Self-Assembly Process of Dodecanuclear Pt(II)-Linked Cyclic Hexagon

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S *Supporting Information*

ABSTRACT: The self-assembly process of a Pt(II)-linked hexagonal macrocycle consisting of six linear dinuclear Pt(II) units and six organic ditopic bent ligands was investigated. The process was monitored by ^1H NMR, and the intermediates in the self-assembly were analyzed by the $n-k$ analysis. It was found that a 1:2 complex of a dinuclear Pt(II) unit and an organic ditopic ligand was exclusively observed as an intermediate with a certain lifetime and that the reaction of the 1:2 complex is the rate-determining step in the supramolecular macrocycle formation. The key 1:2 complex was unambiguously characterized by ^1H and DOSY NMR and ESI-TOF mass measurement.

Macrocycles are of much importance for living organisms because of their highly selective recognition abilities for small molecules, ions, and polymers.[1] In general, macrocycles are synthesized by the cyclization of an acyclic chain molecule. For the synthesis of macrocycles by irreversible covalent bond formation, a high-dilution condition is required so as to prevent the undesired intermolecular reaction leading to too long chain molecules, which cannot convert into the macrocyclic structure.[2] However, it is difficult to perfectly prevent the undesired reaction, and the yields of the macrocycles are low without a few exceptions utilizing a template effect.[3] On the other hand, a supramolecular approach can nearly quantitatively afford a discrete macrocyclic structure from the mixture of the components, taking advantage of the reversibility of the chemical bond.[4] In self-assembly processes, it has been expected that even if longer oligomeric chains are formed, they can convert into the thermodynamically most stable macrocycle by the repetitive recombination of the bonds. At this stage, a question arises whether longer oligomeric chains are really produced during the self-assembly of the supramolecular rings, and if this is true, the next questions are how long the chain molecules grow and how they convert into the supramolecular macrocycle. Herein we report the self-assembly process of a cyclic hexagon, $[Pt_6 1_6]^{12+}$, consisting of six Pt(II) dinuclear complexes, Pt^{2+}, and six organic ditopic ligands **1** (Figure 1). The recently developed $n-k$ analysis and other measurements including NMR and ESI-TOF mass measurements revealed that a 1:2 complex, $[Pt1_2]^{2+}$, was exclusively observed as an intermediate with a certain lifetime during the self-assembly of the cyclic hexagon.

While plenty of examples for self-assembly have been known both in nature and in artificial systems, the detail analysis of the intermediates during self-assembly processes is rare because of
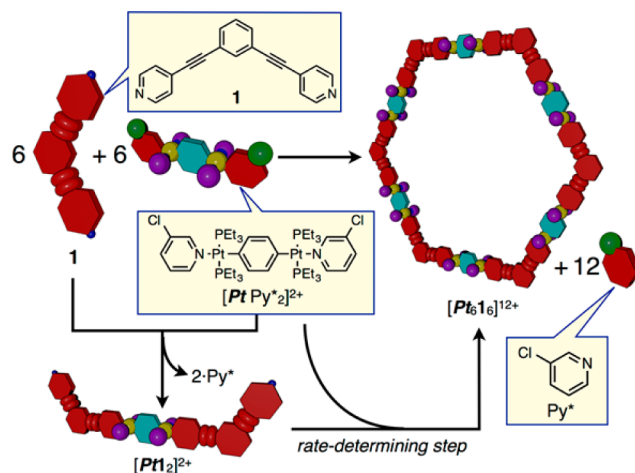

Figure 1. Schematic representation of the self-assembly of a supramolecular cyclic hexagon constructed from ditopic ligand **1** and Pt(II) dinuclear complex, $[PtPy^*_2]^{2+}$ (Pt^{2+}: $Pt(PEt_3)_2C_6H_4Pt(PEt_3)_2$, Py*: 3-chloropyridine). Py* was used so as to quantify Pt^{2+} in the intermediates formed during the self-assembly and to gain information about coordination environment around Pt(II) centers in the intermediates.

