A Molecular Lock

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Received December 23, 1994

We introduce here the concept of a "molecular lock" exploiting the dual character of a platinum(II)–pyridine (Pt(II)–Py) coordinate bond. This bond can be likened to a lock since it is irreversible ("locked") under ordinary conditions but becomes reversible ("released") in highly polar media at elevated temperature (Figure 1a). Incorporation of the molecular lock into a macrocyclic backbone made it possible to *irreversibly* interlock two molecular rings. Thus, molecular ring **1a** involving the Pt(II)–Py bond is on the lock in water and is not in equilibrium with other structures. However, once the lock is "released" by adding $NaNO_3$ and heating at 100 °C, an equilibrium between **1a** and its catenated dimer **2a** arises, and the equilibrium is strongly pushed by polar media toward the catenane. After self-assembling in a high yield, catenane **2a** is again locked up by cooling to room temperature and removing $NaNO_3$ (Scheme 1). This procedure completes molecular manipulation in which an organic architecture is built up molecule-by-molecule.

Interlocking ring structures continue to fascinate chemists, partly in expectation of serving molecular-scale devices.[1,2] Research in this area is now booming, mainly due to the recent development of templated synthetic strategies of Sauvage[3,4] and π-stacking-mediated self-assembly approaches of Stoddart.[5,6] Quite recently, the utilization of the labile nature of a palladium(II)–pyridine (Pd(II)–Py) coordinate bond has realized the quantitative self-assembly of [2]catenane **2b** from two component rings **1b**.[7] This molecular action is ascribed to the dissociation of the Pd(II)–Py bonds that causes a rapid equilibrium between **1b** and **2b**. However, the presence of the equilibrium means that [2]catenane **2b**, once formed, easily dissociates into two separate rings. If the labile coordinate bond can be frozen after the catenane assembles, a complete catenane that does not dissociate into two rings is obtained. Such a one-way formation of a catenane is now achieved in a platinum(II) counterpart system, as described below.

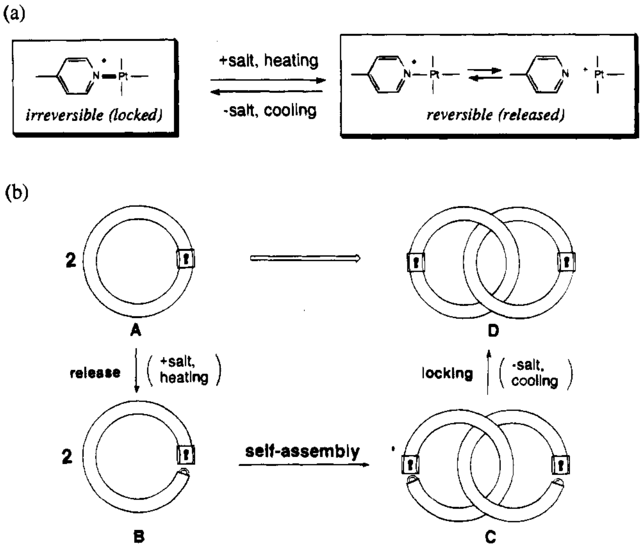
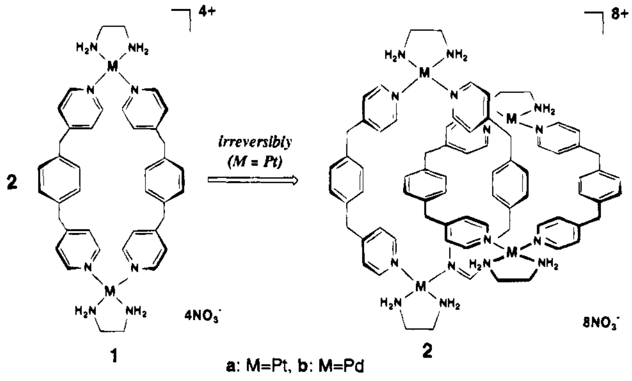
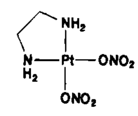


Figure 1. Schematic presentation of the molecular lock. (a) The dual character of a Pt(II)–Py coordinate bond. (b) Irreversible formation of a catenane from two complete rings by the use of the molecular lock.

Scheme 1



Pyridine-based ligand **4** (0.1 mmol) was suspended in D_2O solution (4 mL) of ethylenediamine–platinum(II) nitrate complex **3** (0.1 mmol), and the mixture was heated at 100 °C.



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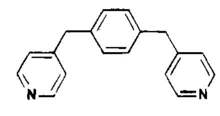

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Ligand **4** gradually dissolved, and after 12 h, ^1H NMR showed high-yield formation of molecular ring **1a** (Figure 2a). The formation of **1a** is kinetically controlled since the dissociation of the Pt(II)–Py bond under the reaction conditions is negligible.[8] However, after sodium nitrate was added to the solution of **1a** ($[NO_3^-] = 5$ M) and the solution was heated at 100 °C, a dramatic change in ^1H NMR spectroscopy was observed: signals of **1a** were gradually transferred into those of **2a**, and the complete formation of **2a** was observed after 24 h (Figure 2b). It was confirmed that catenane **2a**, isolated as its perchlorate salt from the solution, did not dissociate any longer into **1a** in D_2O even at 100 °C.

