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Preparation of Novel Poly[2]catenanes by Direct Bonding of [2]Catenanes

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The preparation of novel poly[2]catenanes by direct bonding of [2]catenanes was investigated. The monomeric catenanes were prepared by cycloamidation of 5-substituted *N,N'*-bis[(4-aminophenyl)methyl]isophthalamides (**2**) and sebacoyl chloride in highly dilute solutions. Polycondensation of dihydroxy[2]catenane (**3b**) and dicarboxy[2]catenane (**3d**) resulted in a product with a low degree of polymerization, and a considerable amount of cyclic dimer (**7**) was formed. The desired novel poly[2]catenane **8** was obtained by azide-alkyne 1,3-dipolar cycloaddition of diazido[2]catenane (**3e**) and diethynyl[2]catenane (**3f**). The number-average molecular weight of the poly[2]catenane was between 3×10^4 and 5×10^4.
Key words: poly[2]catenane, [2]catenane, 1,3-dipoler cycloaddition, polyaddition

1. INTRODUCTION

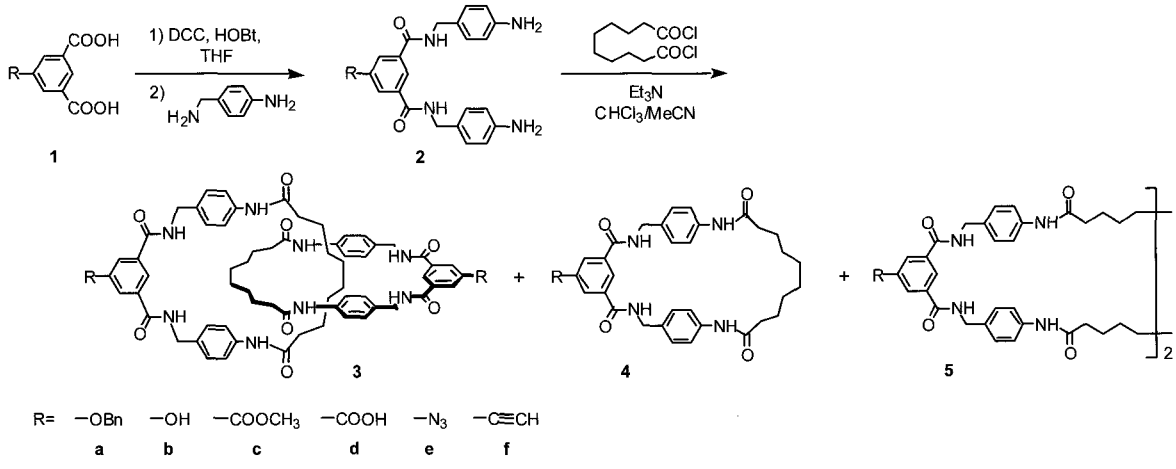
In recent years, much attention has been given to materials with an interlocked molecular structure. Interlocked polymers with a catenane structure, such as polycatenane or poly[2]catenane, are of particular interest due to the expectation of unique properties based on the topological bonds in the catenane structure.[1] Polycatenanes, consisting only of interlocked rings, have not yet been synthesized, since it is difficult to achieve highly effective ring closure. There have been some reports on poly[2]catenanes obtained from [2]catenanes and connector molecules;[2-5] however these are not expected to show special properties due to topological bonds, because the connectors contain flexible covalent bonds. Accordingly, such topologically based properties have not been observed in the reported poly[2]catenanes.

Herein, we report the preparation of novel poly[2]catenanes by direct bonding of two [2]catenanes, without connectors. The poly[2]catenanes are new interlocked polymers which are expected to show unique properties based on the topological bonds.

2. RESULTS AND DISCUSSION

2.1 Preparation of functional [2]catenanes

The synthesis of amide-type [2]catenanes have been studied by Leigh et al.[6-8] Various functional [2]catenanes were prepared from 5-substituted isophthalic acids using Leigh's method. U-shaped diamines (**2**), precursor of [2]catenanes, were prepared by amidation of 5-substituted isophthalic acids (**1**) and 4-aminobenzylamine, and cycloamidation reactions of diamines **2** and sebacoyl dichloride were carried out in highly dilute solutions. The desired [2]catenanes (**3a**, **3c**, **3e**, and **3f**) were obtained in 5 – 17% yield along with [1+1]cyclic compounds **4** and [2+2]macrocycles **5** (Scheme 1). The catenanes were isolated from the mixture by preparative thin layer chromatography. Protected catenanes **3a** and **3c** were converted into dihydroxy (**3b**) and dicarboxy[2]catenane (**3d**) by hydrogenation and hydrolysis, respectively. The catenane structure was determined by ^{1}H-NMR (Fig. 1) and MALDI-TOF MS. It is known that NMR signals of catenanes exhibit a characteristic high-field shift, which distinguishes them from non-catenane cyclic compounds such as **4** and **5**.[6]



Scheme 1 Preparation of [2]catenanes.

