DOSY Study on Dynamic Catenation: Self-Assembly of a [3]Catenane as a Meta-Stable Compound from Twelve Simple Components

Akiko Hori,[a] Kazuhisa Kumazawa,[a] Takahiro Kusukawa,[a] Dillip Kumar Chand,[a] Makoto Fujita,*[a] Shigeru Sakamoto,[b] and Kentaro Yamaguchi[b]

Abstract: Synthesis of [2]catenane **6** has been successfully achieved by the combination of Pd complex **1** and pyridines **2** and **3** at a molar ratio of 2:1:1 in D_2O. A mixture of square molecule **4** (prepared from **1** and **2**) and macrocycle **5** (obtained from **1** and **3**), in which the final ratio of **1**, **2**, and **3** was kept 2:1:1 reorganizes in D_2O/CD_3OD (1:1) to form **6** within one day. However, the same mixture in D_2O shows the formation of novel [3]catenane **7** along with the [2]catenane. In order to make **7**, the theoretical ratio of components **1**, **2**, and **3** should be 3:1:2. Thus, deliberately maintaining such ratio of the above-mentioned molecules, a higher proportion of the [3]catenane is observed in D_2O as found from ^1H NMR spectra of the system. Reorganization of the twelve components to form [3]catenane is supported by studies with the DOSY method. This method is a first attempt to separate, from a mixture, either catenanes or any other supramolecular self-assembly structures. CSI-MS studies further support the assigned catenane super structures **6** and **7**. All the results indicate that the [2]catenane is thermodynamically the most stable structure, while the [3]catenane is a meta-stable self-assembly.

Keywords: catenanes · NMR spectroscopy · palladium · self-assembly · supramolecular chemistry

Introduction

Catenanes as fascinating structures have been a stimulating area of research in the field of synthetic supramolecular chemistry for the last two decades.[1] Further, the use of these interlocked molecules in material research as building blocks for the construction of molecular scale machines and nanomaterials,[2] biological research for the study of DNA replication,[3] and many other applications are subjects of considerable current interest. Various promising synthetic methods exist in literature for the synthesis of catenanes including metal-[4] and organic-templating[5, 6] strategies, and self-assembly strategies.

We have been involved in using the self-assembly of pyridine-appended ligands in the presence of *cis*-protected Pd^{II}/Pt^{II} ions to obtain [2]catenanes.[7] In contrast to the cyclization in which covalent bond formation is the key step, our method is much easier since self-assembly directs to catenane formation in quantitative yields by simply combining suitably designed ligand/ligands with coordinatively unsaturated metal ions (e.g., $[Pd(en)(NO_3)_2]$) under suitable conditions. Such a self-assembly route, as an efficient approach for the construction of catenanes, was reported from our laboratory in 1994, when we observed a novel [2]catenane structure during a study on the metal-directed self-assembly of coordination macrocycles. Recently, our interest is extending towards the synthesis of [3]catenanes, which is of course a more synthetically challenging task. Due to the possibilities of synthetic and technical difficulties, there are not many reports, relative to those of [2]catenane, on the synthesis of [3]catenanes[8] or higher ordered catenanes.[9] In fact, the results presented herein is the first example of characterizing a [3]catenane by a metal-mediated self-assembly route.

The [3]catenane was obtained from the study on an alternative synthesis of a previously published [2]catenane.[7c] During the self-assembly process we observed the formation of a meta-stable intermediate [3]catenane along with the expected [2]catenane structure. The characterization was preliminarily performed by a proton NMR study of the system, followed by DOSY (diffusion-ordered NMR spectroscopy)[10] and CSI-MS (coldspray ionization mass spectrometry)[11] studies. In the DOSY method, two-dimesional NMR spectra are recorded in which the *x* axis represents the chemical shift value and the *y* axis the diffusion constant. The

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[a] Prof. Dr. M. Fujita, A. Hori, K. Kumazawa, Dr. T. Kusukawa,
Dr. D. K. Chand
Department of Applied Chemistry
Graduate School of Engineering, Nagoya University and CREST
Japan Science and Technology Corporation (JST), Chikusaku
Nagoya 464-8603 (Japan)
Fax: (+81)52-789-3199
E-mail: mfujita@apchem.nagoya-u.ac.jp

[b] S. Sakamoto, Prof. Dr. K. Yamaguchi
Chemical Analysis Center, Chiba University
Yayoicho, Inageku, Chiba 263-8522 (Japan)

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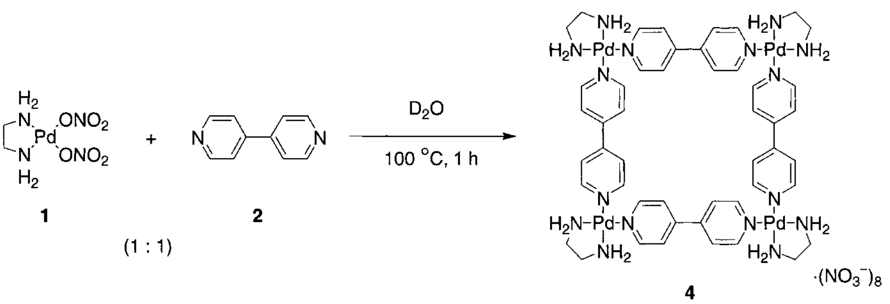
components of the mixture in the NMR tube possess different rates of diffusion, and their corresponding signals appear in different rows of the two-dimensional spectrum. These can be separated into the individual one-dimensional spectra for each component. Although the DOSY NMR method has been utilized earlier for transition-metal-containing coordination complexes[12] and THF-solvated *n*-butyllithium aggregates,[13] our report appears to be the first attempt of using a hitherto unused technique for the detection of either catenanes or any other supramolecular self-assembly structures. The [3]catenane was successfully separated and characterized by the DOSY method.