The overall one-way transformation of **1a** into **2a** is schematically illustrated in Figure 1b. Initially, a molecular ring is on the lock (A). The lock is then released by adding salt and heating (B), allowing the self-assembly of a catenated framework (C). Finally, this framework is locked by removing the salt and cooling (D).

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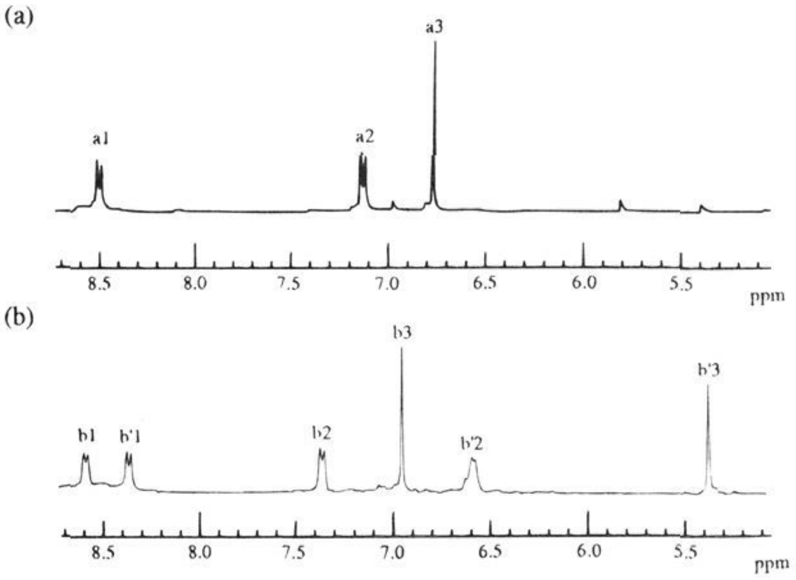


Figure 2. Spectroscopic observation of the transfer of **1a** into **2a** by releasing the molecular lock. Molecular ring **1a** (25 mM) was heated at 100 °C in D_2O solution of $NaNO_3$ (5 M). (a) After 0 h, signals a1, a2, and a3 are assigned as PyH_α, PyH_β, and C_6H_4 protons of **1a**, respectively. (b) After 24 h, signals b and b′ are referred to the outside and inside ligands of **2a**, respectively. Physical data of **1a** and **2a** have been reported.[7]

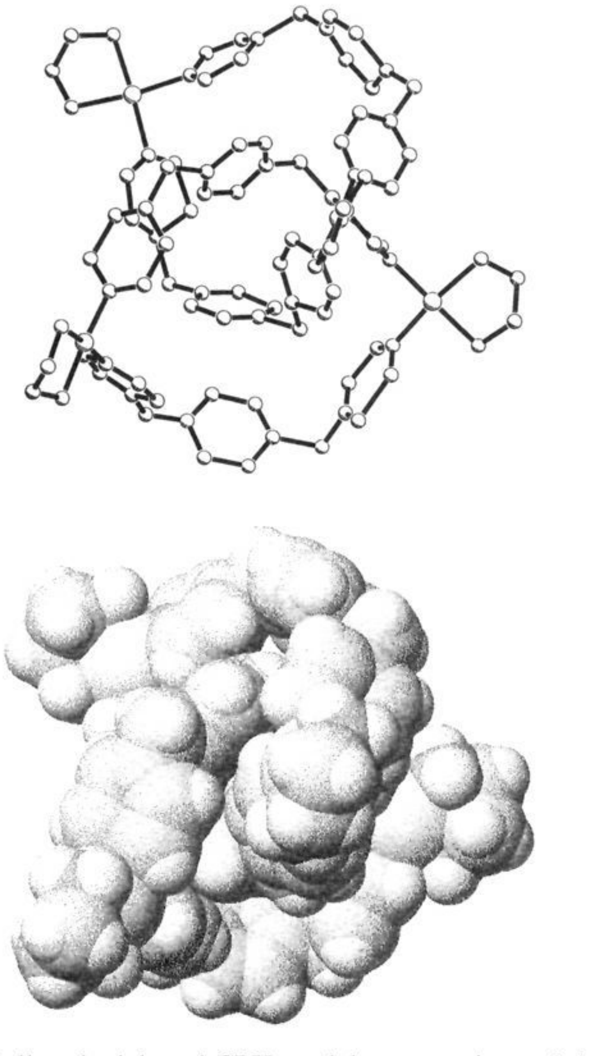


Figure 3. Ball-and-stick and CPK model presentations of the crystal structure of catenane **2a**.

