Made-to-Order Assembling of [2]Catenanes from Palladium(II)-Linked Rectangular Molecular Boxes

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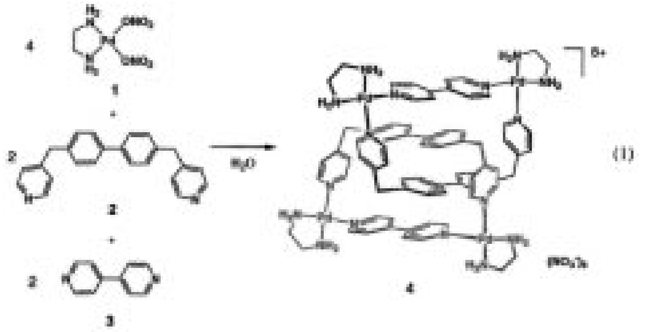
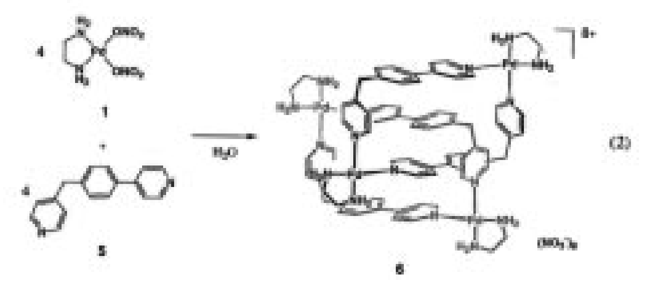
Linked-ring molecules or catenanes have long intrigued chemists because mechanically connected structures are expected to show unique properties which chemically connected molecules have never possessed.[1,2] An ideal methodology for catenane synthesis should allow chemists to design and obtain a variety of catenanes in quantitative yields without synthetic difficulties. Here we show such an ideal catenane synthesis can be achieved by metal-mediated supramolecular self-assembly.[3] That is, designed molecular boxes composed of transition metals and organic ligands are quantitatively catenated if the boxes possess a rectangular cavity with the van der Waals interplane separation of ca. 3.5 Å.[4,5] Thus eight building blocks—four metals and four ligands − are found to self-assemble into [2]catenanes consisting of two rectangular molecular boxes as shown in eqs 1 and 2.





When three compounds, **1**, **2**,[6] and **3**, were combined in water in a 2:1:1 stoichiometry, we observed the self-assembly of a single product which can be assigned as catenane **4**.[7] A simple NMR (Figure 1) agrees well with the structure of catenane **4**. In particular, a very high upfield shift of an aromatic proton appearing at δ 3.8 (assigned as ArH_β) is reliable evidence for the catenane structure. Neither other products nor impurities were found in the crude NMR. In addition, a satisfactory ESI-MS spectrum was obtained (m/z 1011 $[M - (NO_3)_2]^{2+}$; 653.4 $[M - (NO_3)_3]^{3+}$). Addition of $NaClO_4$ to the reaction solution gave **4** (ClO_4 salt) as a pure form in 94% isolated yield.

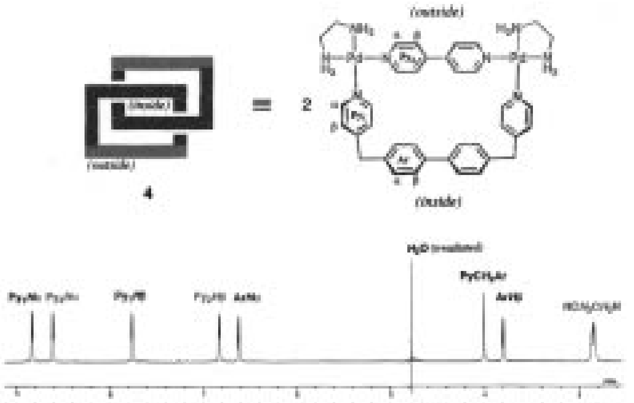


Figure 1. ^1H NMR of catenane **4** (ClO_4 salt) (500 MHz, D_2O, 25 °C, TMS as an external standard).