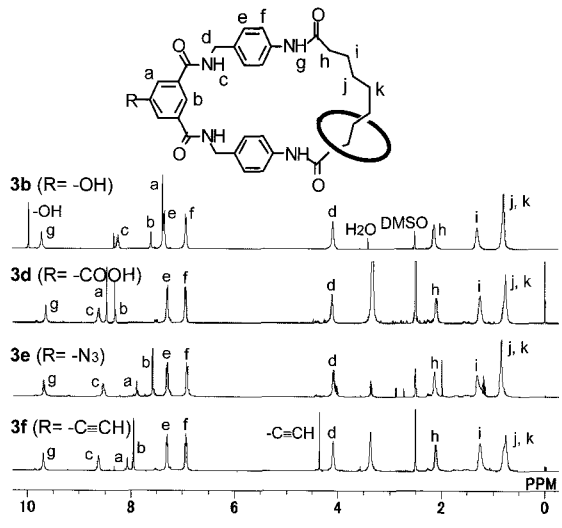
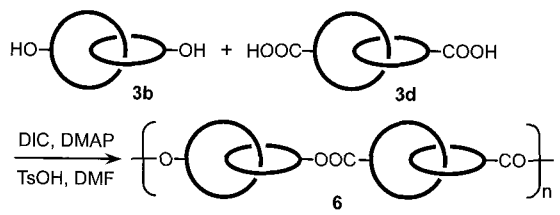


Fig. 1 ^{1}H-NMR spectra of [2]catenanes (400 MHz, DMSO-d_6).

2.2 Synthesis of poly[2]catenanes by direct bonding of [2]catenanes

Poly[2]catenane preparation was first attempted by an esterification reaction between dihydroxy[2]catenane and dicarboxy[2]catenane in the presence of *N,N'*-diisopropylcarbodiimide (DIC) as a coupling reagent (Scheme 2). The reaction proceeded and condensation products were recovered in 74% yield, but the average molecular weight was low ($Mn = 1 \times 10^4 - 2 \times 10^4$, Fig. 2). In addition, it was found that a large amount of



Scheme 2 Preparation of poly[2]catenane **6** from **3b** and **3d** by esterification.

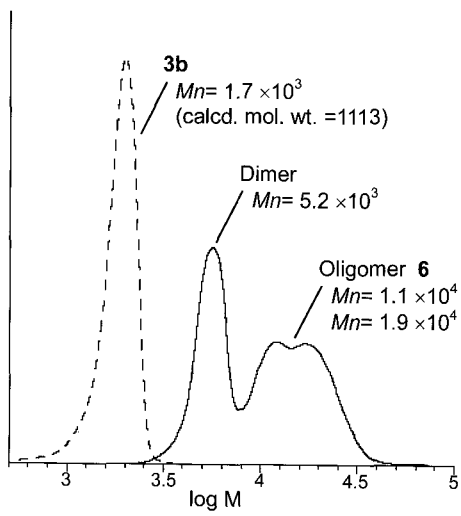


Fig. 2 GPC curves of dihydroxy[2]catenane (**3b**, – – –) and the condensation product (——). Calibration was carried out using polystyrene standards. DMF was used as an eluent.

dimeric product (about 56% of the total product, estimated from GPC peak area) was formed. The dimeric product was isolated from the mixture by taking advantage of its low solubility: treatment of the product mixture with chloroform – methanol (8:2) resulted in the separation of an insoluble fraction from the other soluble products. The MALDI-TOF MS spectrum of the fraction is shown in Fig. 3. The molecular weight indicates that the isolated fraction is the cyclic dimer **7**, which is formed from **3b** and **3d**. The preferential formation of the cyclic dimer can be explained by the flexibility of the ester bond, which induces intramolecular cyclization. Therefore, in order to prevent the formation of a cyclic dimer and obtain a higher molecular weight polymer, a rigid bond is required to connect the two [2]catenane molecules.