several difficulties of their investigation. In most cases, numerous kinds of intermediates can be produced during the self-assembly so that it is intrinsically impossible to detect and quantify all the intermediates. In addition, quick conversion and low symmetry of many intermediates would also make the observation of the intermediates virtually impossible. Recently we developed a method to indirectly analyze the intermediates produced during the coordination self-assembly ($n-k$ analysis).[5] The coordination self-assemblies (here we consider the formation of the cyclic hexagon in Figure 2) are constructed from metal ions (or complexes), **M**, and multitopic ligands, **L**. If the quantification of both the substrates and the products is possible, one can obtain the information about the average composition of the intermediates. Considering the fact that both **L** and the cyclic hexagon can be easily quantified by ^1H NMR, if the quantification of **M** becomes possible by ^1H NMR, the self-assembly process can be simply monitored by ^1H NMR measurement. To realize this, we attached ^1H NMR-detectable monodentate ligands, **X**, to the metal source, **M**. In this system, by quantifying the four species, **L**, MX_2, **X**, and the cyclic hexagon (M_6L_6), we can know the average composition of the
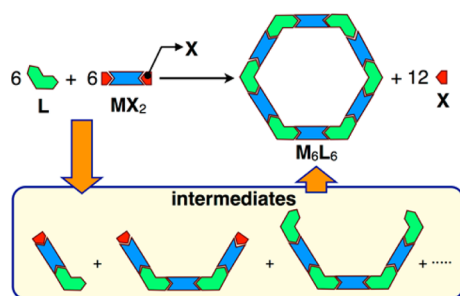
Figure 2. A concept of the $n-k$ analysis for the investigation of self-assembly process of coordination self-assemblies. If **L** and **X** have hydrogen atom(s) which can be detected by ^{1}H NMR, the quantification of **L**, **MX$_2$**, **M$_6$L$_6$**, and **X** becomes possible so that average composition of the intermediates, **M$_a$L$_b$X$_c$** (a, b, and c are numerical values), can be determined.

intermediates, **M$_a$L$_b$X$_c$**. Because a, b, and c are the ratio of each component in the intermediates, more elaborated parameters are defined as follows:

$$n = (N \cdot a - c)/b \qquad (1)$$

$$k = a/b \qquad (2)$$

where N is the number of the available binding sites on **M** for **L**. In the case of **Pt^{2+}**, N is 2. Parameters n and k stand for the average number of **M** (**M** is dinuclear **Pt^{2+}** in this case) binding to one molecule of **L** and metal to ligand ratio in the intermediates, respectively. As the experimentally obtained (n, k) value is the weight-average of the (n, k) values for all the intermediates, here we express the average (n, k) value as ($\langle n \rangle$, $\langle k \rangle$). As for the self-assembly of cyclic structures, n ranges from 1 to 2 and k ranges from 0.5 to 2. The (n, k) values for the possible structures with no more than ten **M** units for the assembly were calculated and were plotted to make an $n-k$ map (Figure 3). The linear intermediates are classified into three
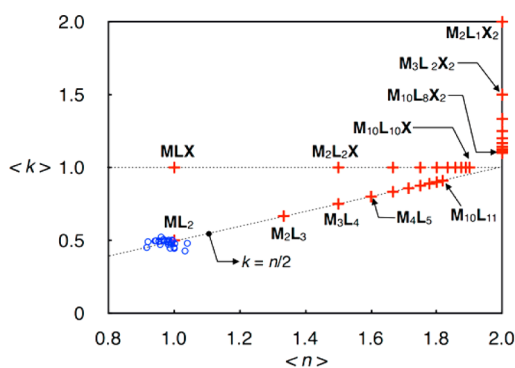

Figure 3. An $n-k$ map for the self-assembly of a cyclic hexagon. The (n, k) values for linear oligomers containing no more than ten **M** (**Pt^{2+}**) are indicated by red crosshairs. The experimentally obtained ($\langle n \rangle$, $\langle k \rangle$) values (5−20000 min) are indicated by blue open circles.

