Short Communication

Synthesis and Switchable Condensation Reaction of Bifunctional [2]Catenane

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Syntheses of mechanically interlocked molecules such as catenanes and rotaxanes have been intensely developed over the past 15 years.1,2 Recently much attention has been devoted to the reactions,3–5 photochemistry,6 and electrochemistry7 of these molecules, especially of novel mechanically interlocking structures. Concerning the reactions of these molecules, novel reactivities would be expected because units of the molecules are located close to each other and with some regular order. However, there are few reports about the reactivities of the parts used to construct these molecules, except for the synthesis of cyclodextrin nanotubes,3 poly[2]catenane,4,7 and a pretzel-shaped molecule8 using mechanically interlocking structures as templates. We have also tried to synthesize bifunctional [2]catenane8 and [2]rotaxane9 monomers aiming at the construction of polymers, where catenane- or rotaxane-type linkages exist in the polymer main chains. Here we report the synthesis of [2]catenane having secondary amino groups on each ring and its condensation reaction resulting in poly[2]catenane or a pretzel-shaped molecule, depending on the absence or presence of a copper(I) ion.

[2]Catenane with azacetylene glycol ethers was synthesized on the basis of the method developed by Sauvage et al.1 The synthesis of diiodide 4 as a tether component of 10 is shown in Scheme 1. The amine in 3,6,12,15-tetraoxa-9-azaheptadecane-1,17-diol (1)10 was protected as a benzylcaramate (Cbz) in 97% yield. Tosylation of 2 and displacement with NaI of the tosylate 3 gave the diiodide 4 with an 80% overall yield.

To construct an interlocked system, the two-step approach11 to catenate was used. The monocyclic compound 6 was prepared by the addition of the diiodide 4 to a solution of the phenanthroline 5 with Cs₂CO₃ in DMF at 65°C in 40% yield (Scheme 2). The copper chelate formed immediately on addition of a CH₃CN solution of Cu(CH₃CN)₄·BF₄ to the cyclic phenanthroline 6 in DMF. Addition of the phenanthroline 5 to this chelate gave the complex 7. The alkylation of 7 with the iodide 4 afforded the catenated complex 8 in 30% yield. Demetallation of 8 was performed with KCN in CH₃CN·H₂O to afford 9 in 86% yield. The Cbz group of 9 was removed with HBr·AcOH12 to give the diamine 10 in 82% yield.

The reaction between the catenated diamine 10 and adipoyl chloride was investigated. To the CH₂Cl₂ solution of the diamine 10 was added adipoyl chloride in the presence of triethylamine. The condensation proceeded smoothly and the pretzel-shaped compound10 11 was obtained (78%) (Scheme 3). The chemical structure of 11 was verified by its ¹H NMR and FAB mass spectra. On the other hand, in order to prevent the equilibrium

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† All new compounds gave satisfactory analytical and spectral data. Selected data for 10: pale yellow crystals (m.p. 205°C).

¹H NMR (CDCl₃): δ 3.08 (t, 8 H, J = 5.1 Hz), 3.60–3.69 (brs, 2 H), 3.70 (brs, 16 H), 3.76 (t, 8 H, J = 4.7 Hz), 3.83 (t, 8 H, J = 5.1 Hz), 4.22 (t, 8 H, J = 5.1 Hz), 7.09 (d, 8 H, J = 8.8 Hz), 7.76 (s, 4 H), 8.03 (d, 4 H, J = 8.5 Hz), 8.27 (d, 4 H, J = 8.5 Hz), 8.30 (d, 8 H, J = 8.8 Hz). FABMS: (m/z) 1220 (M+H⁺). For 11: pale yellow crystals (m.p. 207°C). ¹H NMR (CDCl₃): δ 1.63 (brs, 4 H), 2.34 (brs, 4 H), 3.75–3.48 (br, 32 H), 3.88 (dd, 8 H, J = 5.9, 13.3 Hz), 4.25 (dd, 8 H, J = 5.7, 10.2 Hz), 4.34 (dd, 4 H, J = 6.2, 11.5 Hz), 7.14 (d, 4 H, J = 8.9 Hz), 7.24 (d, 4 H, J = 8.9 Hz), 7.72 (s, 4 H), 8.05 (d, 4 H, J = 8.5 Hz), 8.27 (d, 4 H, J = 8.4 Hz), 8.32 (d, 4 H, J = 8.5 Hz), 8.42 (d, 4 H, J = 8.9 Hz), 8.45 (d, 4 H, J = 8.9 Hz). FABMS: (m/z) 1329 (M+H⁺).
between the two rings of catenane 10, metallation of 10 by addition of Cu(CH$_3$CN)$_4$·BF$_4$ was performed to afford the chelate complex 12. Without isolation, the condensation was carried out using adipoyl dichloride to give the black precipitate 13, which was not soluble in CH$_2$Cl$_2$ but was soluble in DMF or CHCl$_3$. Demetallation of 13, was performed to give a yellow amorphous powder 14 in 66% yield based on the amount of catenane 10. The $^1$H NMR spectrum of 14 in CDCl$_3$ showed broadened peaks, indicating that the mobility of 14 was restricted. The signal assigned to the α-proton (δ 3.08) of the amine group of the azaethylene glycol tether disappeared completely. The existence of the amide group was verified by IR spectral measurements (1650 cm$^{-1}$). Gel permeation chromatography analysis of 14 was performed in DMF eluent, showing a shorter retention time than that of the monomer 10. The $M_n$ (number-average molecular weight) of 14 was calculated to be almost $8.1 \times 10^5$ ($M_n/M_w = 4.1$) against polystyrene standard.

In summary, we have demonstrated that the reaction between two rings of [2]catenane can be switched by use of chelation to copper(1) ion.

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References


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