introduced by some of us 15 years ago, made catenanes and related systems reasonably accessible from a preparative viewpoint.[13] The strategy, based on a precursor that consists of two phenanthroline-type ligands entwined around a copper(I) center, allows the preparation of gram-quantities of the interlocking ring systems in a few steps.

The original [2]catenane that contains two thirty-membered rings could not be used in the frame of the work described in the present report because: i) the appropriate functional groups had to be introduced at the correct positions, that is in an antipodal arrangement with respect to one another and ii) the size of the interlocking rings had to be increased.

The difunctionalized copper [2]catenate **13a** is based on two identical interlocking macrocycles with 2,9-diaryl-1,10-phenanthroline moieties coordinated to the metal center in a tetrahedral geometry. In order to ensure pronounced mobility of the demetalated system (the poly[2]catenand), these macrocycles were designed so as to be rigid and large. The rigidity requirement was satisfied by substituting the 2,9-positions of the phenanthroline core with *p*-biphenyl nuclei. These are linked through their *p'*-positions to a 5-functionalized (hydroxymethyl) resorcinol by triethyleneglycol chains. The resulting macrocycles are thus 45-membered rings (Scheme 4). Since the solubility of polymeric materials is an essential condition for their physicochemical characterization, lipophilic groups (*n*-hexyl chains) were introduced on the 4 and 7 positions of the phenanthroline core,[14] so as to counterbalance the effects of 1,10-phenanthroline and biphenyl units.

The principle of the synthesis of the coordinating interlocking molecules is based on the elaboration of a highly preassembled system and on the generalized three-dimensional template effect mentioned above.[13] In our case, the catenate precursor is the threaded precursor [Cu(**15**·**16**)]$^+$ (Scheme 5), which is obtained quantitatively by threading 4,7-di-(*n*-hexyl)-2,9-di-[4'-(*p*-hydroxyphenyl)phenyl]-1,10-phenanthroline (**16**) through the macrocycle **15** by the use of [Cu(CH_3CN)$_4$$PF_6$] as the template agent.

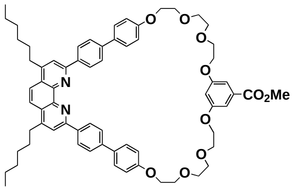


13a M = Cu^+ X = CH_2OH A = PF_6^-

13b M = nil X = CH_2OH A = nil

14a M = Cu^+ X = CO_2Me A = PF_6^-

14b M = nil X = CO_2Me A = nil



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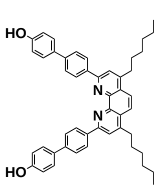

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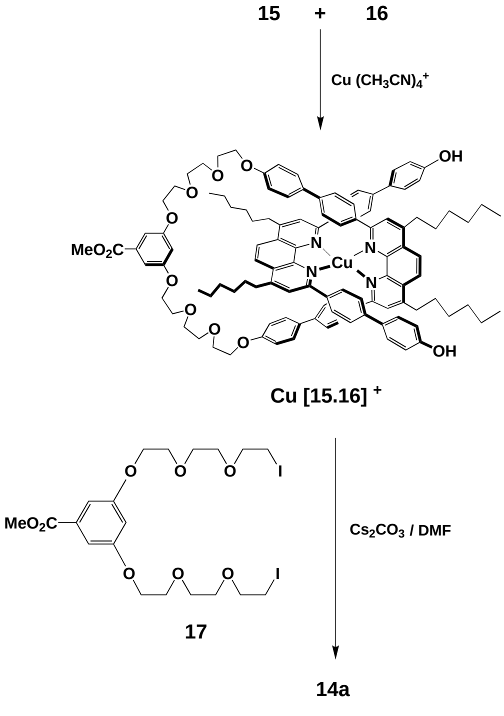
Scheme 4. Catenate monomer **13a**, catenand monomer **13b**, and their synthetic precursors.



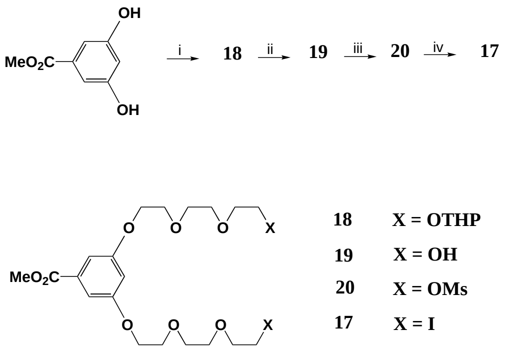
$$\mathbf{14a} \xrightarrow{\text{HDibal}} \mathbf{13a}$$

$$\mathbf{14a} \xrightarrow{CN^-} \mathbf{14b} \xrightarrow{\text{HDibal}} \mathbf{13b}$$

Scheme 5. Synthesis of catenate monomer **13a** and catenand monomer **13b**.

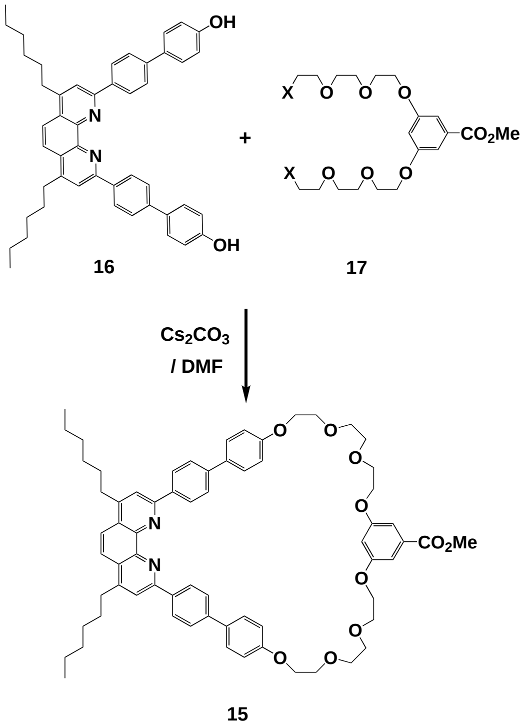
The cyclization of this pseudorotaxane is the key step in the synthesis of the poly[2]catenate precursor **13a**. Under relatively mild reaction conditions, copper [2]catenate **14a** was obtained in 55% yield from the reaction of $[\mathrm{Cu}(\mathbf{15}\cdot\mathbf{16})]^+$ with the dielectrophile **17** in dimethylformamide (DMF) in the presence of Cs_2CO_3 as a base. The bis(hydroxymethyl)-functionalized copper [2]catenate **13a** was then obtained by the reduction of **14a** with diisobutylaluminum hydride (HDibal). Catenand **13b** was prepared by demetalation of **13a** to give **14b**, followed by reduction of the ester groups using HDibal again, in tetrahydrofuran.

The synthesis of the diphenolic compound **16** is described elsewhere.[15] The dielectrophile **17** was prepared in the following manner (Scheme 6): methyl 3,5-dihydroxybenzoate was treated with the OTHP derivative of 2-[2-(2-chloroethoxy)ethoxy]ethanol in a basic medium to afford **18**. Acidic cleavage of **18** led to the dialcohol **19**, which was successively mesylated (compound **20**) and transformed into the diiodo compound **17** by treatment with excess NaI. The synthesis of the macrocycle **15** (Scheme 7) was based on the reaction of the nucleophilic diphenolate derivative of **16** with the dielectrophile **17** under conditions of high dilution (53% yield).