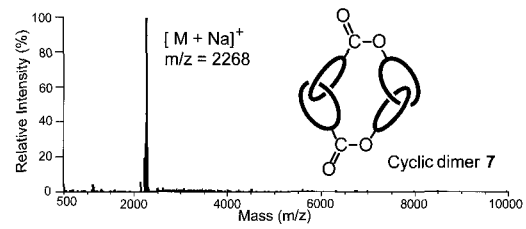
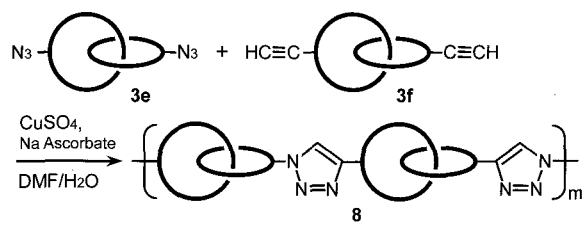


Fig. 3 MALDI-TOF MS spectrum of cyclic dimer **7**.

1,3-Dipolar cycloaddition between an organic azide and an alkyne gives a rigid triazole ring selectively under mild conditions.[9-10] With the aim of synthesizing a poly[2]catenane linked by a triazole ring, we carried out a copper(I) catalyzed azide-alkyne 1,3-dipolar cycloaddition reaction between diazido[2]catenane **3e** and diethynyl[2]catenane **3f** (Scheme 3). A polymeric product **8** with a number-average molecular weight about 3.7×10^4 was obtained quantitatively (Table 1, run 1). The molecular weight was improved by increasing the reaction time and using a larger amount of Cu catalyst, and a *Mn* of 4.6×10^4 was achieved in a 7 h reaction using a threefold amount of the catalyst (Table 1, run 3).



Scheme 3 Preparation of poly[2]catenane **8** from **3e** and **3f** by 1,3-dipolar cycloaddition.

Table 1 Preparation of poly[2]catenane **8**.

Run	Catalyst (equiv.)		Time (day)	Product		
	$CuSO_4 \cdot 5H_2O$	Sodium Ascorbate		Yield (%)	*Mn* ($\times 10^3$)	*Mw* ($\times 10^3$)
1	0.5	2.0	2	100	37	43
2	0.5 × 2	2.0 × 2	4	99	31	49
3	0.5 × 3	2.0 × 3	7	100	46	60

All reactions were carried out at room temperature. *Mn* and *Mw* were determined by GPC on the basis of a polystyrene calibration.

The GPC chromatogram of the product obtained in run 3 is shown in Fig. 4. The chromatogram shows that the amount of the cyclic dimer decreased while that of the high molecular weight product increased (about 66% of the total, estimated from the peak area). It was found that the polymer contained an average of 12 catenanes. Thus, the first preparation of poly[2]catenane by direct bonding of [2]catenanes was achieved.

The TGA thermogram of the polymer gave a 5% weight loss temperature of 344 °C at a heating rate of 10 °C/min in nitrogen, but the mechanical properties of the product could not be measured due to its small quantity.

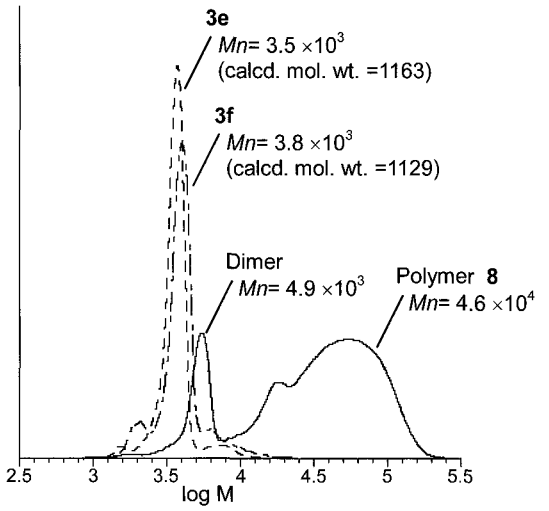


Fig. 4 GPC curves of diazido[2]catenane (**3e**,– – –), diethynyl-[2]catenane (**3f**,– · –) and the run 3 product (——). Calibration was carried out using polystyrene standards, and DMF was used as an eluent.