Results and Discussion

The [3]catenane was observed when we examined the reorganization of square molecule **4** and macrocycle **5** into [2]catenane **6**. Thus we first discuss the self-assembly of individual cyclic compounds (**4** and **5**) and then the formation of the [3]catenane.

Synthesis of square molecule 4 and macrocycle 5: Square molecule **4** and macrocycle **5** can be easily synthesized from the precursors **1**, **2**, and **3** as described in Experimental Section. The complexation reactions to obtain these molecules in aqueous solution go smoothly in a short time (< 1 h) and at 100 °C. Complex **4** was successfully prepared by combining **1** and **2** at a molar ratio of 1:1 in D_2O, instead of EtOH/MeOH/H_2O mixture as reported earlier [Eq. (1)].[14] The new Pd^{II} complex **5** was similarly synthesized from **1** and **3** [Eq. (2)] by mixing both components at a molar ratio of 1:1 in various kinds of solvent systems such as 1) D_2O, 2) CD_3OD, and 3) D_2O/CD_3OD (1:3).

In CD_3OD or D_2O/CD_3OD, signals that are consistent with the formation of macrocycle **5** are clearly obtained. However,



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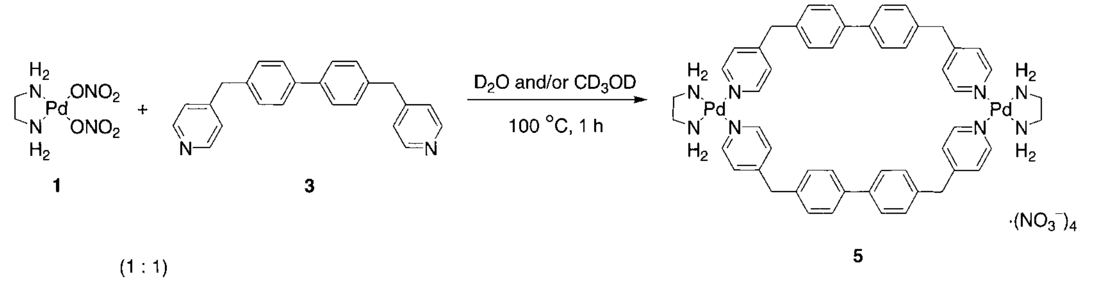

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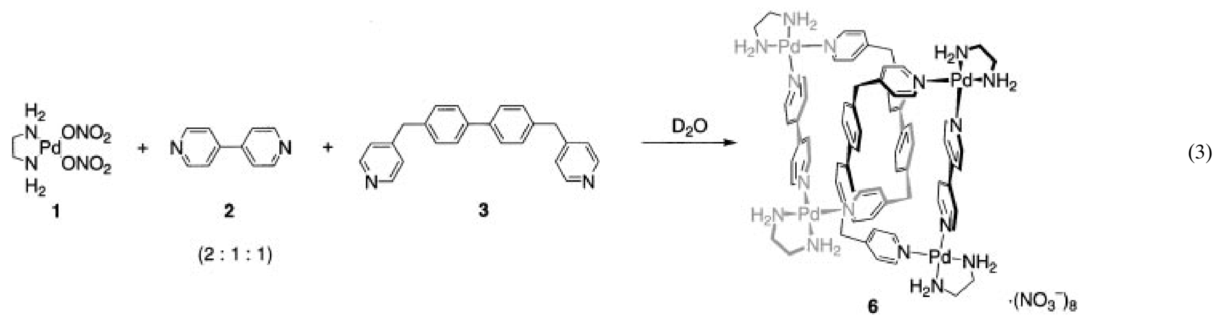

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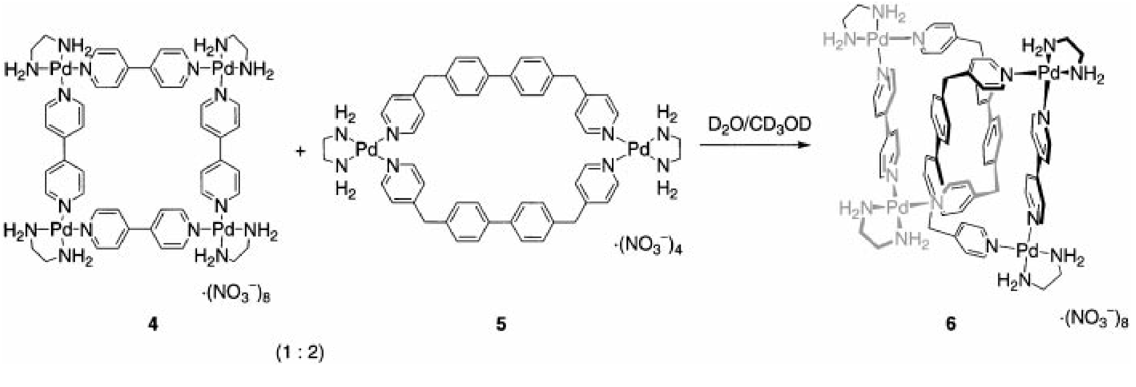