The stability of the solution structure of **4** is remarkable. The dissociation of the catenane into component rings was not observed even at a low concentration (1 mM)[8] or in a less polar media (D_2O-CD_3OD 1:1) in sharp contrast to the behavior of a previously reported catenane[2a] which completely dissociated under these conditions.

A single crystal was obtained from an aqueous solution of **4** (ClO_4 salt) and subjected to the diffraction study using an image plate method at −100 °C.[9] The crystal structure (Figure 2) shows that four aromatic systems very efficiently stack on each other

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(1) For recent development of highly efficient catenane synthesis, see the following: (a) Sauvage, J.-P.; Dietrich-Buchecker, C. O.; Chambron, J.-C. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Ed.; Pergamon Press: Oxford, 1996; Vol. 9, Chapter 2 and references therein. (b) Stoddart, J. F.; Raymo, F.; Amabilino, D. B. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Ed.; Pergamon Press: Oxford, 1996; Chapter 3 and references therein. (c) H-bonding approaches: Hunter, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 5303. Vögtle, F.; Dunnwald, T.; Schmidt, T. *Acc. Chem. Res.* **1996**, *29*, 451. Jonston, A. G.; Leigh, D. A.; Pritchard, R. J.; Deegan, M. D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1396. (d) Hamilton, D. G.; Sanders, J. K. M.; Davies, J. E.; Clegg, W.; Teat, S. J. *J. Chem. Soc., Chem. Commun.* **1997**, 897.

(2) (a) Fujita, M.; Ibukuro, F.; Hagihara, H.; Ogura, K. *Nature* **1994**, *367*, 720. (b) Fujita, M.; Ibukuro, F.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 4175. (c) Fujita, M.; Ibukuro, F.; Seki, H.; Kamo, O.; Imanari, M.; Ogura, K. *J. Am. Chem. Soc.* **1996**, *118*, 899.

(3) (a) Sanders, J. K. M. (Chapter 4); Baxter, P. N. W. (Chapter 5); Constable, E. C. (Chapter. 6); Fujita, M. (Chapter 7) In *Comprehensive Supramolecular Chemistry*; Sauvage, J.-P., Hosseini, M. W., Eds.; Pergamon Press: Oxford, 1996; Vol. 9. This volume includes excellent reviews of the metal-associated self-assembly. See also ref 1a. (b) *Transition Metals in Supramolecular Chemistry*; Fabbrizzi, L., Poggi, A., Eds.; Kluwer Academic Publishers: The Netherlands, 1994.

(4) An organic rectangular box: Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1547.

(5) The term “van der Waals interplane separation” is defined as a surface-to-surface distance in the cavity of the boxes. Though the interplanar separation (atom-to-atom distance) measured with X-ray or MM2 is actually about 7 Å, the surface-to-surface distance is shorter by double the van der Waals radius of an aromatic carbon (ca 3.5 Å).

(6) Preparation and physical data of **2**: see Supporting Information.

(7) Ligand **2** (0.05 mmol) and ligand **3** (0.05 mmol) were suspended in an aqueous solution (1.0 mL) of Pd(II) complex **1** (0.10 mmol), and the mixture was stirred at 70 °C for 2 h to give a clear solution. Addition of $NaClO_4$ aqueous solution (1 M, 1.0 mL) to the solution precipitated **4** (ClO_4 salt, 94% yield) as a pure cleam yellow powder. Physical data of **4**: see Supporting Information.

(8) Detection of **4** by ESIMS means **4** exisits even at ESIMS concentration (ca 0.1 mM).

