

Short Communication

## Synthesis and Switchable Condensation Reaction of Bifunctional [2]Catenane

Satoru Shimada,\* Keiichiro Ishikawa and Nobuyuki Tamaoki\*

National Institute of Materials and Chemical Research, 1–1 Higashi, Tsukuba, Ibaraki 305, Japan

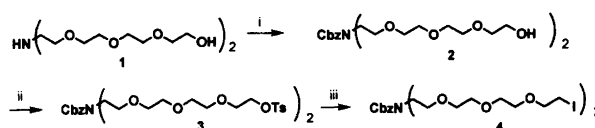
Shimada, S., Ishikawa, K. and Tamaoki, N., 1998. Synthesis and Switchable Condensation Reaction of Bifunctional [2]Catenane. – Acta Chem. Scand. 52: 374–376. © Acta Chemica Scandinavica 1998.

Syntheses of mechanically interlocked molecules such as catenanes and rotaxanes have been intensely developed over the past 15 years.<sup>1,2</sup> Recently much attention has been devoted to the reactions,<sup>3–5</sup> photochemistry,<sup>6</sup> and electrochemistry<sup>2</sup> 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,<sup>3</sup> poly[2]catenane,<sup>4,7</sup> and a pretzel-shaped molecule<sup>5</sup> using mechanically interlocking structures as templates. We have also tried to synthesize bifunctional [2]catenane<sup>8</sup> and [2]rotaxane<sup>9</sup> 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 **10** with azaethyleneglycol tethers was synthesized on the basis of the method developed by Sauvage *et al.*<sup>1</sup> 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**)<sup>10</sup> was protected as a benzylcarbamate (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 approach<sup>1</sup> 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 Cs<sub>2</sub>CO<sub>3</sub> in DMF at 65 °C in 40% yield (Scheme 2). The copper chelate formed immediately on addition of a CH<sub>3</sub>CN

\* To whom correspondence should be addressed.

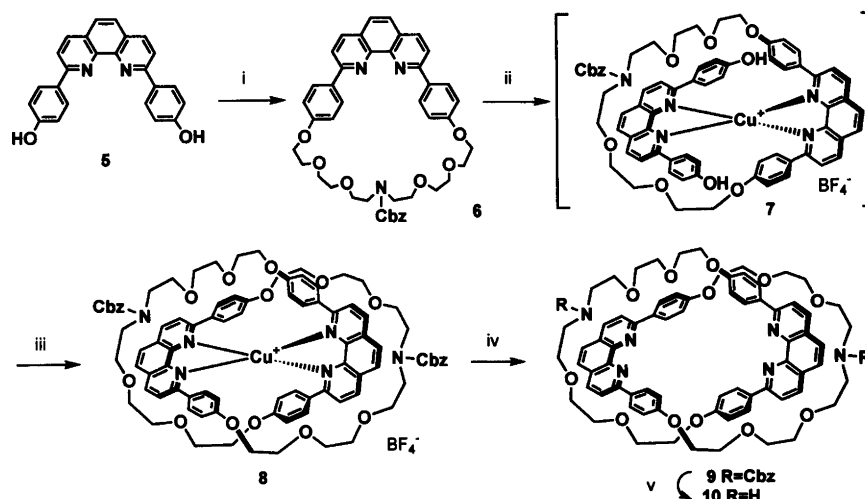


Scheme 1. Synthesis of diiodide **4**: i, CbzCl, K<sub>2</sub>CO<sub>3</sub>, EtOH, rt, 12 h, 97%; ii, TsCl, pyridine, cat. DMAP, CH<sub>2</sub>Cl<sub>2</sub>, rt, 12 h, 80%; iii, NaI, acetone, rfl., 12 h, 98%.

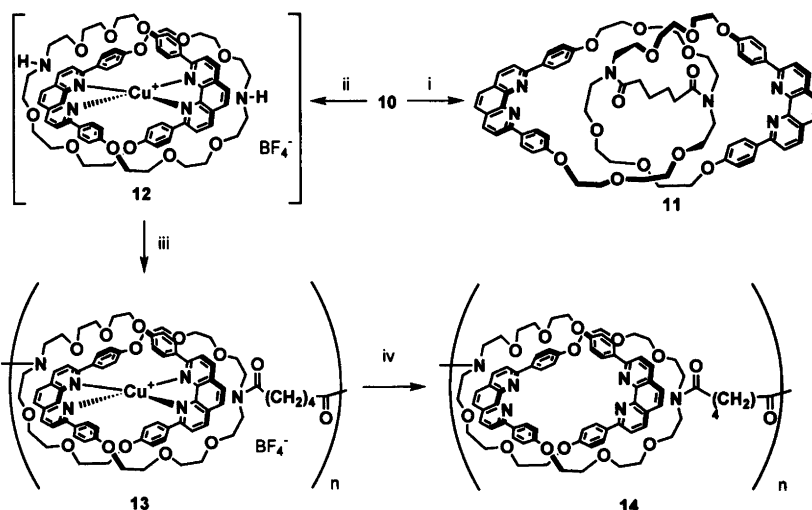
solution of Cu(CH<sub>3</sub>CN)<sub>4</sub>·BF<sub>4</sub> to the cyclic phenanthroline **6** in DMF. Addition of the phenanthroline **5** to this chelate gave the complex **7**. The alkylation of **7** with the iodide **4** afforded the catenated complex **8** in 30% yield. Demetallation of **8** was performed with KCN in CH<sub>3</sub>CN–H<sub>2</sub>O to afford **9** in 86% yield. The Cbz group of **9** was removed with HBr–AcOH<sup>11</sup> to give the diamine **10**<sup>†</sup> in 82% yield.