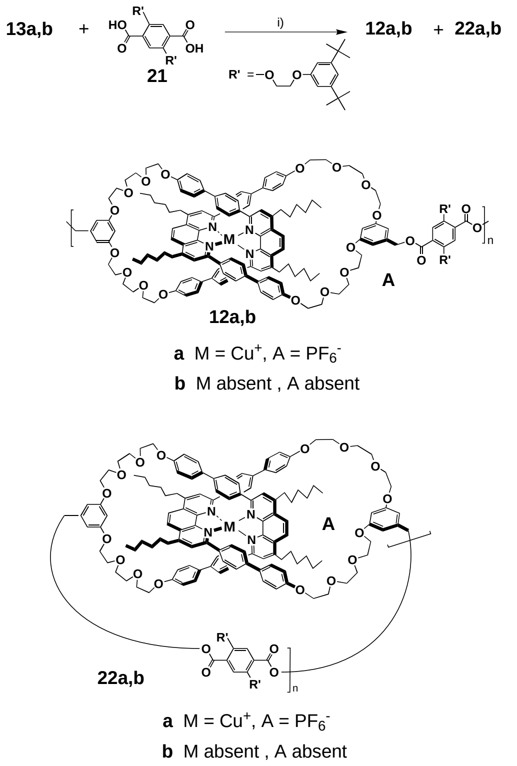


Scheme 6. Synthetic pathway to dielectrophile **17**: i) Cl(-CH_2-CH_2-O)$_3$-THP, NaH, DMF; ii) pyridine·HCl, EtOH; iii) MsCl, Et_3N, CH_2Cl_2; iv) NaI, acetone.

A rigid diacid was designed as a structural unit to connect the catenate or catenand moieties in the polymers. This diacid **21** (see Scheme 8), which is a derivative of terephthalic acid, bears four *tert*-butyl groups in order to provide good solubility for the diacid in the polymerization solvent (dichloromethane) and to contribute to the solubility of the polymers.[10, 11]



Scheme 7. Synthesis of the macrocycle **15**.



Scheme 8. Synthesis of oligo- and poly[2]catenates (**12a**, **22a**) and oligo- and poly[2]catenands (**12b**, **22b**). i) 4-(*N*,*N*′-dimethylamino)pyridine/*p*-toluenesulfonic acid 1:1 complex, *N*,*N*′-diisopropylcarbodiimide.

Polymer synthesis and characterization: The copolymerization of catenate **13a** or catenand **13b** with the highly soluble terephthalic spacer **21** was carried out with the polyesterification method of Moore and Stupp (Scheme 8).[10a, 16] This mild polymerization method, which uses *N*,*N*′-diisopropylcarbodiimide as a dehydrating agent and 4-(*N*,*N*′-dimethylamino)pyridinetoluene-*p*-sulfonic acid 1:1 complex as a catalyst, has the advantage of functioning in dichloromethane, a solvent in which catenate **13a** is especially soluble. The polymerization products were soluble in chlorinated solvents, *N*,*N*′-dimethylformamide, and tetrahydrofuran; no insoluble fraction was observed. The purification was carried out by precipitation in a large volume of methanol.

*Cyclic oligo[2]catenand **22 b***: The polymerization of catenand **13b** was conducted for three days at −10 °C, then two days at 0 °C, and finally one day at room temperature to afford the cyclic oligo[2]catenand **22b** in 77 % yield. The structure of the oligo[2]catenand **22b** was elucidated by ^{1}H and ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), and viscometry.

In the ^{1}H NMR spectrum of the polymerization product of catenand **13b**, all peaks were broadened compared to those of the corresponding monomers, as expected for oligomers or polymers. Typical resonances of the terephthalic ester spacer and of the interlocked macrocycles were present and no evidence of ring-opening or dethreading during polymerization was observed. New resonances appeared, namely the benzyl ester protons at $\delta = 5.17$, and no benzyl proton signal at $\delta = 4.43$ for the catenand **13b** was present in the corresponding polymer spectra. Accordingly, the ^{13}C NMR spectra indicated that the characteristic resonance of the carboxyl carbon atom of the acidic moiety at $\delta = 163.8$ was shifted to $\delta = 164.9$ for the ester groups. The absence of end groups can be caused by either high molecular weight poly[2]catenand **12b**, by cyclic oligo[2]catenand **22b**, or by a mixture of both. Evidence for the presence of cyclic oligo[2]catenand **22b** was provided by GPC (Diol columns (Merck), in *N,N'*-dimethylformamide (DMF)) which indicated a number-average molecular weight (M_n) of only 2500. Even if the more compact structure of catenane segments with respect to polystyrene standards is considered, these GPC data show that only oligomers have been obtained. Previously reported GPC data in chloroform[11] overestimated the presence of high molecular weight polymers, namely number-average molecular weight ($M_n = 4.2 \times 10^3$) and weight-average molecular weight ($M_w = 1.8 \times 10^6$). Presumably, as a result of the acidic character of chloroform, protonation of the phenanthrolines of the catenane units leads to the formation of strong dipolar moments on the oligomers which then aggregate by dipole–dipole interactions and, therefore, bias the molecular weight distribution.[17] The viscometry study in DMF indicated that no significant increase in the viscosity was observed, corroborating the conclusions made from the GPC data that only oligomers were reached. Therefore, it is concluded that cyclic oligo[2]catenands **22b** were obtained which explains the absence of end groups evidenced from ^{1}H and ^{13}C NMR spectroscopy.

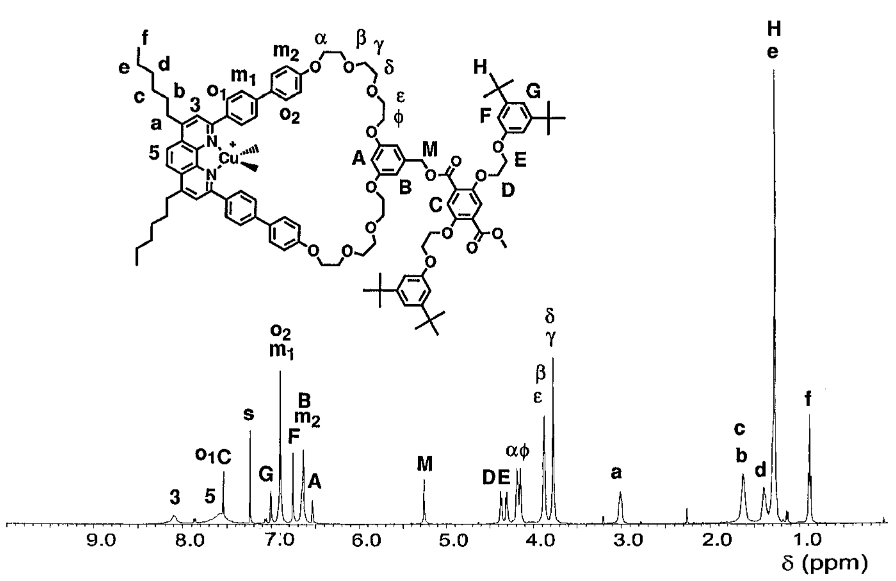


Figure 1. ^{1}H NMR spectrum of poly[2]catenate **12a** in $CDCl_3$ at 500 MHz (s = solvent).

It is easily understandable from the mobility of the macrocycles of the catenand that cyclic oligo[2]catenands **22b** are formed preferentially over linear oligo- and poly[2]catenands **12b**. In the course of the polyesterification reaction, when an oligo[2]catenand carries two complementary end groups, namely, the acid function of the spacer and the alcohol function of the catenand, the mobility of the macrocycles of the catenand units preferentially allows an intramolecular cyclization rather than an intermolecular reaction which would lead to an increase in the molecular weight.[12b] This documents, however, the chemical reactivity of the catenanes, whereby the reactivity of a functional group on a macrocycle is influenced by the presence of another functional group on the other macrocycle.[1e, 18]

*Poly[2]catenate **12 a***: The polymerization of catenate **13a** was carried out at −20 °C for six days to afford the poly[2]catenate **12a** in 94 % yield. The structure was elucidated by ^{1}H and ^{13}C NMR spectroscopy, as well as by matrix-assisted laser-desorption time-of-flight mass spectrometry (MALDI-TOF MS).[19]

The characteristic features of the ^{1}H spectrum of the poly[2]catenate **12a** (Figure 1) are: i) all peaks were broadened compared to their corresponding monomers, as expected for polymers; ii) typical resonances of the interlocked macrocycles of the catenane monomer were present which indicates that no ring opening and dethreading has occurred during the polymerization; iii) resonances attributed to the diacyl moiety were also observed; iv) new resonances appeared, namely benzyl ester protons at $\delta = 5.25$; v) in agreement, ^{13}C NMR spectra indicated that the characteristic resonance of the carboxyl carbons of the acid moieties at $\delta = 163.8$ was shifted to $\delta = 165.0$ characteristic for ester groups. The end-group analysis of the ^{1}H spectrum revealed that a low-intensity resonance at $\delta = 4.63$, attributed to the benzyl protons of catenate end groups was observed. Assuming the equiprobable occurrence of catenate and spacer end groups, integration gives a relative concentration of end groups of 4 %. Since the formation of cyclic and linear oligo- and poly[2]catenates are possible, a reliable average degree-of-polymerization (DP) cannot be derived (see below). The use of Carother's equation, $DP = 1/(1-p)$, which relates DP to the yield p, is meaningless because of the low amount of monomers used for the polymerization and the unavoidable loss of polymer upon precipitation and filtration.

