

## Quantitative and Spontaneous Formation of a Doubly Interlocking [2]Catenane Using Copper(I) and Palladium(II) as Templating and Assembling Centers

Fumiaki Ibukuro,<sup>†,‡</sup> Makoto Fujita,<sup>\*,†,§,||</sup>  
Kentarō Yamaguchi,<sup>||</sup> and Jean-Pierre Sauvage<sup>\*,†</sup>

Laboratoire de Chimie Organo-Minérale  
UMR 7513 du CNRS, Université Louis Pasteur  
Insitut Le Bel, 4 rue Blaise Pascal  
67070 Strasbourg, France

The Graduate University for Advanced Studies  
Myodaiji, Okazaki 444-8585, Japan

Coordination Chemistry Laboratories

Institute for Molecular Science and CREST

Japan Science and Technology Corporation (JST)

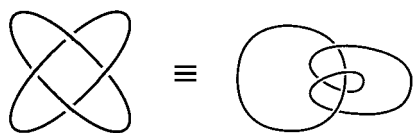
Myodaiji, Okazaki 444-8585, Japan

Chemical Analysis Center, Chiba University

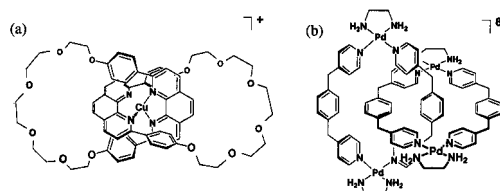
Inageku, Chiba 263-8522, Japan

Received July 9, 1999

Template strategies and self-assembly have recently undergone an explosive development, making possible the synthesis of many fascinating and complex structures using only relatively simple procedures.<sup>1</sup> By combining building blocks coming from various families of molecules, the structure of the resulting multicomponent systems can, in principle, be varied infinitely at will. Here, we report a new strategy for catenane synthesis,<sup>2</sup> which enabled us to obtain a 4-crossing [2]catenane quantitatively incorporating two different metal centers: 4 Pd(II) and 2 Cu(I).

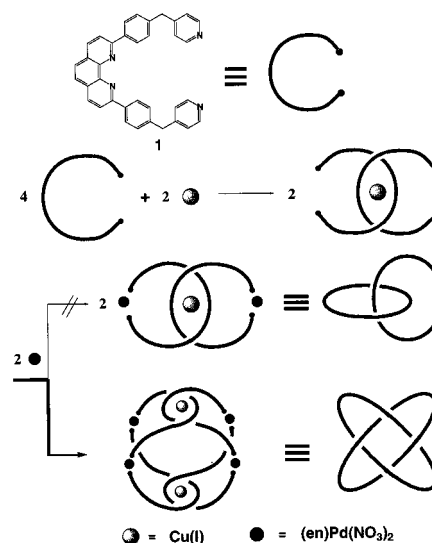


Doubly interlocking catenanes are chiral, and have complex topologies which have only been described recently.<sup>3</sup> Our approach is to combine the two methods, based on coordination chemistry, which are termed as “template” and “self-assembly” strategies. In the template strategy which has been developed in the course of the last 15 years, copper(I) complexes have been used as precursors, affording simple to topologically very complex catenanes.<sup>2c</sup> On the other hand, the self-assembly process furnishes



**Figure 1.** Prototypical interlocking molecules prepared by (a) template<sup>4</sup> and (b) self-assembly<sup>5</sup> strategies.