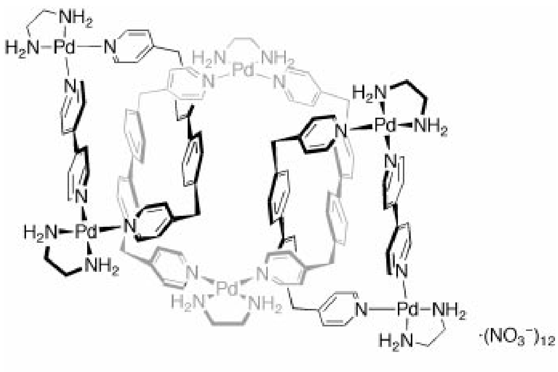
(4)

when the ^1H NMR spectrum was recorded in D_2O, no signal other than that of ethylenediamine moiety could be seen for this molecule, probably due to the slow conformational change of the macrocyclic framework on the NMR timescale. Evaporation of D_2O followed by the addition of CD_3OD and rerecording the NMR spectrum resulted in a spectrum which is similar to that obtained from the synthesis of the macrocycle utilizing CD_3OD as solvent. Further ^1H and ^{13}C NMR spectra for the complex were completely assigned with the help of H-H COSY and C-H COSY spectra.

Self-assembly of catenanes: We reported earlier[7c] that the combination of **1**, **2**, and **3** in one pot at a molar ratio of 2:1:1 in D_2O leads to the formation of [2]catenane **6** [Eq. (3)]. On the other hand, ligands **2** and **3**, upon reaction with **1**, give the square-type molecule **4** and macrocycle **5**, respectively [Eqs. (1) and (2)].

Since the self-assembly of these compounds is a thermodynamic event, we planned to combine **4** and **5** at a molar ratio of 1:2, for which the final ratio of the components **1**, **2**, and **3** would be 2:1:1, in expectation of the reorganization of **4** and **5** into catenane **6** [Eq. (4)].

During the study on the reorganization, we observed also the formation of a new molecule that is characterized as [3]catenane **7**. Subsequently, the stoichiometry of the components was tailored to prepare [3]catenane **7** in a higher proportion.



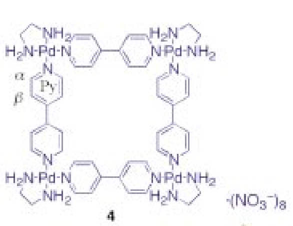
[3]catenane **7**

The structure of [2]catenane **6** has been unambiguously characterized by NMR spectroscopy, ESI-MS, and X-ray crystallographic analysis.[7c] In the ^1H NMR spectrum, five aromatic signals out of six possible aromatic signals appear in the usual region. Another aromatic signal, assigned as ArH_β, has a remarkable upfield shift that is a reliable evidence for the interlocked structure. The conformation of the molecule is that in which there is a minimum repulsion among the positively charged metal centers.

Similarly, in case of the structure of [3]catenane **7**, out of ten aromatic signals, two signals again exhibited a very high upfield shift as the corresponding hydrogens are positioned in the shielded region of interlocked molecule **7**. By using H-H COSY and NOESY spectra of the system, the complete assignment of all the peaks were carried out. The conformation may be suggested as that depicted here in which there is a compromise among the metal centers so as to achieve minimum repulsion. This conformation was again suggested by molecular mechanics calculation and is discussed vide infra.

Reorganization of 4 and 5 into [2]catenane 6 and [3]catenane 7

In D_2O/CD_3OD (1:1): In this mixed solvent we did not observe the formation of [3]catenane **7**, but a smooth reorganization of **4** and **5** into [2]catenane **6**. A solution of **4** in D_2O and **5** in D_2O/CD_3OD (1:3) were combined under the conditions given in Equation (4); thus the final solution was a 1:1 mixture of D_2O/CD_3OD. The solution was shaken in the NMR tube and kept at 25 °C and the ^1H NMR spectrum was monitored at different time intervals (Figure 1) at ambient temperature. After five minutes peaks due to the square molecule **4** and macrocycle **5** could be observed. After 30 minutes very small additional peaks appeared, which became pronounced after 2.5 hours. These new peaks resemble those of [2]catenane **6** and became further pronounced



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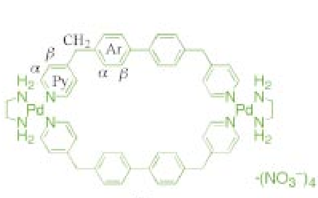

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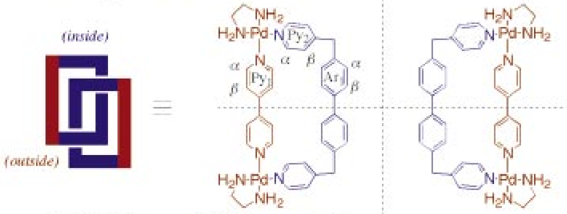


[2]catenane **6**

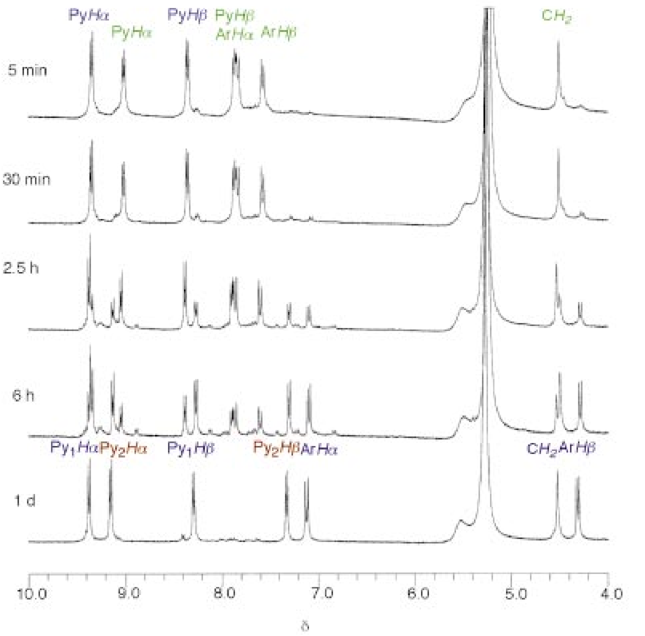


Figure 1. ^1H NMR spectra showing the self-assembly of [2]catenane **6** by reorganization of the molecular square **4** and macrocycle **5** at ambient temperature (300 MHz, D_2O/CD_3OD (1:1), 25 °C, TMS as an external standard).