3. EXPERIMENTAL

3.1 Preparation of 5-benzyloxyisophthalic acid (**1a**)

A mixture of dimethyl 5-hydroxyisophthalate (4.20 g), benzyl chloride (3.80 g), and potassium carbonate (4.15 g) in acetone (30 ml) was refluxed for 24 h. The reaction mixture was then evaporated and the residue was dissolved in hot cyclohexane. Insoluble inorganic salts were filtered off, and the filtrate was cooled to ambient temperature. Crystallized dimethyl 5-benzyloxyisophthalate was collected by filtration and dried. The ester was hydrolyzed in refluxed methanol in the presence of KOH for 4 h. The mixture was evaporated, dissolved in water, and acidified using HCl. After filtration and drying of the resulting precipitate, acid **1a** was obtained in 71% yield as a colorless powder.

^{1}H-NMR (TMS, DMSO-d_6): δ (ppm) = 13.33 (br, 2H), 8.11 (s, 1H), 7.75 (s, 2H), 7.49 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 5.25 (s, 2H). ^{13}C-NMR (TMS, DMSO-d_6): δ (ppm) = 166.31, 158.49, 136.52, 132.59, 128.50, 127.98, 127.64, 122.44, 119.50, 69.70.

3.2 Preparation of 1,3,5-benzenetricarboxylic acid monomethyl ester (**1c**)

A mixture of trimethyl 1,3,5-benzenetricarboxylate (2.53 g) and a 1.0 M aqueous solution of NaOH (20 ml) in methanol (200 ml) was refluxed for 24 h. After removal of the solvent, the residue was dissolved in water and acidified with HCl, giving a precipitate, monoester **1c**, which was collected by filtration and dried under reduced pressure (90% yield).

^{1}H-NMR (TMS, DMSO-d_6): δ= 13.65 (br, 2H), 8.66 (s, 1H), 8.64 (s, 2H), 3.93 (s, 3H). ^{13}C-NMR (TMS, DMSO-d_6): δ= 165.72, 164.85, 133.88, 133.36, 132.08, 130.70, 52.71.

3.3 Preparation of *N,N'*-bis[(4-aminophenyl)methyl]-5-benzyloxyisophthalamide (**2a**)

A solution of *N,N'*-dicyclohexylcarbodiimide (1.69 g) in THF (20 ml) was added dropwise to a solution of **1a** (1.07 g) and 1-hydroxybenzotriazole monohydrate (1.26 g) in THF (10 ml) at 0 °C. The mixture was stirred for 6 h in an ice bath and filtered. The filtrate was added slowly to a solution of 4-aminobenzylamine (0.93 ml) in THF (20 ml) and stirred at room temperature for 48 h under a N_2 atmosphere. Half of the solvent was removed by evaporation, and chloroform was added to the remainder. The solution was washed with saturated aqueous $NaHCO_3$ and evaporated to give diamine **2a** in 72% yield.

Further 5-substituted *N,N'*-bis[(4-aminophenyl)-methyl]isophthalamides **2c**, **2e**, and **2f** were prepared using the same method.

N,N'-Bis[(4-aminophenyl)methyl]-5-benzyloxyisophthalamide (2a)

^{1}H-NMR (TMS, DMSO-d_6): δ= 8.91 (bt, J = 5.6 Hz, 2H), 7.97 (s, 1H), 7.64 (s, 2H), 7.47 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 8.4 Hz, 4H), 6.51 (d, J = 8.4 Hz, 4H), 5.20 (s, 2H), 4.97 (b, 4H), 4.30 (d, J = 5.6 Hz, 4H). ^{13}C-NMR (TMS, DMSO-d_6): δ= 165.19, 158.20, 147.56, 136.67, 136.11, 128.48, 128.38, 127.96, 127.72, 126.32, 118.88, 116.03, 113.68, 69.65, 42.49.

N,N'-Bis[(4-aminophenyl)methyl]-5-methoxycarbonylisophthalamide (2c)

^{1}H-NMR (TMS, DMSO-d_6): δ= 9.17 (bt, J = 6.0 Hz, 2H), 8.61 (s, 1H), 8.56 (s, 2H), 6.98 (d, J = 8.8 Hz, 4H), 6.52 (d, J = 8.8 Hz, 4H), 4.97 (b, 4H), 4.32 (d, J = 4.3 Hz, 4H), 3.91(s, 3H). ^{13}C-NMR (TMS, DMSO-d_6): δ= 165.42, 164.56, 147.62, 135.35, 130.78, 130.18, 129.97, 128.48, 126.14, 113.68, 52.52, 42.62.