### Scheme 1. General Strategy for the Preparation of Doubly Interlocking [2]Catenanes



in one chemical step sophisticated structures, including interlocking rings, from very simple molecular fragments and under mild conditions.<sup>2j</sup> The two prototypical molecules made using these approaches are the copper(I) catenane<sup>4</sup> and the four-palladium interlocking ring system<sup>5</sup> of Figure 1. Several previous reports deal with catenane formation for which the ring-forming reaction is based on transition metal coordination.<sup>6–11</sup>

The first strategy we have used is summarized in Scheme 1. Ligand (1) contains both phenanthroline and pyridine units in its structure. It was expected that phenanthroline units would coordinate to Cu(I) and pyridine rings would interact with Pd(II), leading to the sequence of reactions indicated in Scheme 1. In fact, the hypothetical simple [2]catenane built around one Cu(I) center only would be highly strained and thus very unstable. It was anticipated that the doubly interlocking dimer-like structure of Scheme 1 would be favored.

Indeed, following this route, the target catenane **3**<sup>10+</sup> was quantitatively obtained, first as nitrate salt and, after anion exchange, as its hexafluorophosphate salt (Scheme 2). The reaction of the pyridine-based ligand (1) (0.03 mmol) and

<sup>†</sup> Université Louis Pasteur.

<sup>‡</sup> The Graduate University for Advanced Studies.

<sup>§</sup> Coordination Chemistry Laboratories, Institute for Molecular Science. Present address: Department of Applied Chemistry, School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan.

<sup>||</sup> CREST, Japan Science and Technology Corporation (JST).

<sup>||</sup> Chemical Analysis Center, Chiba University.

(1) Sauvage, J.-P.; Hosseini, W., volume Eds. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Ed.; Pergamon Press: Oxford, UK., 1996; Vol. 9 and references therein.

(2) For leading references in the field of catenanes, see: (a) Schill, G. In *Catenanes, Rotaxanes, and Knots*; Academic Press: New York, 1971. (b) Frisch, H. L.; Wasserman, E. *J. Am. Chem. Soc.* **1961**, *83*, 3789–3795. (c) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Rev.* **1987**, 759–810. (d) Chambon, J.-C.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Top. Curr. Chem.* **1993**, *165*, 131–162. (e) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725–2828. (f) Hunter, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 5303–5311. (g) Vögtle, F.; Dünwald, T.; Schmidt, T. *Acc. Chem. Res.* **1996**, *29*, 451–460. (h) Leigh, D. A.; Murphy, A.; Smart, J. P.; Deleuze, M. S.; Zerbetto, F. *J. Am. Chem. Soc.* **1998**, *120*, 6458–6467. (i) Hamilton, D. G.; Davis, J. E.; Prodi, L.; Sanders, J. K. M. *Chem. Eur. J.* **1998**, *4*, 608–620. (j) Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53. (k) Sauvage, J.-P.; Dietrich-Buchecker, C. O. In *Catenanes, Rotaxanes, and Knots*; Wiley-VCH: Weinheim, New York, Eds. 1999.

(3) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Commun.*, **1999**, 615.

(4) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kintzinger, J.-P. *Tetrahedron Lett.* **1983**, *24*, 5098.

(5) Fujita, M.; Ibukuro, F.; Hagihara, H.; Ogura, K. *Nature* **1994**, *367*, 720–723.

(6) Piguet, C.; Bernardinelli, G.; Williams, A. F.; Bocquet, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 582.

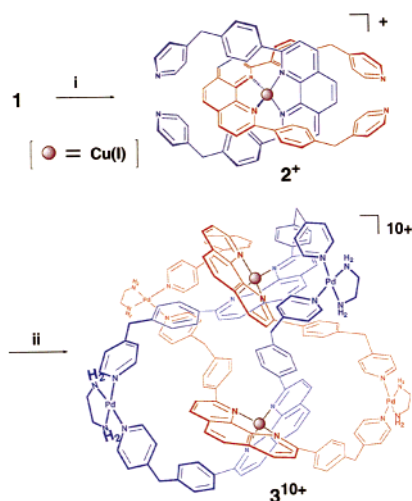
(7) Cárdenas, D. J.; Gaviña, P.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1997**, *119*, 2656–2644.

(8) Cárdenas, D. J.; Sauvage, J.-P. *Inorg. Chem.* **1997**, *36*, 2777–2783.