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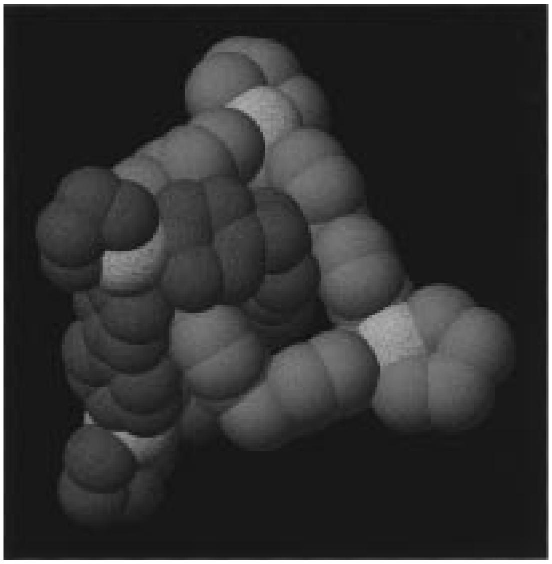
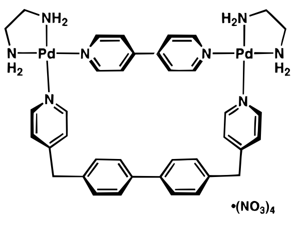


Figure 2. CPK presentation of the crystal structure of **4.**

with distances of 3.2−3.6 Å. Two rectangular boxes interlock so that a maximum aromatic stack is obtained. As a result, the cross angle of two rings was arranged to ca. 77 degree. Crystallography as well as NMR spectroscopy showed that the self-assembled catenane **4** consisted of a single conformational isomer with 4,4′-bipyridine located outside although there are many possible isomers which, for example, have 4,4′-bipyridine ligand(s) located inside. The exclusive formation of this isomer is most probably due to minimization of electrostatic repulsion among Pd^{2+} ions.

It is noteworthy that the remarkable thermodynamic stability of catenane **4** overcame a combination problem which should arise in a self-assembly from lager sets of components.[10] At least, formation of three component rings **7**−**9** is possible because their thermodynamic stability is comparable. Nevertheless, catenane **4** self-assembled as a sole product. This result shows that, *having an ideal van der Waals separation (3.5 Å) in its framework, only rectangular box* **7** *can be stabilized by fillind its cavity with another copy of itself.*



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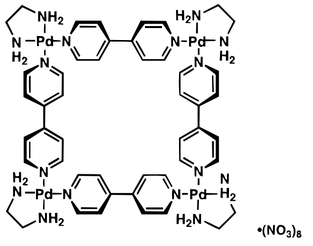

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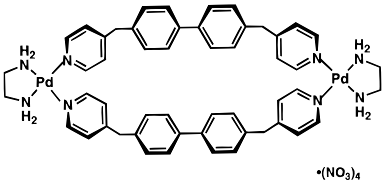

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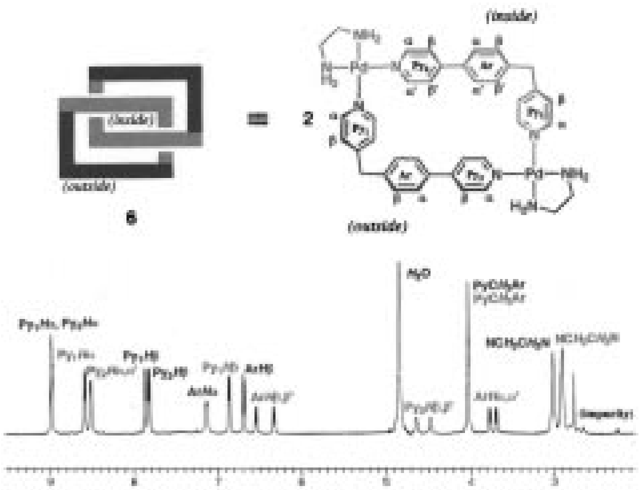

Figure 3. ^1H NMR of catenane **6** from the crude reaction solution (400 MHz, D_2O, 25 °C, TMS as an external standard).