N,N'-Bis[(4-aminophenyl)methyl]-5-azidoisophthalamide (2e)

^{1}H-NMR (TMS, DMSO-d_6): δ= 9.04 (t, J = 5.6 Hz, 2H), 8.18 (t, J = 1.6 Hz, 1H), 7.70 (d, J = 1.6 Hz, 2H), 6.98 (d, J = 8.4 Hz, 4H), 6.51 (d, J = 8.4 Hz, 4H), 4.97 (b, 4H), 4.30 (d, J = 5.6 Hz, 4H). ^{13}C-NMR (TMS, DMSO-d_6): δ= 164.51, 147.60, 139.97, 136.38, 128.41, 126.12, 123.10, 120.14, 113.67, 42.55.

N,N'-Bis[(4-aminophenyl)methyl]-5-ethynylisophthalamide (2f)

^{1}H-NMR (TMS, DMSO-d_6): δ= 9.07 (t, J = 6.0 Hz, 2H), 8.41 (t, J = 1.2 Hz, 1H), 8.10 (d, J = 1.2 Hz, 2H), 7.01 (d, J = 8.4 Hz, 4H), 6.53 (d, J = 8.4 Hz, 4H), 4.98 (b, 4H), 4.35 (s, 1H), 4.32 (d, J = 5.6 Hz, 4H). ^{13}C-NMR (TMS, DMSO-d_6): δ= 164.54, 147.54, 135.23, 132.49, 128.43, 126.92, 126.18, 121.84, 113.70, 82.30, 81.78, 42.58.

3.4 Preparation of dibenzyloxy[2]catenane (**3a**)

A solution of diamine **2a** (0.48 g) in acetonitrile (8 ml) was diluted with chloroform (250 ml), and a solution of sebacoyl dichloride (0.21 ml) and triethylamine (0.31

ml) in chloroform (50 ml) was added dropwise over 5 h. After stirring at room temperature for 24 h under a N_2 atmosphere, the resulting precipitate was filtered off and the filtrate was washed with 1M-HCl and saturated aqueous $NaHCO_3$. The organic layer was evaporated and dibenzyloxy[2]catenane (**3a**) was isolated from the residue in 17% yield by preparative thin layer chromatography using chloroform–methanol (93:7) as an eluent.

Further [2]catenanes **3c**, **3e**, and **3f** were prepared using the same method.

Dibenzyloxy[2]catenane (3a)

^{1}H-NMR (TMS, DMSO-d_6): δ= 9.78 (b, 4H), 8.42 (b, 4H), 7.79 (s, 2H), 7.54 (s, 4H), 7.45-7.39 (m, 10H), 7.35 (d, J = 8.0 Hz, 8H), 6.93 (d, J = 8.0 Hz, 8H), 4.98 (s, 4H), 4.10 (b, 8H), 2.17 (b, 8H), 1.33 (m, 8H), 0.83 (m, 16H). ^{13}C-NMR (TMS, DMSO-d_6): δ= 171.45, 165.91, 158.16, 138.12, 136.56, 136.30, 132.51, 128.46, 128.20, 127.94, 127.62, 118.80, 117.97, 116.44, 69.43, 43.13, 36.05, 29.14, 28.01, 25.25.

Dimethoxycarbonyl[2]catenane (3c)

^{1}H-NMR (TMS, DMSO-d_6): δ= 9.70 (b, 4H), 8.65 (b, 4H), 8.50 (s, 2H), 8.38 (s, 4H), 7.32 (d, J = 7.3 Hz, 8H), 6.95 (d, J = 7.3 Hz, 8H), 4.14 (s, 8H), 3.90 (s, 6H), 2.14 (b, 8H), 1.29(m, 8H), 0.81 (m, 16H). ^{13}C-NMR (TMS, DMSO-d_6): δ= 171.49, 165.36, 165.82, 138.05, 135.33, 132.71, 130.53, 129.96, 129.83, 128.27, 118.95, 52.52, 43.08, 36.02, 28.99, 27.92, 25.26.