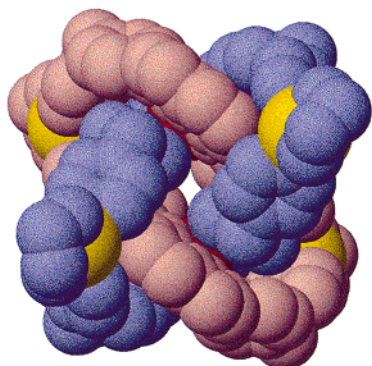
(9) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494 and references therein.

(10) Whang, D.; Park, K.-M.; Heo, J.; Ashton, P.; Kim, K. *J. Am. Chem. Soc.* **1998**, *120*, 4899–4900.

(11) Mingos, D. M. P.; Yau, J.; Menzer, S.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1894–1895.

Scheme 2. Preparation of  $3^{10+}$  <sup>a</sup>

<sup>a</sup> (i)  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (0.5 equiv to **1**); (ii)  $(\text{en})\text{Pd}(\text{NO}_3)_2$  (2.0 equiv to  $2^+$ ).



**Figure 2.** A molecular modeling of  $3^{10+}$  optimized by MM2 force-field calculation with Cerius<sup>2</sup> 3.5 package program. For simplicity, only one enantiomer is represented throughout the paper.

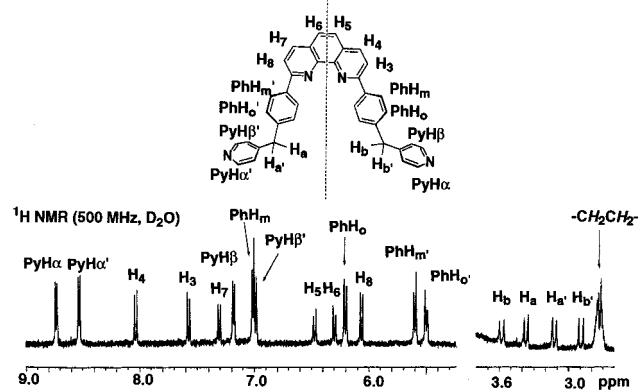
$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (0.015 mmol) in acetonitrile (1 mL) immediately gave the catenane precursor ( $2^+$ ). To this mixture, an aqueous solution (1 mL) of  $(\text{en})\text{Pd}(\text{NO}_3)_2$  ( $\text{en} = 1,2$ -diaminoethane, 0.03 mmol) was added, and the reaction mixture was stirred for 1 h at room temperature to give the doubly interlocking catenane compound ( $3^{10+}$ ). This quantitative catenane formation was monitored by NMR experiment when the reaction was carried out in a deuterated solvent. The reaction solution was poured into aqueous  $\text{KPF}_6$  (0.6 mmol, 5 mL) to give a red-brown precipitate, which was filtered and dried. With this simple method, catenane  $3^{10+}$  was isolated in almost quantitative yield as  $\text{PF}_6$  salt (92%). It was fully characterized by elemental analysis and various spectroscopic methods (1D- and 2D-NMR, and ESI-MS) as discussed later.<sup>12</sup>

This remarkable assembly process leads in a surprisingly efficient fashion to a 10-component architecture (six metals and four ligands). Catenane  $3^{10+}$  consists of two doubly interlocked 50-membered rings. An optimized structure is depicted in Figure 2, which shows the absence of any distortion in the framework. The possibility of a simple, two-crossing [2]catenane consisting of the same components is excluded because this molecule is unable to chelate two  $\text{Cu(I)}$  centers at the same time due to too large distortion of the chelated structure.