A previous attempt[11] to characterize the molecular weight distribution of poly[2]catenate **12a** by GPC in chloroform gave the values $M_n = 5.5 \times 10^4$ and $M_w = 1.8 \times 10^6$. However, poly[2]catenate **12a** contains one copper(I) complex and the PF_6^- counterion per repeat unit; their presence creates strong dipole moments along the oligomer and polymer chain.[17] It is expected that aggregation as a result of dipolar interactions occurs and leads to an overestimation of the molecular weight distribution. This holds, of course, for other characterization methods in solution, such as light scattering, osmometry, and viscometry, which are all hampered by aggregation.[17] MALDI-TOF MS has the advantage of being insensitive to aggregation phenomena in solution[17] and thus was used to investigate the molecular weight distribution of poly[2]catenate **12a**. Interestingly, signals that correspond to oligo[2]-catenates with $n = 1-4$ were successfully observed. Theoretical masses and experimental values for $n = 1-4$ are presented in Table 1.

Table 1. Theoretical and MALDI-TOF experimental masses of the poly[2]catenate **12a**.[a]

	$n(SC^+)_n \cdot (X^-)_{n-1}$, cyclic **22a**	$(SC^+)_n \cdot (X^-)_{n-1}$ linear **12a**	$(SC^+)_n - S \cdot (X^-)_{n-1}$ linear **12a + 21**	$C^+ - (SC^+)_n \cdot (X^-)_{n-1}$ linear **12a + 13a**
1	2797 (2796)	2814 (2814)	[b], (3458)	5113 (5111)
2	5740 (5737)	5756 (5755)	[b], (6399)	8056 (8052)
3	8678 (8678)	[c], (8696)	[c], (9340)	[c], (10993)
4	11700[d] (11619)	11700[d], (11637)	[c], (12281)	[c], (13934)

[a] C^+ = catenate, S = spacer, $X^- = PF_6^-$, the number given in brackets is the theoretical mass. [b] Peaks not observed. [c] Very low signal-to-noise ratio. [d] Low signal-to-noise ratio.

An important feature is the formation of both linear and cyclic oligo[2]catenates for $n = 1$ and 2. Indeed, a space-filling model indicates that oligo[2]catenate **22a**, which contains only one repeat unit, does not lead to a dramatic strain because of the high flexibility of polyether bridges. No indication of any cyclic species could be obtained for $n = 3$ and 4 owing to a poor resolution of the corresponding signals. The absence of signals for $n > 4$ does not rule out the existence of higher oligo- and poly[2]catenates; it simply shows that they are not observable by MALDI-TOF MS (see below). Thus, the exact molecular weight distribution of oligo- and poly[2]catenates is not directly accessible because of their strongly polar character and the intrinsic limitation of MALDI-TOF MS. Clearly, only an indirect characterization is possible, namely, the demetalation of poly[2]catenate **12a** to yield poly[2]catenand **12b**.

*Poly[2]catenand **12b***: The poly[2]catenand **12b** was obtained in 81% yield by the reaction of poly[2]catenate **12a** with a large excess of potassium cyanide in tetrahydrofuran at room temperature for one day (Scheme 3). The course of the reaction was monitored by the disappearance of the metal-to-ligand charge-transfer band at $\lambda \approx 440$ nm which is characteristic of the phenanthroline copper(I) complex of the poly[2]catenate **12a**.[20]

The ^1H NMR spectrum shows the typical resonances of the terephthalate moiety, of the interlocked macrocycles, and the presence of benzyl alcohol protons at $\delta = 4.38$, which are attributed to catenand end groups. Assuming the equiprobable occurrence of catenate and spacer end groups, then integration gives a relative abundance of end groups of 4%. The same end-group concentration for the poly[2]catenate **12a** and the poly[2]catenand **12b** demonstrates, within the limit of experimental error, that no benzyl ester hydrolysis took place during demetalation. It is, therefore, suggested that the molecular weight distribution of poly[2]catenand **12b** accurately represents that of poly[2]catenate **12a**. The ^{13}C NMR spectrum exhibits, besides the characteristic resonance of ester groups at $\delta = 165.0$, a comparable resonance pattern to oligo[2]catenand **22b**. Definite evidence of the presence of high molecular weight poly[2]catenand **12b** is provided by viscometry and GPC in DMF. In particular, the specific viscosity, n_{sp}, increased with concentration, which is typical for high molecular weight polymers. Extrapolation to zero concentration yields a value of intrinsic viscosity reaching $1.09\,cL\,g^{-1}$. The macromolecular characteristics of poly[2]catenand **12b** are presented in Table 2. Standard calibration with polystyrene gave the values $M_n = 16500$, $M_w = 30500$ Da and peak molecular weight at $M_p = 37500$ Da. These values are very probably underestimated because of the more compact structure of poly[2]catenand **12b** compared to a polystryrene coil of similar molecular weight.[10a] A universal calibration was used to circumvent this problem.[21] The principle of the universal calibration relies on the observation that in a given solvent, the product of the intrinsic viscosity $[\eta]$ times the molecular weight M is a direct measure of the hydrodynamic volume of the polymer coil, and determines the retention time in the chromatographic column.[21] Since the chains of poly[2]catenand **12b** may be swollen in DMF to a different extent compared to a polystryrene standard of equal molecular weight, the hydrodynamic volumes will not necessarily be equivalent.[22a] This can be compensated for by applying a correction based on the Mark–Houwink–Sakurada equation[22] [Eq. (1)], which relates $[\eta]$ to M, and K and α are system-specific constants that

$$[\eta] = KM^{\alpha} \tag{1}$$

depend on the polymer, solvent, and temperature. Equation (1) contains two unknowns: K and α, whereas only the intrinsic viscosity $[\eta]$ of the poly[2]catenand **12b** is known.

Table 2. Macromolecular characteristics of poly[2]catenand **12b** from GPC in DMF

Calibration	M_n	DP	M_w	M_p	M_w/M_n
polystrene standard	16500	6	30500	37500	1.85
$\alpha = 0.5$, $K = 0.0494\,mL\,g^{-1}$	22000	8	47000	63000	2.12
$\alpha = 0.8$, $K = 0.002\,mL\,g^{-1}$	25000	9	42000	55000	1.68

Therefore, the problem remains unresolved.[23] However, while no unique solution can be obtained, reasonable estimates are possible by employing the two limiting values of α: it is well-established for flexible polymers at room temperature that $0.5 \leq \alpha \leq 0.8$, depending on the solvent quality. Notably, $\alpha = 0.5$ corresponds to θ conditions, that is, a solvent in which the polymer under investigation is close to precipitation, and $\alpha = 0.8$ corresponds to a random coil in a good solvent.

It can be seen from Figure 2 that the molecular weight distribution is not strongly influenced by the choice of α. Specifically, $\alpha = 0.5$ yields $M_n = 22\,000$ Da which corresponds to a DP of 8, $M_w = 47\,000$ Da, and peak molecular weight at $M_p = 63\,000$ Da. While $\alpha = 0.8$ affords comparable values: that is, $M_n = 25\,000$ Da which corresponds to a DP of 9, $M_w = 42\,000$ Da, and $M_p = 55\,000$ Da. The molecular weight averages calculated with universal calibration are considerably higher than the values obtained with polystyrene standards; this corroborates the suggested compact structure of **12b**. The polydispersity index (M_w/M_n) is slightly more sensitive to the choice of α: namely 2.1 and 1.7 for $\alpha = 0.5$ and 0.8, respectively. However, to a first approximation M_w/M_n remains close to 2.0, which is the generally observed value for polycondensation products.