after six hours. After one day no peaks other than those of **6** could be seen. This indicates the formation of solely the [2]catenane and conveys the idea that the product is a more stable assembly than compounds **4** and **5**.

In D_2O: The same experiment was performed in D_2O instead of the mixed solvent, while keeping other conditions similar to the reaction in D_2O/CD_3OD. The NMR spectrum was monitored in a similar fashion (Figure 2). After 5 min peaks due to square **4** were seen, but no peaks for macrocycle **5** were observed. This is in accordance with the fact that macrocycle **5** exhibits no peaks in D_2O. However, there were many small peaks observed. After six hours a new set of peaks were observed at the expense of the intensity of the peaks due to **4**. While peaks marked with a black disk were assigned for [2]catenane **6**, there still remained several unassigned signals (marked with asterisks). These new signals were analyzed very carefully, and we assigned them to the formation of the new [3]catenane **7**. After one day, signals of both **6** and **7** became clear along with those of **4**. However, after seven days the amount of **6** increased, while that of **7** decreased. Finally after sixteen days **6** became the major product with only a small amount of **7**. The ratio of compounds **4**, **6**, and **7** were calculated at different points in time from the integration ratio of the concerned signals in ^1H NMR spectra. After six hours, one day, seven days, and sixteen days the ratio observed for **4**:**6**:**7** are 2.0:0.7:1.0, 1.1:1.3:1.0, negligible:3.5:1.0, and 0.0:11.7:1.0, respectively.

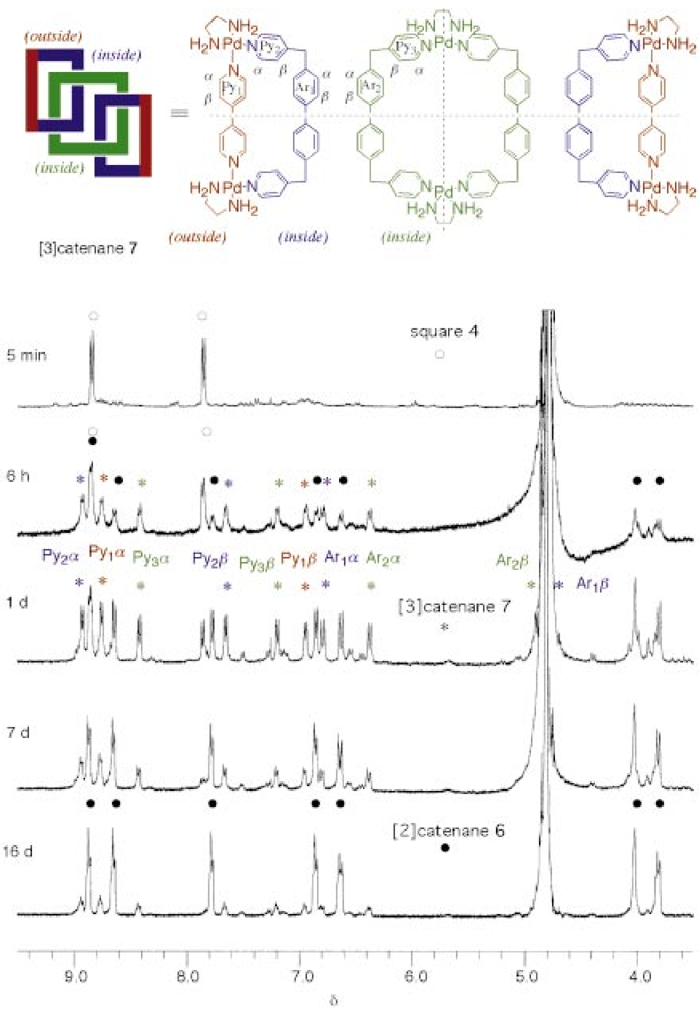


Figure 2. ^1H NMR spectra showing the formation and equilibrium of [2]catenane **6** and [3]catenane **7** from a mixture of the molecular square **4** and macrocycle **5** (300 MHz, D_2O, 25 °C, TMS as an external standard).