The 4-crossing [2]catenane structure was evidenced by ESI-MS and NMR spectroscopy. ESI-MS showed prominent peaks corresponding to  $[\mathbf{3}^{10+} \cdot n\text{PF}_6^-]^{(10-n)+}$  with  $n = 3, 4,$  and  $5$ .<sup>13</sup> These

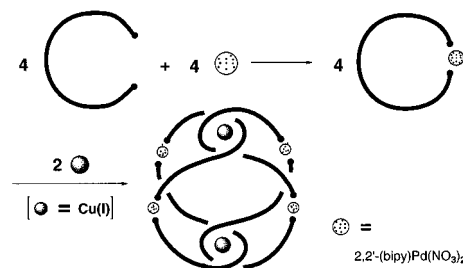
(12) Characterization of  $3^{10+}$ : also see Supporting Information.

(13) ESI-MS data of compound  $3^{10+}$ : ESI-MS ( $\text{CH}_3\text{CN}$ )  $m/z$  1289.1 [ $3^{10+} - (\text{PF}_6^-)_3$ ]<sup>3+</sup>, 930.4 [ $3^{10+} - (\text{PF}_6^-)_4$ ]<sup>4+</sup>, 715.3 [ $3^{10+} - (\text{PF}_6^-)_5$ ]<sup>5+</sup>.



**Figure 3.**  $^1\text{H}$  NMR spectrum of catenane  $3^{10+}$ .

## Scheme 3. Second Approach for the Preparation of Doubly Interlocking [2]Catenanes via Preformed Ring Molecules



data are clear evidence that the complex formed contains four  $\text{Pd(II)}$ , two  $\text{Cu(I)}$ , and four molecules of **1** and that it cannot be a simple [2]catenane.  $^1\text{H}$  NMR also strongly supported the structure of  $3^{10+}$ : (i) the four ligands of  $3^{10+}$  are all equivalent; (ii) each ligand is disymmetric as evidenced by the presence of the 14 individual signals in the aromatic region; and (iii) the two protons of the  $\text{PyCH}_2$  group (see Figure 3) are diastereotopic. Furthermore, 2D  $^1\text{H}$  NMR afforded the expected linkage connectivity of the ligand.

The second approach is based on the catenation reaction from preformed  $\text{Pd(II)}$ -linked components, thus taking advantage of the reversible nature of the  $\text{Pd(II)}-\text{N}$  bond (Scheme 3). Bipy ( $2,2'$ -bipyridine) was selected as an ancillary palladium(II) ligand instead of  $\text{en}$  so as to avoid coordination of the  $\text{Pd}$  centers to the phenanthroline unit of **1**, making the formation of square planar complexes very unlikely because of steric reasons. When **1** and  $(\text{bipy})\text{Pd}(\text{NO}_3)_2$  were mixed in  $\text{CD}_3\text{CN}:\text{D}_2\text{O}$  (1:1), quantitative formation of a monomer ring was observed.<sup>14</sup> Subsequent addition of  $\text{Cu}(\text{CH}_3\text{CN})_4^+$  led to the formation of a doubly interlocking catenane, which is analogous to  $3^{10+}$ , with bipy on each  $\text{Pd(II)}$ .<sup>14</sup> The formation of the same product by the two different routes confirms that it is a strict self-assembled unit. This reaction was also quantitative within the mixing time. As expected, bipy units are all equivalent, but each of them is disymmetric in good accordance with the expected structure. This procedure shows the potentiality of reversible ring-closing and -opening processes for constructing interlocking rings, analogous to previous work.<sup>5</sup>

**Acknowledgment.** We thank Dr. C. O. Dietrich-Buchecker for helpful discussion. We are also grateful to Dr. T. Kusukawa and J. D. Sauer for NMR. JSPS is appreciated with financial support to F.I.

**Supporting Information Available:** Experimental details, NMR (1D and 2D) and ESI-MS data of catenane complexes **3** and its bipy-protected analogue, and the optimized geometry of **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA992391R

(14) Physical properties of the bipy monomer ring and the bipy catenane (ESI-MS,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, Elemental Analysis, etc.): see Supporting Information.