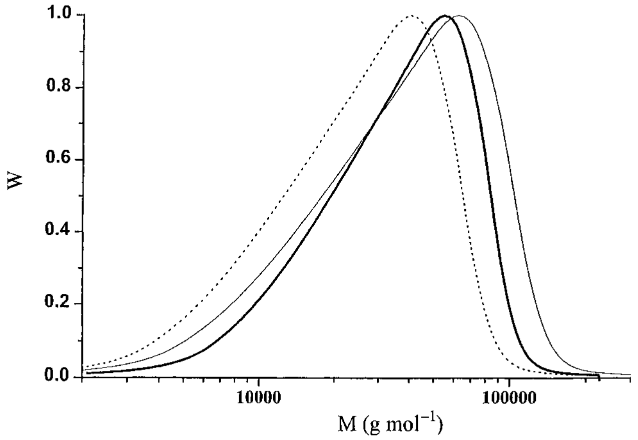


Figure 2. GPC trace in DMF of poly[2]catenand **12b** relative to polystyrene calibration (dotted line), and with a universal calibration where $\alpha = 0.5$ (solid line) and $\alpha = 0.8$ (bold solid line).

The molecular weight distribution of poly[2]catenand **12b** was also investigated by MALDI-TOF MS[19] (Figure 3). Signals of $m/z \leq 41\,000$, which correspond to $n = 15$, were observed. This in good agreement with the presence of high molecular weight polymers deduced from GPC. The resolution of the MALDI-TOF MS spectrum of poly[2]catenand **12b** was sufficient to support the presence of the cyclic oligo[2]catenand and the linear oligo[2]catenand, which bear a spacer on one side and a catenand on the other in the low molecular weight tail, up to $n = 2$, of the molecular weight distribution. However, the ratio between cyclic and linear oligomers could not be deduced because of the poor signal-to-noise ratio. The signals that correspond to poly[2]catenands **12b** terminated by two spacers and two catenane end-groups were also acquired; however, they are of lower intensity and appear broader.

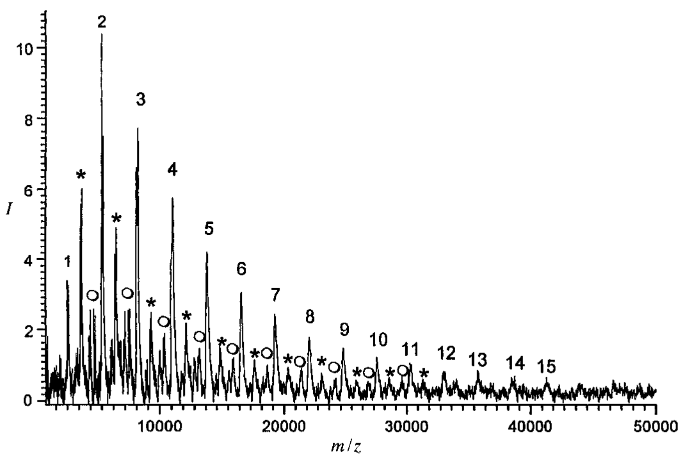


Figure 3. MALDI-TOF mass spectrum of poly[2]catenand **12b** (n refers to = (spacer–catenand)$_n$ with $n = 1,2,3$ to 15; * refers to (spacer–catenand)$_n$–spacer; ○ refers to catenand–(spacer–catenand)$_n$).

To summarize this section, the copolymerization of catenand **13b** with the spacer **21** leads preferentially to the formation of cyclic oligo[2]catenates **22b** because of the high relative mobility of the constitutive macrocycles of catenand **13b**. Conversely, the polymerization of catenate **13a** with the spacer **21** proceeds successfully to afford high molecular weight poly[2]catenates **12a**. The highly polar nature of poly[2]catenate **12b** renders its characterization difficult. Fortunately, the facile demetalation reaction allows the transformation of poly[2]catenate **12a** into poly[2]catenand **12b** without degradation, and thus its full characterization.

Solution properties of poly[2]catenand 12b: It is expected that the properties in solution and, in particular, the overall conformation of poly[2]catenand **12b** will reflect the unusual mobility elements that result from the introduction of topological bonds into a polymer main chain.[10b] The mobility elements present in a catenane unit are depicted in Figure 4.

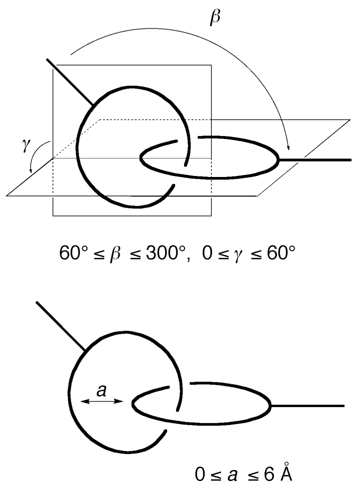


Figure 4. The mobility elements contained in catenand monomer units of **12b** and **22b**: rotational motions β and γ, and elongational motion a.

One should differentiate between the rotational mobility elements (β, γ) and the elongational mobility element a. Specifically, γ is defined by the angle between the planes of the catenane macrocycles and corresponds to rocking motions, which are also present in numerous polymers. On the other hand, the angle between the two spacers connected to the catenane unit, β, is an element of mobility which has not yet been introduced into a polymer main chain. Taking into account the thickness of the catenane macrocycles, one could estimate β to vary between 60 and 300°. Therefore, it is anticipated that little correlation will exist between the spatial orientation of neighboring monomer segments of poly[2]catenand **12b** and that it will represent the closest synthetic equivalent of the freely jointed chain model. In this model a real polymer chain is replaced by an equivalent chain consisting of N rectilinear segments, the spatial orientations of which are mutually independent (Figure 5).[24, 25]

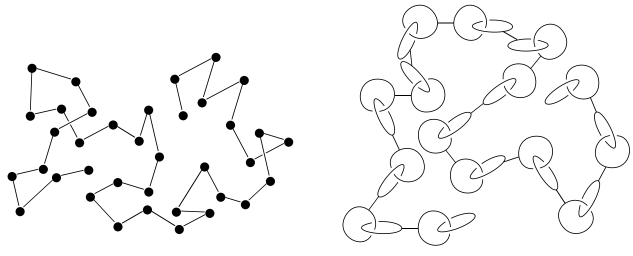


Figure 5. Snapshots of the conformation of the freely jointed chain model (top) and of the poly[2]catenane (bottom).

The elongational mobility element, a, is also characteristic of the relative motions of a catenane made of large macrocycles and is defined as the maximum allowed translational degree-of-freedom of one ring, considered as mobile, within the other, taken as fixed. In the present case, taking into account the ring size and the thickness of the organic groups, a could be roughly estimated as varying freely from 0 to 6 Å. Similarly to β, a has not yet been introduced in a polymer main chain.

Assuming that the poly[2]catenand **12b** can be adequately represented by the freely jointed chain model, the Kuhn segment length (l_k) has been estimated from GPC and viscometry results in DMF. The l_k value of a polymer chain is a characteristic of its equilibrium flexibility in a given solvent. The smaller the Kuhn segment length, the more flexible is the polymer chain. Typically, l_k values range from 15–30 Å for highly flexible polymers to 150–300 Å for rigid rods.[26] For flexible coils under θ conditions, l_k is defined according to Equation (2), where N is the number of repeat units, l is the length of the repeat unit, and R_g the radius of gyration. The Fox–Flory equation [Eq. (3)][22] relates the

$$l_k = 6R_g^2/Nl \tag{2}$$

$$[\eta] = \phi(6R_g^2)^{3/2}/M \tag{3}$$

intrinsic viscosity to R_g, where M is the molar mass, ϕ is the Flory viscosity constant. The combination of Equations (2) and (3) with the Mark–Houwink–Sakurada equation [Eq. (1)], allows the calculation of l_k, where K_θ is the

$$l_k = K_\theta^{2/3}\phi^{-2/3}M_o/l \tag{4}$$

viscosity constant for $\alpha = 0.5$ and M_o/l the molar mass per unit length. With $K_\theta = 0.0494\,\mathrm{mL\,g^{-1}}$ (Table 2), $\phi = 2.7 \times 10^{23}\,\mathrm{mol^{-1}}$,[27] $M_o = 2734\,\mathrm{g\,mol^{-1}}$, and $l = 32$ Å, a Kuhn length of $l_k = 27$ Å is obtained as a crude estimation (Figure 6).