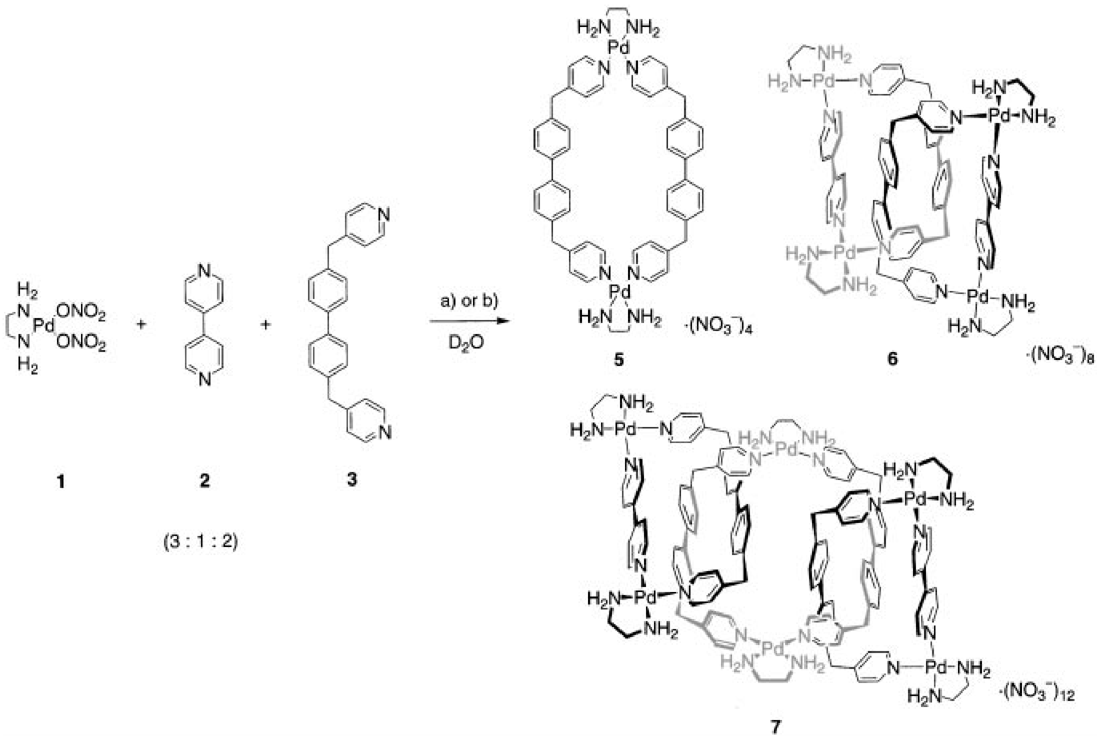
Synthesis of [3]catenane 7--a meta-stable product: Theoretically the ratio of **1**, **2**, and **3** necessary for the formation of the [2]catenane **6** is 2:1:1, while that for the formation of [3]catenane **7** is 3:1:2. Considering the results of the last section it is clear that even if we used the ratio of components for making **6**, we still observed the formation of **7**. Thus it should be worth using the molar ratio for making exclusively **7** in order to understand more about the equilibrium of **6** and **7**. Accordingly, we examined a one-pot reaction of compounds **1**, **2**, and **3** at a ratio of 3:1:2 in D_2O (Scheme 1 method a). The reaction was carried out at 60 °C for 30 minutes, and the ^1H NMR spectrum was then recorded. The data showed the formation of [2]catenane **6** and [3]catenane **7** in a ratio of 4.0:1.0. Macrocycle **5**, though not observed in the spectrum, must be formed in the same amount as [2]catenane **6**. This result suggests that the equilibration between **5**, **6**, **7** favors the [2]catenane.

The reorganization of **4** and **5** gave a higher proportion of **7** as a meta-stable component as discussed earlier. Thus we examined the reorganization of **7** from **1**, **2**, and **5** (**5** was generated in situ from **1** and **3**), for which the final ratio of the components **1**, **2**, and **3** would be 6:2:4 (Scheme 1 method b). First compounds **1** and **3** were mixed at a molar ratio of 3:2 in D_2O and were stirred at 60 °C for 30 minutes to obtain macrocycle **5**. Subsequently, the required amount of compound **2** (i.e., one equivalent molar ratio) was added. The mixture was brought to 25 °C and was monitored by ^1H NMR spectroscopy after six hours stirring. Here the ratio of **6** and **7** was calculated to be 2:3 (Figure 3). After 15 hours the ratio became 1:1 and slowly after a long time of 36 hours it became 4:1. This final ratio almost remained constant even after two to three weeks.

The above two experiments let us conclude that the equilibrium ratio of **6** and **7** under the reaction conditions is 4:1, but we can observe much higher proportion of [3]catenane **7** (the ratio being 2:3) as a meta-stable component during the reorganization process.[15]

Structure optimizations for catenanes were carried out using Cerius^2 program.[16] The energy-minimized structure is represented in Figure 4. The δH value for the formation of [3]catenane **7** from [2]catenane **6** and macrocycle **5** [Eq. (5)] was estimated to be $-24.06\ \mathrm{kcal\,mol^{-1}}$. Thus the formation of **7** is favored in terms of enthalpy. Probably the high entropy cost in the formation of [3]catenane makes it difficult to obtain [3]catenane **7** exclusively under thermodynamic control.

DOSY NMR study of [2]catenane/[3]catenane: [3]Catenane **7** obtained in a high proportion by the reorganization method was subjected to a DOSY NMR study. The solution of the reaction given in Equation (4) in D_2O after one day was found



Scheme 1. Self-assembly of [2]catenane **6** and [3]catenane **7** by two methods. a) Components **1**, **2**, and **3** were combined together in D_2O. b) Addition of **2** to a solution of **1** and **3** in D_2O (which assembles to form **5**).