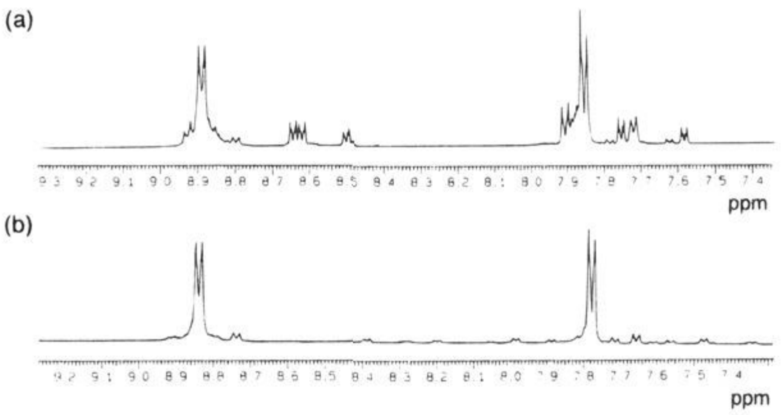
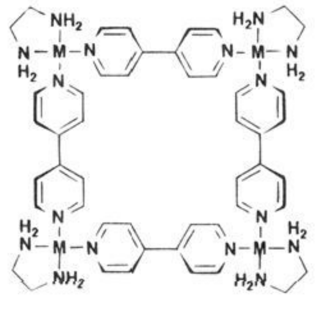


Figure 4. Spectroscopic observation of transfer of an oligomeric mixture into **5a** by releasing the molecular lock. The oligomeric mixture given by mixing **3** (10 mM) and 4,4′-bipyridine (10 mM) was heated at 100 °C in D_2O solution of $NaNO_3$ (5 M). (a) After 0 h. (b) After 24 h. Doublet signals appearing at δ 8.82 and 7.78 are referred to the PyH_α and PyH_β protons of **5a**, respectively. Physical data of **5a** have been reported.[8]

Crystallography showed that the catenated structure of **2a** exists (Figure 3).[9] Single crystals were obtained from aqueous solution of **2a** (12.5 mM) containing $NaNO_3$ (5 M) by allowing the solution to stand at 15 °C for several days. It was found that boat-shaped two molecular rings interlock with edge-to-face aromatic−aromatic contact[10] that probably induces the self-assembly of the catenated structure in polar media. Counter-anions and water molecules of crystallization seem highly disordered since two NO_3^- ions and water molecules were missing in the crystallographic study even in the measurement at 173 K.

The concept of the molecular lock was next applied to the preparation of the fully locked tetranuclear Pt(II) macrocycle **5a**. When **3** was treated with 4,4′-bipyridine (1 mol equiv) in D_2O, an intractable oligomer mixture was initially formed as kinetic products (Figure 4a). After the lock was released by addition of $NaNO_3$ and heating at 100 °C, however, the mixture was converged to the thermodynamically most favorable **5a** structure (Figure 4b), which was isolated in 50% yield as a locked form by adding $NaClO_4$. In the absence of $NaNO_3$, very slow transfer from kinetic products into **5a** was observed at 100 °C; however, more than a month was required to accomplish the transfer in a high yield.[8] A significant difference between **5a** and a palladium(II) counterpart **5b**[11] was demonstrated by comparing their stability. Addition of (en)Pd$(NO_3)_2$ (2.4 mol equiv) to **5b** in D_2O resulted in redistribution of products, giving a mixture of **5b** (ca. 50%) and two acyclic components having Pd:bpy = 1:2 and 2:3 stoichiometries. In striking contrast, **5a** was kept intact upon addition of **3** since its structure had been locked.



$\cdot(NO_3)_8$

5a: M = Pt
5b: M = Pd

Acknowledgment. This work was financially supported by the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Crystallographic data for **2a** (32 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instruction.

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[9] A very unstable single crystal of **2a** was carefully sealed in a capillary and used for the measurement. Crystal data are as follows: Empirical formula, $C_{80}H_{96}N_{24}O_{24}Pt_4 \cdot xH_2O$ (x = ca. 4.0); formula weight, 2558.14; crystal color, habit, colorless, prismatic; crystal dimensions, 0.25 × 0.25 × 0.50 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 17.351(2), b = 23.520(2), and c = 26.219(3) Å, β = 92.22(1)°; V = 10691(1) Å^3; space group, $P2_1/n$ (No. 14); Z value, 4; D_{calc} = 1.61 g cm^{-3}; F_{000} = 4992.00; μ (Cu Kα) = 98.15 cm^{-1}; radiation, Cu Kα (λ = 1.541 78 Å); temperature, 173.0 K; number of reflections measured, total 16 145, unique, 15 533 (R_{int} = 0.099); structure solution, direct methods; refinement, full-matrix least-squares; function minimized, $\sum\omega(F_o - F_c)^2$; number of observations ($I > 3.00\sigma(I)$), 4157; variables, 937; residuals, R = 0.116, R_w = 0.161.

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