This value must be taken as the upper limit, since the swelling of the polymer coil in a good solvent has not been taken into account and would result in a further decrease of l_k.[28] Clearly, the unusual elements of mobility of poly[2]catenand **12b**, that arise from the topological bonds as well as from the flexibility of the ethyleneoxy bridges and of the benzyl ester bonds, must be considered to account for the low value of the Kuhn segment length. Moreover, the upper limit of $l_k = 27$ Å of poly[2]catenand **12b** is comparable to that of a flexible polymer in a good solvent, for example, $l_k = 25$ Å for polystyrene in benzene.[29] This observation also confirms that little correlation exists between the spatial orientation of neighboring monomer segments of poly[2]catenand **12b** and that this polymer is correctly described by the Freely Jointed Chain model (Figure 5). Clearly, these preliminary results on the Kuhn segment length of the poly[2]catenanes **11** and **12b** stress the importance of the mobility contained in the catenane units on the conformation of these polymers.

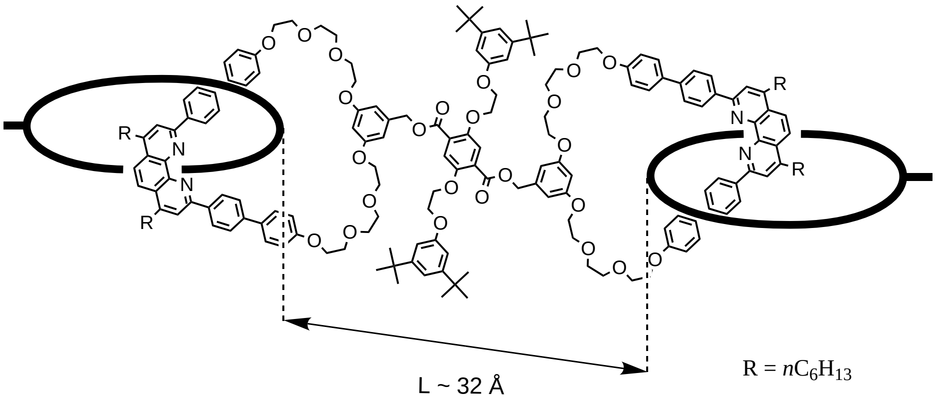


Figure 6. Estimation of the length of a monomer repeat unit of poly[2]catenand **12b**.

Solid-state properties: Thermogravimetric analysis (TGA) showed that poly[2]catenate **12a** is stable up to 210 °C, whereas oligo[2]catenand **22b** and poly[2]catenand **12b** exhibit a higher thermal stability, of up to 300 °C. Differential scanning calorimetry (DSC) was performed to investigate the presence of melting and glass transitions which correspond to first- and second-order phase transitions, respectively. No melting transitions were observed for oligo[2]catenand **22b**, poly[2]catenand **12b**, and poly[2]catenate **12a** in the range from room temperature to the decomposition temperature. It is informative to investigate T_g as a function of the oligo- and poly[2]catenane structure, since the higher the flexibility of the polymer chain, the lower is the glass transition.[22a] Specifically, glass transitions, determined from the second heating curve and taken at the midpoint of the change in heat capacity, were observed at 75 °C for oligo[2]catenand **22b** and poly[2]catenand **12b**, and at 80 °C for poly[2]catenate **12a**. The comparison between T_g of poly[2]catenand **12b** and poly[2]catenate **12a** indicates that it only slightly decreases on removal of the copper(I) ion.

Conclusions

The syntheses of large bifunctional catenate and catenand monomers and their copolycondensation with a spacer have been developed. Specifically, catenand monomers lead mainly to the formation of cyclic oligo[2]catenands **22b**, whereas a linear high molecular weight poly[2]catenate **12a** resulted from the use of catenate monomers. Demetalation of the poly[2]catenate **12a** afforded a poly[2]catenand **12b** without degradation. From a structural viewpoint, poly[2]catenand **12b** contains topological and covalent bonds, that is, the repeat units are mechanically connected to one another. A reliable and comprehensive structure elucidation of the oligo[2]catenands **22b**, poly[2]catenate **12a**, and poly[2]catenand **12b** was established. Moreover, a characterization of the solution properties of poly[2]catenand **12b** in DMF was carried out, and the upper limit of the Kuhn segment length was found to be 27 Å, which is lower than the length of a monomer unit (32 Å). In the solid-state, poly[2]catenate **12a** and poly[2]catenand **12b** exhibit a glass transition temperature at 80 °C and 75 °C, respectively. This synthetic and characterization work paves the way to the large-scale production of poly[2]catenanes and the detailed investigation of their potentially intriguing physical properties.

Experimental Section

Measurements: ^{1}H NMR spectra were acquired on Bruker WP200 SY, Bruker AM400, Varian Gemini 200, Bruker AC300, and Bruker AMX500 spectrometers. Melting points were determined on a Bioblock IA8103 apparatus and are uncorrected. GPC analyses in $CHCl_3$ were performed with PL-gel columns (Spectra Physics PSS SDV 8, 600 × 10^3 Å, 5 mm pore widths). GPC analyses were carried out on a Diol column (Merck 100/300/1000 Å) connected to a UV/Vis detector. Calibration was based on polystyrene standards with narrow molecular weight distributions. Field-desorption mass spectrometric analyses were performed on a VG analytical ZAB2-SE-FPD: (8 kV). Mass spectra were obtained either by chemical ionization (CI-MS), by positive-ion fast atom bombardment (FAB-MS) or by electrospray (ES-MS) mass spectrometry. MALDI-TOF measurements were performed with a Bruker Reflex mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at $\lambda = 337$ nm (LSI N_2 Laser, 10^6–10^7 W cm^{-1}, 100 µm diameter spot). The instrument can be used in a linear and a reflection mode. The reflection detector consists of a dual micro-channel plate for high resolution analysis of polymers below 10000 Da. The linear detector consists of a conversion dynode followed by a microchannel plate, a scintillator, and a photomultiplier. This detector is advantageous for characterization of the polymer molecular weight distribution. The matrix for all experiments was 1,8,9-trihydroxyanthracene. Samples were prepared by dissolving the polymer in $CHCl_3$ at a concentration of 10^{-4} mol L^{-1}. This solution (10 mL) was added to 10 mL of a 0.1 mmol mL^{-1} matrix solution, dissolved in $CHCl_3$. The mixture (1 mL) was applied to the multistage target and air-dried. The ions were accelerated to 33.65 kV and in reflection mode, reflected with 35 kV. Polystyrene ($M_p = 6000$ Da) was used for an external calibration, immediately before measurement. The mass accuracy, thus determined, is ≈0.05%. Thermal analysis was carried out on a Mettler DSC30 differential scanning calorimeter (heating rate: 20 K min^{-1}). Viscometry was carried out on a Ubblehode capillary viscosimeter in DMF.

Solvents and reagents: $[Cu(CH_3CN)_4BF_4]$ was prepared by the reduction of $Cu(BF_4)_2$ with excess Cu powder in CH_3CN under argon at room temperature. The mixture was stirred until the solution was completely bleached. All other chemicals were of the best grades commercially available and were used without further purification. The following compounds were synthesized as described in the literature: 2,5-bis[2-(3,5-(di-*tert*-butylphenoxy)ethoxy]terephthalic acid catalyst complex (4-*N*,*N*′-dimethylamino-pyridine/*p*-toluenesulfonic acid 1:1).[16] Diethyl 2,5-dihydroxyterephtalate, dibromoethane, *tert*-butylphenol, and diisopropylcarbodiimide were purchased from Aldrich.