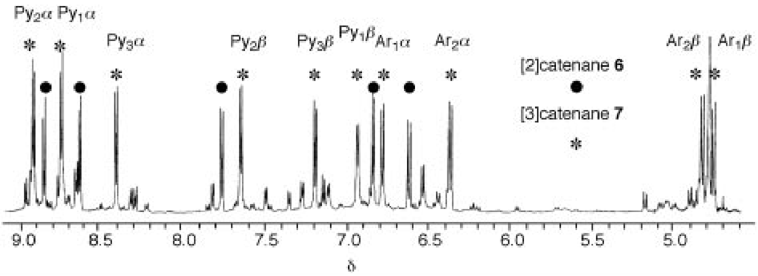
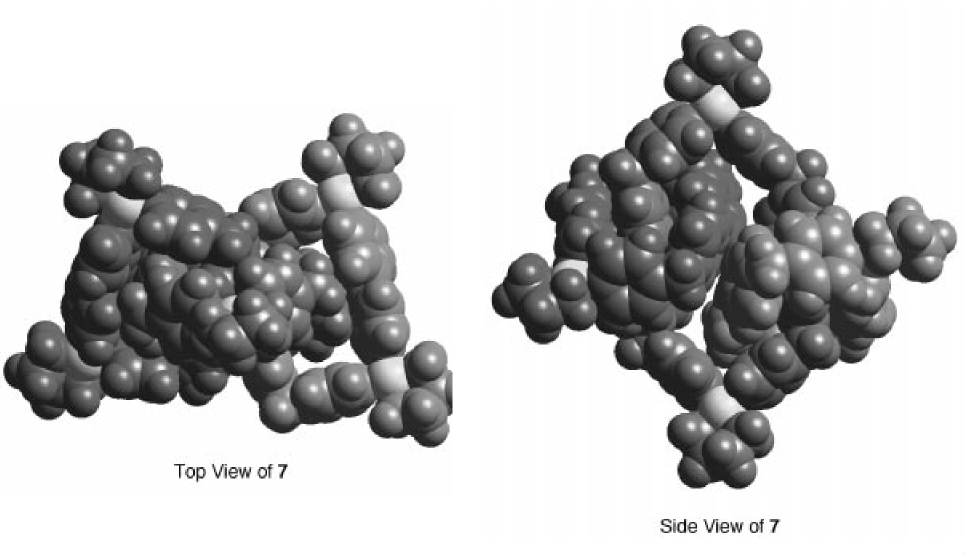


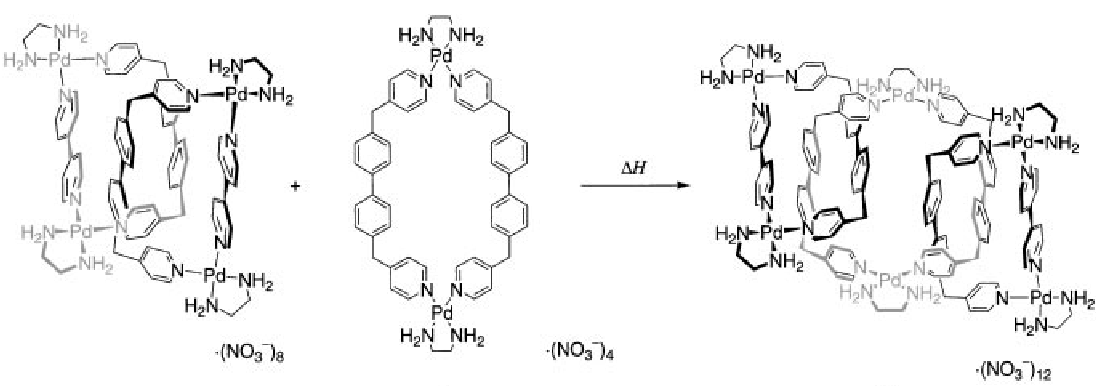
Figure 3. ^{1}H NMR spectrum obtained by combining the macrocycle **5**, which was prepared in situ, and the component **2** (spectrum recorded after 6 h), for which the final ratio of **1**, **2** and **3** is 3:1:2 (500 MHz, D_2O, 25 °C, TMS as an external standard).


Top View of 7

Side View of 7

Figure 4. Energy-minimized structure (MD and MM2) of the [3]catenane **7** performed with the Cerius^2 program.

to be a mixture of three major components. The differences in diffusion rates of the molecules allowed the separation of these components by the DOSY method and were assigned as the anticipated molecular square **4**, [2]catenane **6**, and [3]catenane **7** (Figure 5). Similarly, the solution of the reaction shown in Scheme 1 by method b (after 6 h) showed the existence of **6** and **7** (Figure 6). We observed another component in this mixture, which was seen as very small peaks in the earlier study of the ^{1}H NMR spectrum (see Figure 3) and were not assigned. The new component can be seen in the middle region between the slices a and b of Figure 6. The DOSY study indicates that the size of the new molecule is between that of **6** and **7**. This component is assumed to be different kind of [2]catenane, such as **8**, which is formed during the conversion of **7** to **6**. Existence of structure **8** was supported by CSI-MS as described below.