Diazido[2]catenane (3e)

^{1}H-NMR (TMS, DMSO-d_6): δ= 9.68 (b, 4H), 8.53 (b, 4H), 7.89 (s, 2H), 7.57 (s, 4H), 7.29 (d, J = 8.0 Hz, 8H), 6.90 (d, J = 8.0 Hz, 8H), 4.08 (b, 8H), 2.13 (b, 8H), 1.30 (m, 8H), 0.84 (m, 16H), ^{13}C-NMR (TMS, DMSO-d_6): δ= 171.43, 165.03, 139.82, 138.01, 136.46, 132.65, 128.27, 122.21, 120.34, 118.86, 43.02, 36.02, 28.98, 27.96, 25.22.

Diethynyl[2]catenane (3f)

^{1}H-NMR (TMS, DMSO-d_6): δ= 9.69 (b, 4H), 8.63 (b, 4H), 8.07 (s, 2H), 7.96 (s, 4H), 7.30 (d, J = 8.0 Hz, 8H), 6.94 (d, J = 8.0 Hz, 8H), 4.36 (s, 2H), 4.10 (b, 8H), 2.11 (b, 8H), 1.26 (m, 8H), 0.76 (m, 16H). ^{13}C-NMR (TMS, DMSO-d_6): δ= 171.43, 165.00, 137.97, 135.30, 132.88, 132.69, 128.22, 126.09, 121.82, 118.88, 82.24, 81.90, 42.93, 36.00, 28.87, 27.88, 25.23.

3.5 Preparation of dihydroxy[2]catenane (**3b**)

Dibenzyloxy[2]catenane (**3a**, 0.105 g), 10% Pd/C (0.121 g), and DMF (2.0 ml) as a solvent were placed in a 30 ml autoclave. After stirring under 0.5 MPa of H_2 at room temperature for 24 h, the catalyst was removed by filtration. The filtrate was evaporated and dihydroxy-[2]catenane (**3b**) was obtained quantitatively.

^{13}C-NMR (TMS, DMSO-d_6): δ= 171.40, 166.06, 157.25, 138.12, 136.13, 132.61, 128.23, 118.77, 117.13, 115.94, 79.18, 43.04, 36.06, 29.10, 27.99, 25.28.

3.6 Preparation of dicarboxy[2]catenane (**3d**)

A mixture of dimethoxycarbonyl[2]catenane (**3c**, 0.10 g) and LiCl (0.18 g) in DMF (1.7 ml) was refluxed for 48 h under a N_2 atmosphere. The solvent was distilled off under reduced pressure. The residue was dissolved in water and then acidified by addition of 1M-HCl, resulting in the formation of a precipitate. Dicarboxy[2]-catenane (**3d**) was obtained in 52% yield after filtration.

Dicarboxy[2]catenane (3d)

^{1}H-NMR (TMS, DMSO-d_6): δ= 9.67 (b, 4H), 8.65 (b, 4H), 8.48 (s, 2H), 8.31 (s, 4H), 7.31 (d, J = 8.0 Hz, 8H), 6.95 (d, J = 8.0 Hz, 8H), 4.12 (s, 8H), 2.11 (b, 8H), 1.26(m, 8H), 0.76 (m, 16H). ^{13}C-NMR (TMS, DMSO-d_6): δ= 171.49, 165.46, 165.25, 138.01, 135.19, 132.86, 131.32, 130.65, 129.46, 128.26, 118.91, 43.02, 36.03, 29.06, 27.89, 25.27.

3.7 Preparation of poly[2]catenane (**6**) by esterification

A solution of dicarboxy[2]catenane (**3d**, 11.7 mg), DIC (0.012 ml), and 4-(dimethylamino)pyridine p-toluenesulfonate (20 mg) in DMF (0.05 ml) was stirred at room temperature for 1 h under a N_2 atmosphere. Dihydroxy[2]catenane (**3b**, 11.7 mg) solution in DMF (0.05 ml) was added to the mixture and stirred at room temperature for 7 days. The polymeric product was recovered in 74% yield by addition of methanol (5 ml) and filtration.

3.8 Preparation of poly[2]catenane (**8**) by 1,3-dipolar cycloaddition

To a solution of diazido[2]catenane (**3e**, 10.5 mg) and diethynyl[2]catenane (**3f**, 10.2 mg) in DMF (0.1 ml), copper(II) sulfate pentahydrate (1.1 mg), sodium ascorbate (3.6 mg), and water (0.01 ml) were added, and the mixture was stirred at room temperature for 2 days under a N_2 atmosphere. After precipitation by addition of water and subsequent filtration, poly[2]catenane was obtained in quantitative yield.

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