Compound 18: Sodium hydride (3.27 g, 60% suspended in oil, 82 mmol) was added to a degassed solution of methyl 3,5-dihydroxybenzoate (6.0 g, 36 mmol) in DMF (100 mL) at room temperature. The mixture was stirred for 0.5 h and then heated to 85 °C. To this was added 2-(2′-(2″-chloroethoxy)ethoxy)ethyl 2-tetrahydro-2*H*-pyran ether (18.95 g, 75 mmol) dissolved in DMF (30 mL). After stirring at 85 °C for 48 h, the heterogeneous brown solution was evaporated to dryness and the residue taken up with a mixture of diethyl ether and aqueous NaOH (10 mass%). The organic layer was washed twice with an aqueous solution of NaOH (10 mass%), once with dilute HCl (0.05 mol L^{-1}), and twice with water. It was then dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by flash column chromatography (silica gel, CH_2Cl_2), to give pure **18** (20.33 g, 33.8 mmol, 95% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta = 7.18$ (d, $J = 2.3$ Hz, 2H), 6.68 (t, $J = 2.3$ Hz, 1H), 4.62 (t, $J = 3.4$ Hz, 2H), 4.13 (t, $J = 4.8$ Hz, 4H), 3.88 (s, 3H), 4.00–3.80 (m, 8H), 3.80–3.40 (m, 16H), 1.95–1.40 (m, 12H); anal. calcd for $C_{30}H_{48}O_{12}$ (%): C 59.99, H 8.05; found: C 60.06, H 8.19.

Dialcohol 19: Pyridinium *p*-toluenesulfonate (418 mg, 1.66 mmol) dissolved in methanol (10 mL) was added to a solution of **18** (500 mg, 0.83 mmol) in refluxing methanol (100 mL). After 2 h stirring at reflux, the solvent was removed and the residue taken up in CH_2Cl_2. The organic solution was washed twice with water, dried over Na_2SO_4, and evaporated to dryness. The crude product was purified by flash column chromatography (silica gel; CH_2Cl_2 containing 1.0–2.0% MeOH) to give pure **19** (317 mg, 0.73 mmol, 88% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta =$ 7.18 (d, $J = 2.3$ Hz, 2H), 6.72 (t, $J = 2.3$ Hz, 1H), 4.14 (t, $J = 4.7$ Hz, 4H), 3.88 (s, 3H), 3.84 (t, $J = 4.7$ Hz, 4H), 3.75–3.65 (m, 12H), 3.59 (t, $J = 4.5$ Hz, 4H); anal. calcd for $C_{20}H_{32}O_{10}$ (%): C 55.55, H 7.46; found: C 55.60, H 7.35.

Dimesylate 20: To a solution of **19** (317 mg, 0.73 mmol) and triethylamine (1.23 mL, 890 mg, 8.8 mmol) in CH_2Cl_2 (100 mL) at 0 °C was added mesyl chloride (0.34 mL, 4.4 mmol) in CH_2Cl_2 (25 mL) over a period of 20 min. After stirring for 2.5 h at 0 °C, the solution was washed twice with water, dried over Na_2SO_4, and evaporated to dryness. The crude product was purified by flash column chromatography (silica gel; CH_2Cl_2 containing 0.5–1.0% MeOH), to give pure **20** (396 mg, 0.67 mmol, 92% yield) as a pale yellow oil. ^{1}H NMR ($CDCl_3$): $\delta = 7.18$ (d, $J = 2.3$ Hz, 2H), 6.68 (t, $J = 2.3$ Hz, 1H), 4.37 (t, $J = 4.5$ Hz, 4H), 4.13 (t, $J = 4.6$ Hz, 4H), 3.89 (s, 3H), 3.83 (t, $J = 4.6$ Hz, 4H), 3.75–3.70 (unresolved t, 4H), 3.70–3.65 (m, 8H), 3.05 (s, 6H); anal. calcd for $C_{22}H_{36}O_{14}S_2$ (%): C 44.89, H 6.16; found: C 44.71, H 6.19.

Diiodide compound 17: A solution of **20** (4.0 g, 6.8 mmol) and NaI (20.4 g, 136 mmol) in acetone (250 mL) was refluxed for 12 h. The solvent was removed and the yellow oil taken up in CH_2Cl_2. The resulting solution was washed twice with water, dried over Na_2SO_4, and evaporated to dryness.

The crude product was purified by flash column chromatography (silica gel, CH_2Cl_2) to give pure **17** (3.796 g, 5.82 mmol, 86% yield) as a pale yellow oil. ^1H NMR ($CDCl_3$): $\delta = 7.19$ (d, $J = 2.3$ Hz, 2H), 6.70 (t, $J = 2.3$ Hz, 1H), 4.15 (t, $J = 4.7$ Hz, 4H), 3.89 (s, 3H), 3.85–3.80 (unresolved t, 4H), 3.80–3.70 (unresolved t, 4H), 3.70–3.60 (m, 8H), 3.25 (t, $J = 6.9$ Hz, 4H)); anal. calcd for $C_{20}H_{30}O_8I_2$ (%): C 36.83, H 4.64; found: C 37.17, H 4.74.

Macrocycle 15: To an argon-flushed suspension of Cs_2CO_3 (1.00 g, 3.1 mmol) in DMF (135 mL) maintained at 60 °C was added dropwise a mixture of **16** (582 mg, 0.85 mmol) and **17** (730.54 mg, 1.12 mmol) in DMF (75 mL) over a period of 16 h with efficient stirring. The mixture was stirred at this temperature for 5 h. DMF was removed under high vacuum and the residue taken up in CH_2Cl_2. The CH_2Cl_2 layer was washed twice with water, dried over Na_2SO_4, and evaporated to dryness to give a crude yellow product (4.89 g). It was purified by flash column chromatography (silica gel, CH_2Cl_2 containing 0–1.0% MeOH) to give pure macrocycle **15** (487 mg, 0.449 mmol, 53% yield) as a pale yellow solid. M.p. 162–164 °C; ^1H NMR ($CDCl_3$): $\delta = 8.58$ (d, $J = 8.4$ Hz, 4H), 8.02 (s, 2H), 8.00 (s, 2H), 7.79 (d, $J = 8.4$ Hz, 4H), 7.66 (d, $J = 8.7$ Hz, 4H), 7.24 (d, $J = 2.5$ Hz, 2H), 7.04 (d, $J = 8.7$ Hz, 4H), 6.72 (t, $J = 2.3$ Hz, 1H), 4.24 (t, $J = 4.9$ Hz, 4H), 4.16 (t, $J = 4.7$ Hz, 4H), 4.00–3.85 (m, 8H), 3.87 (s, 3H), 3.78 (s, 8H), 3.20 (t, $J = 7.7$ Hz, 4H), 2.00–1.80 (m, 4H), 1.60–1.25 (m, 12H), 0.91 (t, $J = 6.9$ Hz, 6H); anal. calcd for $C_{68}H_{76}N_2O_{10}$ (%): C 75.53, H 7.08, N 2.59; found: C 75.40, H 7.13, N 2.37; FAB-MS: *m/z*: calcd for $[\mathbf{15}+H^+]^+$: 1082.4; found: 1081.4.

Pre-rotaxane [Cu(15·16)]·PF$_6$: A solution of $[Cu(CH_3CN)_4PF_6]$ (121 mg, 0.326 mmol) in degassed acetonitrile (20 mL) was added by cannula to a stirred solution of **15** (320 mg, 0.296 mmol) in CH_2Cl_2 (20 mL) at room temperature under argon. After stirring for 0.5 h at room temperature, a solution of **16** (203 mg, 0.296 mmol) in degassed THF (20 mL) was added and the solution turned dark red immediately. Subsequently, the solution was stirred for 2 h under argon at room temperature. The solvents were removed under reduced pressure to afford a dark red solid of crude $[Cu(\mathbf{15}\cdot\mathbf{16})]PF_6$ in nearly quantitative yield (584 mg, 0.296 mmol). This compound was utilized without further purification. M.p. 121–123 °C; ^1H NMR ($CDCl_3$): $\delta = 8.06$ (s, 2H), 7.91 (s, 2H), 7.60–7.35 (m, 12H), 7.27 (d, $J = 2.3$ Hz, 2H), 7.00–6.80 (m, 16H), 6.82 (t, $J = 2.1$ Hz, 1H), 6.61 (d, $J = 8.2$ Hz, 4H), 6.55 (d, $J = 8.2$ Hz, 4H), 4.30–4.15 (m, 8H), 4.00–3.90 (m, 8H), 3.88 (s, 3H), 3.84 (s, 8H), 3.00–2.80 (m, 8H), 1.65–1.45 (m, 8H), 1.45–1.20 (m, 24H), 0.90 (m, 12H).