6 **5** **7** (5)

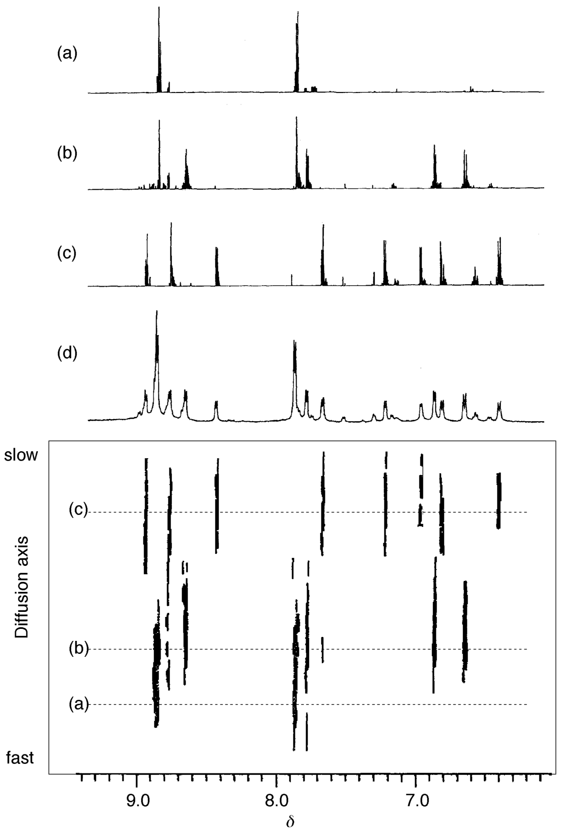


Figure 5. Diffusion-ordered ^{1}H NMR (DOSY) spectrum of a solution obtained from the reorganization of **4** and **5** in D_2O. The slices of the two-dimesional DOSY spectrum for the diffusion coefficients of a) the molecular square **4**, b) [2]catenane **6**, and c) [3]catenane **7** are shown. d) Complete ^{1}H NMR spectrum of the mixture.

CSI-MS study: CSI-MS has been proved as a powerful tool to characterize labile self-assembling metal complexes in solution.[11] Thus the solution of the reaction shown in Scheme 1 (method b) was subjected to CSI-MS study to obtain the exact mass of the catenanes as suggested by NMR spectroscopic study. The peaks were observed for catenanes **6**, **7**, and **8** (Figure 7). The peak at *m/z* 1012 corresponds to $[\mathbf{6}-2\,NO_3]^{2+}$ and that at 1071 can be assigned to $[\mathbf{7}-3\,NO_3]^{3+}$ confirming the existence of [2]catenane and [3]catenane, respectively. Further the peaks at 1102 can be assigned as $[\mathbf{8}-2\,NO_3]^{2+}$; this confirms the formation of the proposed species of intermediate size concluded earlier from DOSY study.

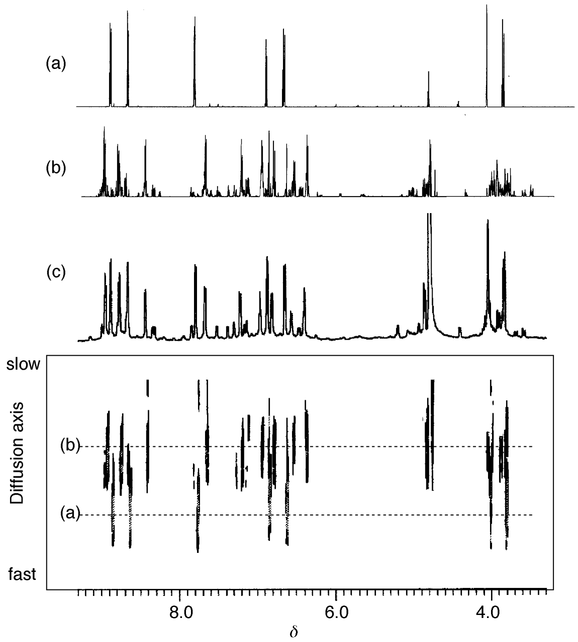
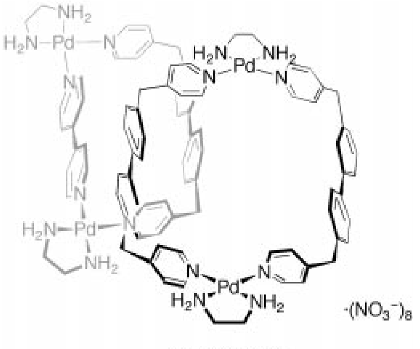


Figure 6. Diffusion-ordered ^{1}H NMR (DOSY) spectrum of a solution obtained from the self-assembly of the components **1**, **2**, and **3**. The slices of the two-dimensional DOSY spectrum for the diffusion coefficients of a) the [2]catenane **6** and b) [3]catenane **7** are shown. c) Complete ^{1}H NMR spectrum of the mixture.



[2]catenane **8**

In conclusion, the findings present here indicate that while the [2]catenane is a thermodynamically stable product, a kinetically stable [3]catenane exists during the process of the self-assembly. It might be possible to achieve the formation of

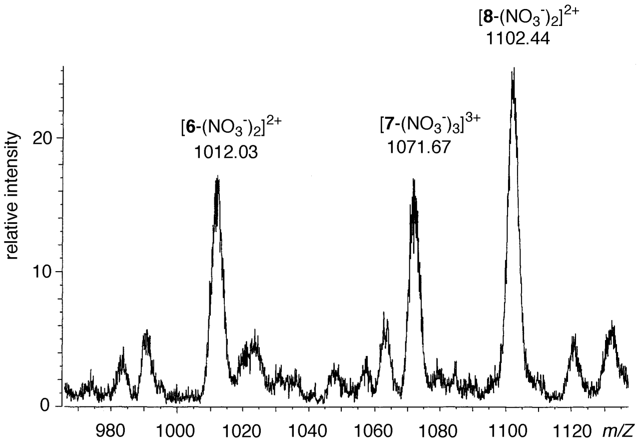


Figure 7. CSI-MS of a mixture of [2]catenane **6**, [3]catenane **7**, and [2]catenane **8**.

stable [3]catenanes by ligand design and through molecular mechanics calculations based on the results described above.