The reaction between the catenated diamine **10** and adipoyl chloride was investigated. To the CH<sub>2</sub>Cl<sub>2</sub> solution of the diamine **10** was added adipoyl chloride in the presence of triethylamine. The condensation proceeded smoothly and the pretzel-shaped compound<sup>5</sup> **11** was obtained (78%) (Scheme 3). The chemical structure of **11** was verified by its <sup>1</sup>H NMR and FAB mass spectra. On the other hand, in order to prevent the equilibrium

<sup>†</sup> All new compounds gave satisfactory analytical and spectral data. Selected data for **10**: pale yellow crystals (m.p. 205 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 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<sup>+</sup>). For **11**: pale yellow crystals (m.p. 207 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 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, 4 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<sup>+</sup>).



**Scheme 2.** Synthesis of [2]catenane **10**: i, **4**,  $\text{Cs}(\text{CO}_3)_2$ , DMF,  $60^\circ\text{C}$ , 24 h, 40%; ii, **5**,  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ ,  $\text{CH}_3\text{CN}$ -DMF, rt, 1 h; iii, **4**,  $\text{Cs}(\text{CO}_3)_2$ , DMF,  $60^\circ\text{C}$ , 7 d, 30% (for two steps); iv, KCN,  $\text{CH}_3\text{CN}$ - $\text{H}_2\text{O}$ , rt, 10 min, 86%; v, HBr-AcOH, rt, 1 h, 82%.



**Scheme 3.** Condensation reaction of [2]catenane **10**: i,  $\text{ClOC}(\text{CH}_2)_4\text{COCl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{Et}_3\text{N}$ , rt, 78%; ii,  $\text{Cu}(\text{CH}_3\text{CN})_3\text{BF}_4$ ,  $\text{CH}_3\text{CN}$ , rt; iii,  $\text{ClOC}(\text{CH}_2)_4\text{COCl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{Et}_3\text{N}$ , rt; iv, KCN,  $\text{CH}_3\text{CN}$ - $\text{H}_2\text{O}$ , rt, 10 min, 66% (for three steps).

between the two rings of catenane **10**, metallation of **10** by addition of  $\text{Cu}(\text{CH}_3\text{CN})_4 \cdot \text{BF}_4$  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  $\text{CH}_2\text{Cl}_2$  but was soluble in DMF or  $\text{CHCl}_3$ . Demetallation of **13**, was performed to give a yellow amorphous powder **14** in 66% yield based on the amount of catenane **10**. The  $^1\text{H}$  NMR spectrum of **14** in  $\text{CDCl}_3$  showed broadened peaks, indicating that the mobility of **14** was restricted. The signal assigned to the  $\alpha$ -proton ( $\delta$  3.08) of the amine group of the azaethyleneglycol tether disappeared completely. The existence of the amide group was verified by IR spectral measurements ( $1650\text{ cm}^{-1}$ ). 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  $8.1 \times 10^5$  ( $M_w/M_n=4.1$ ) 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(I) ion.

**Acknowledgments.** This work was supported by the Proposal-Based Advanced Industrial Technology R&D Program (Research on 'Synthesis of Polymer Objects') of the New Energy and Industrial Technology Development Organization (NEDO) of Japan. We thank Dr. J.-P. Sauvage and Dr. Y. Geerts for discussion and advice. We also thank Dr. M. Asai, Dr. T. Shimizu and Dr. H. Matsuda for their help at various stages of the project.

## References

1. (a) Dietrich-Buchecker, C. O., Sauvage, J. P. and Kintzinger, J. P. *Tetrahedron Lett.* 24 (1983) 5095; (b) Dietrich-Buchecker, C. O. and Sauvage, J. P. *Tetrahedron* 46 (1990) 503.
2. Anelli, P. L., Ashton, P. R., Ballardini, R., Balzani, V., Delgado, M., Gandolfi, M. T., Goodnow, T. T., Kaifer, A. E., Philp, D., Pietraszkiewicz, M., Prodi, L., Reddington, M. V., Spencer, A. M. Z., Stoddart, J. F., Vincent, C. and Williams, D. J. *J. Am. Chem. Soc.* 114 (1992) 193 and references cited therein.
3. Harada, A., Li, J. and Kamachi, M. *Nature* 364 (1993) 516.
4. (a) Geerts, Y., Muscat, D. and Müllen, K. *Macromol. Chem. Phys.* 196 (1995) 3425; (b) Weidmann, J.-L., Kern, J.-M., Sauvage, J.-P., Geerts, Y., Muscat, D. and Müllen, K. *J. Chem. Soc., Chem. Commun.* (1996) 1243; (c) Muscat, Witte, A., Köhler, W., Müllen, K. and Geerts, Y. *Macromol. Rapid Commun.* 18 (1997) 233.
5. Jäger, R., Schmidt, T., Karbach, D. and Vögtle, F. *Synlett* 8 (1996) 723.
6. Chambron, J. C., Harriman, A., Heitz, V. and Sauvage, J. P. *J. Am. Chem. Soc.* 115 (1993) 6109.
7. Ashton, P. R., Huff, J., Menzer, S., Parsons, I. W., Preece, J. A., Stoddart, J. F., Tolley, M. S., White, A. J. P. and Williams, D. J. *Chem. Eur. J.* 2 (1996) 31.
8. Shimada, S., Tamaoki, N. and Ishikawa, K. *Abstracts of XXth International Symposium on Macrocyclic Chemistry* (1995) 6.
9. Tamaoki, N. and Shimada, S. *Acta Chem. Scand.* 51 (1997) 1138.
10. Maeda, H., Furuyoshi, S., Nakatsuji, Y. and Okahara, M. *Tetrahedron* 38 (1982) 3359.
11. Ishai, D. B. and Berger, A. *J. Org. Chem.* 17 (1952) 1564.

Received July 1, 1997.