Copper(I) [2]catenate 14a: A solution of $[Cu(\mathbf{15}\cdot\mathbf{16})]PF_6$ (270 mg, 0.137 mmol), **17** (98 mg, 0.150 mmol), $[Cu(CH_3CN)_4PF_6]$ (51 mg, 0.137 mmol), L-(+)-ascorbic acid (17 mg, 0.096 mmol), and Cs_2CO_3 (223 mg, 0.684 mmol) was stirred in DMF (100 mL) under argon at 50 °C for 2 h. A further portion of **17** (98 mg, 0.150 mmol) was added and the mixture heated for a further 16 h. DMF was removed under high vacuum and the dark red residue taken up in CH_2Cl_2. The resulting solution was treated for 2 h with a large excess of KPF_6, dissolved in a minimum amount of water. By means of this anion exchange reaction, it was possible to isolate **14a**, originally formed as carbonate, iodide, and hexafluorophosphate, as its PF_6^- salt exclusively. The resulting organic layer was washed twice with water, dried over Na_2SO_4, and evaporated to dryness to yield 462 mg of a dark red solid. Flash column chromatography [i) silica gel, CH_2Cl_2 containing 0.25–0.75% MeOH; ii) aluminum oxide, CH_2Cl_2 containing 0.1–0.5% MeOH] gave pure **14a** (178 mg, 0.075 mmol, 55% yield) as a dark red solid. M.p. 95–97 °C; ^1H NMR ($CDCl_3$): $\delta = 8.06$ (s, 4H), 7.63 (s, 4H), 7.58 (d, $J = 8.2$ Hz, 8H), 7.27 (unresolved d, 4H), 6.94 (s, 16H), 6.81 (t, $J = 2.2$ Hz, 2H), 6.67 (d, $J = 8.2$ Hz, 8H), 4.30–4.15 (m, 16H), 4.00–3.85 (m, 16H), 3.88 (s, 6H), 3.84 (s, 16H), 3.02 (t, $J = 7.5$ Hz, 8H), 1.70–1.50 (m, 8H), 1.50–1.20 (m, 24H), 0.91 (t, $J = 6.3$ Hz, 12H); FAB-MS: *m/z*: calcd: 2226.3 $[\mathbf{14a}]^+$, 1144.9 $[\mathbf{15}+Cu]^+$; found: 2225.1, 1143.5.

Copper(I) [2]catenate 13a: A solution of diisobutylaluminum hydride in toluene (0.4 mL, 1.5 mol L^{-1}, 0.6 mmol) was added to a degassed solution of **14a** (50 mg, 0.021 mmol) in THF (25 mL) cooled to −10 °C. After 1 h stirring at −10 °C, a further portion of diisobutylaluminum hydride (0.2 mL, 1.5 mol L^{-1}, 0.3 mmol) was added. The mixture was stirred for 10 min and then a saturated solution of $NaPF_6$ in water was added. THF was removed and the yellow residue taken up in CH_2Cl_2, washed with a saturated aqueous solution of $NaPF_6$, washed twice with water, dried over Na_2SO_4, and evaporated to dryness. The dark red crude product was purified by column chromatography [i) silica gel, CH_2Cl_2 containing 1.0–2.0% MeOH; ii) aluminum oxide, CH_2Cl_2 containing 1.0–2.0% MeOH) to give the pure [2]catenate **13a** (31 mg, 0.0134 mmol, 64% yield) as a dark red solid. M.p. 92–94 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 8.07$ (s, 4H; H5,6), 7.63 (s, 4H; H3,8), 7.58 (d, $J = 8.3$ Hz, 8H; H_{o1}), 6.94 (s, 16H; H_{o2},H_{m2}), 6.67 (d, $J = 8.3$ Hz, 8H; H_{m1}), 6.63 (d, $J = 2.2$ Hz, 4H; H_B), 6.54 (t, $J = 2.2$ Hz, 2H; H_A), 4.65 (s, 4H; H_M), 4.27–4.18 (m, 16H; H_a,H_f), 3.98–3.90 (m, 16H; H_b,H_e), 3.79 (s, 16H; H_g,H_d), 3.03 (t, $J = 7.8$ Hz, 8H; H_a), 1.70–1.60 (m, 8H; H_b), 1.48–1.37 (m, 8H; H_c), 1.37–1.25 (m, 16H; H_d,H_e), 0.92 (t, $J = 6.8$ Hz, 12H; H_f); ^{13}C NMR ($CDCl_3$): $\delta = 160.3$, 158.9, 155.4, 150.7, 143.9, 143.5, 140.8, 137.5, 131.6, 128.7, 127.5, 126.9, 124.6, 123.3, 122.1, 115.0, 105.7, 100.7, 71.0, 70.0, 69.7, 67.7, 67.6, 65.3, 32.4, 31.6, 30.0, 29.3, 22.6, 14.1; FAB-MS: *m/z*: calcd for $[\mathbf{13a}]^+$: 2170.2; found: 2168.9.

[2]Catenand 14b: KCN (110 mg, 1.7 mmol) dissolved in water (6 mL) was added to **14a** (500 mg, 0.21 mmol) in CH_3CN (30 mL) and CH_2Cl_2 (15 mL). The characteristic dark red color of the stirred solution disappeared progressively whereas free ligand precipitated as a pink solid. After the mixture had been stirred for 5 h at room temperature, addition of more KCN (27 mg, 0.42 mmol) allowed completion of the demetalation. The mixture was stirred for 2 h, the resulting pale yellow solution was evaporated to dryness, and then taken up in CH_2Cl_2/H_2O. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were carefully washed with water (three times), dried over Na_2SO_4, and evaporated to dryness. The crude yellow product was purified by flash column chromatography (silica gel, CH_2Cl_2 containing 1.5–2.5% MeOH) to give pure free ligand **14b** (309 mg, 0.143 mmol, 68% yield) as a yellow solid. M.p. 89–91 °C; ^1H NMR ($CDCl_3$): $\delta = 8.55$ (d, $J = 8.1$ Hz, 8H), 8.00 (s, 4H), 7.97 (s, 4H), 7.73 (d, $J = 8.3$ Hz, 8H), 7.56 (d, $J = 8.7$ Hz, 8H), 7.15, (d, $J = 2.2$ Hz, 4H), 6.96 (d, $J = 8.7$ Hz, 8H), 6.62, (t, $J = 2.2$ Hz, 2H), 4.14 (t, $J = 4.9$ Hz, 8H), 4.05 (t, $J = 4.4$ Hz, 8H), 3.90–3.75 (m, 22H), 3.70 (s, 16H), 3.16, t, $J = 7.6$ Hz, 8H), 1.95–1.70 (m, 8H), 1.55–1.20 (m, 24H), 0.89 (t, $J = 6.9$ Hz, 12H); FAB-MS: *m/z*: calcd: 2163.7 $[\mathbf{14b}+H]^+$, 1082.4 $[\mathbf{15}+H]^+$; found: 2162.7, 1081.5.