Experimental Section

Material and methods: All the chemicals were of reagent grades and used without any further purification. Ethylenediamine was used for the *cis*-protection of Pd^{II}, as described earlier,[14] to obtain $[Pd(en)(NO_3)_2]$ (**1**). While, 4,4′-bipyridyl **2** was obtained from Tokyo Kasei Ind., the ligand **3** was prepared following the procedure as reported earlier.[7c] The square complex **4** was also reported earlier from our group.[11] However, we have now prepared the complex **4** using an alternative solvent as described below. The NMR data of [2]catenane **6** obtained during the course of the reactions reported in this work agrees well with that of the previously published data of the same [2]catenane.[7c] Deuterated solvents were acquired from Cambridge Isotopic Laboratories and used as such for the complexation reactions and NMR measurements. ^1H NMR spectral data were recorded either on a JEOL AL300 MHz or Bruker DRX500 spectrometer. These data were collected at ambient temperature unless otherwise noted, and the chemical shift values reported here are with respect to external TMS standard. ^{13}C NMR, H-H COSY, and C-H COSY spectra were recorded on the Bruker AMX500 spectrometer. CSI-MS (Coldspray ionization mass spectroscopy) data were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700T, JEOL) equipped with the CSI source. DOSY spectra were collected on a Bruker DRX500 instrument equipped with a z axis gradient amplifier, operating at 500.13 MHz for ^1H observation, and a BBO probe with z axis gradient coil, at 300 K without spinning. The LED-BP (longitudinal eddy current delay, bipolar gradient pulse for diffusion) program[17] was performed for DOSY spectrum. The gradient duration was 3 ms, and the strength (G) was varied during the experiment (at least 128 times for each experiment). Diffusion times were 40 to 100 ms. Data processing was accomplished with XWINNMR 2.1 (Bruker) and ILT (inverse laplace transform, Bruker).

Synthesis of $[\{Pd(en)(4,4'\text{-bipyridyl})\}_4](NO_3)_8$ (4): Complex **1** (0.0232 g, 0.08 mmol) was added to a suspension of **2** (0.0125 g, 0.08 mmol) in D_2O (4 mL). The mixture was stirred at 100 °C for 1 h to affording the square complex **4** quantitatively. ^1H NMR (300 MHz, D_2O, 25 °C, TMS): $\delta = 8.6$ (d, 16H; Py_α), 7.6 (d, 16H; Py_β).

Synthesis of $[\{Pd(en)[4,4'\text{-}(4\text{-pyridylmethyl})\text{biphenyl}]\}_2](NO_3)_4$ (5): Complex **1** (0.0116 g, 0.08 mmol) was added to a suspension of **3** (0.0135 g, 0.004 mmol) in CD_3OD (4 mL). The mixture was stirred at 100 °C for 1 h to afford the macrocycle **5** quantitatively. The above reaction was carried out using D_2O as the solvent, for which a very broad pattern in the NMR spectrum was observed. However, evaporation of the solvent followed by the addition of CD_3OD gave an NMR spectrum which was similar to that obtained from the synthesis of the macrocycle with CD_3OD as the solvent. The complexation reaction to synthesize macrocycle **5** was further carried out in a solvent system of D_2O/CD_3OD (1:3). In this case the NMR signals were not broad, but indicative of the macrocycle. ^1H NMR (500 MHz, D_2O/CD_3OD (1:3), 25 °C, TMS): $\delta = 9.07$ (d, 8H; Py_α), 7.91 (t, 16H; Ar_α, Py_β), 7.65 (d, 8H; Ar_β), 4.55 (s, 8H; $ArCH_2$), 3.33 (s, 8H; en); ^{13}C NMR (125 MHz, D_2O/CD_3OD (1:3), 25 °C, TMS): $\delta = 156.64$ (q_c), 151.30 (Py_α), 139.57 (q_c), 137.74 (q_c), 129.77 (Ar_β), 127.53 and 127.46 (Ar_α/Py_β), 47.14 (en), 40.35 ($ArCH_2$); elemental analysis calcd (%) for $C_{52}H_{56}N_{12}O_{12}Pd_2 \cdot 3H_2O$: C 47.75, H 4.78, N 12.85; found C 47.87, H 4.65, N, 12.75.

Reorganization of 4 and 5

In D_2O/CD_3OD: A preformed solution of the macrocycle **5** in D_2O/CD_3OD (1:3) (0.4 mL, 10 mM in Pd^{II}) was added to a preformed solution of the square complex **4** in D_2O (0.2 mL, 20 mM in Pd^{II}) prepared as described above. The solution, which had a D_2O/CD_3OD ratio of 1:1, was stirred at 25 °C and then ^1H NMR spectra were recorded after 5 min, 30 min, 2.5 h, 6 h, and 1 d.

In D_2O: The reaction as mentioned above was repeated, but with D_2O only for all the steps, while keeping the concentration of ligands and metal ions fixed. ^1H NMR spectra were recorded after 5 min, 6 h, 1 day, 7 days and 16 days.

One pot synthesis of 7

Method a: Ligand **3** (0.0200 g, 0.06 mmol) was added to a suspension of **2** (0.0047 g, 0.03 mmol) in D_2O (3 mL) followed by the addition of complex **1** (0.0260 g, 0.09 mmol). The mixture was stirred at 60 °C for 0.5 h to obtain a clear solution. The ^1H NMR spectrum was recorded immediately.

Method b: Compounds **1** and **3** were stirred at 60 °C for 0.5 h and cooled down to RT and macrocycle **5** was formed. Compound **2** was added to this solution, and the reaction mixture was stirred for another 6 h. The ^1H NMR spectrum was then recorded.

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