Catenane **6** also self-assembled quantitatively from **1** and ligand **5** (eq 2).[11] Thus, **1** and **5**[12] were combined in a 1:1 ratio in D_2O. Careful analysis of the self-assembled product by 1D and 2D NMR techniques showed that observed signals are perfectly assigned as the catenane structure **6** (Figure 3).[13] A strong structural evidence is four aromatic signals appearing at very high field (Ar*H*α, δ 3.7; Ar*H*α′, d 3.8; $Py_2H\beta'$, δ 4.45; $Py_2H\beta$, δ 4.65) due to the efficient aromatic stack of four aromatic systems as observed in the solid structure of **4**. Interestingly, four couples on inside Py(1) and phenylene became unequivalent ($Py_2H\beta$ and $Py_2H\beta'$, Ar*H*α and Ar*H*α′, and Ar*H*β and Ar*H*β′).[14] This observation showed the restriction of rotation of the Py(1) and phenylene rings. In contrast, inside Py(2) and outside aromatic rings do not have such differentiated couples suggesting that these rings can freely rotate. The molecular weight was confirmed by ESI-MS with a series of $[M - (NO_3)_n]^{n+}$ ($n = 2-4$) peaks. Addition of $NaClO_4$ to the solution precipitated pure **6** as a ClO_4 salt in 87% isolated yield.

Two successful examples of catenane self-assembly led us to conclude that the self-assembly of [2]catenanes is now designable. That is, catenanes self-assemble from multispecies if component rings involve reversible bonds and have a van der Waals interplane separation of ca. 3.5 Å inside the cyclic framework. The procedure is very simple: just combine the components in water! Therefore, our method provides the simplest, most efficient, and made-to-order way to catenanes.

Supporting Information Available: Experimental procedures, physical data, and crystallographic data of **4** and **6** (70 pages). See any current masthead page for ordering and Internet access instructions.

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(9) Crystal data: trigonal, $P\bar{1}$ (#2); $a = 16.161(10)$, $b = 25.73(3)$, $c = 13.777(3)$ Å, $V = 4976(5)$ Å^3; $z = 2$; $F(000) = 2464$; $\mu(\mathrm{Mo}K\alpha) = 10.11$ cm^{-1}; $\lambda(\mathrm{Mo}\ K_\alpha) = 0.71070$ Å; temp, −100 °C.; 6590 reflections measured, 3944 observed ($I > 4.50\sigma(I)$); 1032 number of parameters; $R = 0.163$; $Rw = 0.197$. The high R value is due to unavoidable disorder of counterions.

(10) Multicomponent self-assembly: Baxter, P. N.; Lehn, J.-M.; DeCian, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 69. Baxter, P. N.; Lehn, J.-M.; Kneisel, B. O.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1978.

(11) Ligand **5** (0.06 mmol) was suspended in an aqueous solution (1.2 mL) of Pd(II) complex **1** (0.06 mmol), and the mixture was stirred at 60 °C for 0.5 h to give a clear solution. Addition of $NaClO_4$ aqueous solution (1 M, 1.5 mL) to the solution precipitated **6** (ClO_4 salt, 87% yield) as a pure cleam yellow powder. Physical data of **6**: see Supporting Information.

(12) Preparation and physical data of **5**: see Supporting Information.

(13) The structure of catenane **6** was also supported by X-ray crystallography. Despite many efforts, however, the high degree of disorder of nitrate ions and solvent molecules could not be avoided, and the quality of the diffraction data is poor ($R = 0.266$; $Rw = 0.331$). The crystal structure: see Supporting Information.

(14) The structure of catenane **6** is characterized in terms of "topological chirality". Due to this chirality, otherwise equivalent proton couples on the aromatic rings become diastereotopic if free turn of the rings is restricted. Preparation and optical resolution of a topologically chiral catenane: Mitchell, D. K.; Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 930.