[2]Catenand 13b: To a degassed solution of **14b** (283 mg, 0.13 mmol) in THF (125 mL) cooled to −10 °C was added a solution of diisobutylaluminum hydride in toluene (3.5 mL, 1.5 mol L^{-1}, 5.2 mmol). After 0.5 h stirring at −10 °C, an additional portion of diisobutylaluminum hydride (1.5 mL, 2.2 mmol) was added to the red solution, which was then stirred for a further 15 min. The solution was hydrolyzed with an aqueous solution of HPF_6 (pH = 1 according to a pH paper test), THF was removed, and the yellow residue taken up in $CH_2Cl_2/(H_2O + HPF_6)$. NaOH was added to the aqueous layer to give pH = 9 and then extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were washed with slightly basic water (pH = 9) and twice with water, dried over Na_2SO_4, and evaporated to dryness. The crude yellow product was purified by flash column chromatography (silica gel, CH_2Cl_2 containing 1.5–2.5% MeOH) to give pure [2]catenand **13b** (200 mg, 0.095 mmol, 73% yield) as a yellow solid. M.p. 95–97 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 8.55$ (d, $J = 8.6$ Hz, 8H; H_{o1}), 8.01 (s, 4H; H5,6), 7.98 (s, 4H; H3,8), 7.72 (d, $J = 8.3$ Hz, 8H; H_{m1}), 7.56 (d, $J = 8.8$ Hz, 8H; H_{o2}), 6.96 (d, $J = 8.8$ Hz, 8H; H_{m2}), 6.46 (d, $J = 2.1$ Hz, 4H; H_{II}), 6.30 (t, $J = 2.0$ Hz, 2H; H_I), 4.44 (s, 4H; H_M), 4.14 (t, $J = 5.1$ Hz, 8H; H_a), 3.99 (t, $J = 4.7$ Hz, 8H; H_f), 3.82, (t, $J = 4.9$ Hz, 8H; H_b), 3.77 (t, $J = 4.7$ Hz, 8H; H_e), 3.69 (s, 16H; H_g,H_d), 3.18 (t, $J = 7.8$ Hz, 8H; H_a), 1.84 (m, 8H; H_b), 1.55–1.40 (m, 8H; H_c), 1.40–1.25 (m, 16H; H_d,H_e), 0.90 (t, $J = 7.0$ Hz, 12H; H_f); ^{13}C NMR ($CDCl_3$): $\delta = 160.0$, 158.5, 155.8, 149.3, 146.8, 144.0, 141.5, 138.1, 133.4, 128.2, 128.0, 127.0, 126.5, 121.4, 119.6, 115.1, 105.4, 100.3, 70.9, 70.8, 69.9, 69.6, 67.5, 67.4, 64.7, 33.0, 31.7, 30.6, 29.4, 22.6, 14.1; FAB-MS: *m/z*: calcd for $[\mathbf{13b}+H]^+$: 2107.7; found: 2106.9.

Oligo[2]catenand 22b: A two-necked flask (10 mL) was charged, under argon, with the diol **13b** (119 mg, 56.5 µmol), the substituted terephthalic acid **21** (37.3 mg, 56.5 µmol), the catalyst complex 4-*N*,*N'*-dimethylaminopyridine/*p*-toluene sulfonic acid 1:1 (33 mg, 113 µmol, 2 equiv), and dry dichloromethane (1.3 mL). The reaction mixture was cooled to −10 °C and diisopropylcarbodiimide (0.1 mL) was added. The mixture was stirred for three days at −10 °C, two days at 0 °C, and then one day at room temperature. The crude polymer was purified by precipitation in methanol to afford 120 mg as a yellow powder in 77% yield. The ^1H and ^{13}C NMR spectra of the various batches were comparable, specifically: ^1H NMR (500 MHz, $CDCl_3$, 30 °C): $\delta = 8.54$ (s, 8H, arom.), 7.80–7.30 (m, 26H, arom.), 7.05–6.85 (m, 10H, arom.), 6.72 (m, 4H, arom.), 6.54 (s, 4H, arom.), 6.35 (m, 2H, arom.), 5.18 (m, 4H, aliph.), 4.40–3.60 (m, 56H, aliph.), 3.04 (m, 8H, aliph.), 2.06 (s, 8H, aliph.), 1.72 (s, 8H, aliph.), 1.44 (s, 8H, aliph.), 1.31 (s, 8H, aliph.), 1.26 (s, 8H, aliph.), 1.23 (s, 36H, aliph.), 0.88

(s, 12H, aliph.); ^{13}C NMR (125.75 MHz, CDCl$_3$, 30°C): $\delta = 164.9$ (C=O); 160.1, 158.8, 158.1, 155.3, 152.3, 152.2, 141.8, 137.9, 128.1, 127.0, 126.9, 126.4, 121.6, 118.3, 115.3, 115.1, 109.0, 106.8, and 100.9 (arom.); 70.9, 69.9, 69.3, 67.6, 67.5, 66.8, 66.3, 34.9, 33.0, 32.9, 31.7, 30.4, 29.7, 29.4, 22.6, and 14.1 (aliph.)

Poly[2]catenate 12a: A two-necked flask (10 mL) was charged, under argon, with the diol **13a** (214.6 mg, 92.7 µmol), the substituted terephthalic acid **21** (61.4 mg, 92.7 µmol), the catalyst complex 4-*N*,*N*′-dimethylaminopyridine/*p*-toluene sulfonic acid 1:1 (60 mg, 204 µmol, 2.1 equiv) and dry dichloromethane (2 mL). The reaction mixture was cooled to −20°C and diisopropylcarbodiimide (0.27 mL) was added. The mixture was stirred for six days at −20°C. The crude polymer was purified by precipitation in methanol to afford 256 mg of a violet powder (94% yield). ^{1}H NMR (500 MHz, CDCl$_3$, 30°C): $\delta = 8.10$ (s, 4H, arom.), 7.75–7.40 (m, 12H, arom.), 7.00 (s, 2H, arom.), 6.90 (s, 16H, arom.), 6.75 (s, 4H, arom.), 6.63 (s, 12H, arom.), 6.53 (s, 2H, arom.), 5.26 (s, 4H, aliph.), 4.63 (benzyl alcohol end-groups), 4.37 (m, 4H, aliph.), 4.30 (m, 4H, aliph.), 4.17 (s, 8H, aliph.), 4.15 (s, 8H, aliph.), 3.87 (s, 8H, aliph.), 3.77 (s, 8H, aliph.), 3.00 (s, 8H, aliph.), 1.63 (s, 16H, aliph.), 1.40 (s, 8H, aliph.), 1.28 (s, 44H, aliph.), 0.88 (t, 12H, aliph.); ^{13}C NMR (125.75 MHz, CDCl$_3$, 30°C): $\delta = 163.6$ (C=O); 158.9, 157.6, 156.8, 151.0, 150.9, 136.6, 126.2, 124.0, 123.0, 117.1, 114.0, 113.5, 107.7, 105.5, 99.8, and 99.1 (arom.); 69.5, 68.6, 68.3, 68.1, 66.2, 65.4, 65.0, 33.6, 31.1, 30.1, 28.6, 27.9, 21.2, and 12.7 (aliph.).

Poly[2]catenand 12b: To a solution of poly[2]catenate **12a** (200 mg) in THF (30 mL) was added KCN (500 mg). The reaction mixture was stirred for one day at room temperature until the characteristic violet color of poly[2]catenate had disappeared. Precipitation in methanol afforded 150 mg of **12b** as a yellow powder (81% yield). ^{1}H NMR (500 MHz, CDCl$_3$, 30°C): $\delta = 8.51$ (s, 4H, arom.), 8.00–7.89 (m, 8H, arom.), 7.75–7.35 (m, 18H, arom.), 6.96 (s, 2H, arom.), 6.91 (d, 8H, arom.), 6.70 (s, 4H, arom.), 6.52 (s, 4H, arom.), 6.33 (s, 2H, arom.), 5.16 (s, 4H, aliph.), 4.38 (s, end groups, 4%), 4.37–4.22 (m, 8H, aliph.), 4.10 (s, 8H, aliph.), 3.96 (s, 8H, aliph.), 3.77–3.64 (m, 32H, aliph.), 3.10 (s, 8H, aliph.), 1.77 (s, 8H, aliph.), 1.43 (s, 8H, aliph.), 1.31 (s, 8H, aliph.), 1.24 (m, 44H, aliph.), 0.86 (t, 12H, aliph.); ^{13}C NMR (125.75 MHz, CDCl$_3$, 30°C): $\delta = 165.0$ (C=O); 162.5, 160.1, 158.5, 158.1, 155.4, 152.3, 152.2, 149.2, 146.8, 141.5, 137.9, 133.3, 128.1, 128.0, 126.8, 124.4, 125.3, 121.4, 119.3, 118.3, 115.3, 115.1, 109.1, 106.7, and 100.8 (arom.); 70.8, 69.8, 69.6, 69.3, 67.5, 67.4, 66.8, 66.3, 36.4, 34.9, 32.9, 31.7, 31.4, 30.5, 29.7, 29.4, 22.6, and 14.1 (aliph.).

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