groups. The (n, k) values for **M$_a$L$_{a+1}$X$_0$**, both of whose terminals are **L**, are on the straight line of $k = n/2$. The (n, k) values for **M$_a$L$_{a-1}$X$_2$**, both of whose terminals are **X**, are on the straight line of $n = 2$. The (n, k) values for **M$_a$L$_a$X$_1$**, which have **L** and **X** on both the terminals, are on the straight line of $k = 1$. In every group, with the number of **M** in the intermediate increasing, its (n, k) value becomes close to (2, 1), which is the (n, k) value of the cyclic structures. Therefore, from the time

variation of the ($\langle n \rangle$, $\langle k \rangle$) value, one can determine which group of the intermediates is predominantly produced and how long the chain molecules grow during the self-assembly process.[6]

The cyclic hexagon investigated in this report is composed of dinuclear Pt(II) complexes, **Pt^{2+}**, and ditopic ligands with two pyridyl groups, **1** (Figure 1). A similar cyclic hexagon possessing a substituent on **1** was reported by Yang et al.[7] As various self-assembled structures using multinuclear organometallic Pt(II) complexes with organic ligands bearing pyridyl groups have been intensively reported by Stang[8] and others,[9] the cyclic hexagon, **[Pt$_6$1$_6$]$^{12+}$**, is expected to be a good prototype for investigating the self-assembly process of this class of entities. As mentioned above, in order to obtain the average composition of the intermediates, **M$_a$L$_b$X$_c$**, it is necessary to quantify the four species in the equation shown in Figure 2. For this purpose, we chose 3-chloropyridine (Py*) as a monodentate ligand, **X**. Because Py* possesses weaker coordination ability than the pyridyl groups of **1**, the equilibrium will shift toward the cyclic hexagon.

The self-assembly of the cyclic hexagon was monitored by ^{1}H NMR at 298 K in CD$_3$NO$_2$ (Figure 4), and the time variation
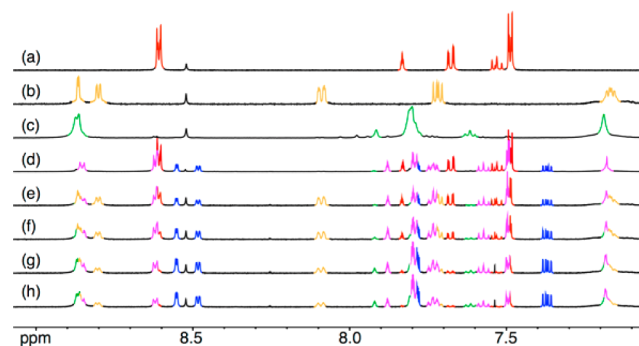
Figure 4. Partial ^{1}H NMR spectra (aromatic region) of each component for the cyclic hexagon and the reaction mixture (500 MHz, CD$_3$NO$_2$, 298 K). (a) **1**, (b) **[PtPy^*_2]$^{2+}$**, (c) **[Pt$_6$1$_6$]$^{12+}$**, (d) a mixture of **[Pt1_2]$^{2+}$**, **1**, and Py*, and the reaction mixture monitored at (e) 13.5 h, (f) 1 d, (g) 3 d, and (h) 6 d. Signals colored in red, yellow, green, blue, and purple indicate **1**, **[PtPy^*_2]$^{2+}$**, **[Pt$_6$1$_6$]$^{12+}$**, Py*, and **[Pt1_2]$^{2+}$**, respectively.

of the four components is shown in Figure 5a. The reaction reached the equilibrated state in 2 weeks to form the cyclic hexagon in 50% yield. The reason for the nonquantitative formation of the ring would be the coordination ability of Py* that slightly competes with the pyridyl groups of **1**. While the consumption of **1** reached over 90%, that of **[PtPy^*_2]$^{2+}$** was <70%. Interestingly, the release of Py* was the same as the consumption of **[PtPy^*_2]$^{2+}$** during the self-assembly. This means that the pyridyl groups of **1** occupied both the coordination sites of **Pt^{2+}** in the intermediates. This result suggests that the ligand exchange of Py* in **[PtPy^*_2]$^{2+}$** with **1** took place with strong positive cooperativity probably due to the *trans* effect on Pt(II) center[10] and that the ring formation from the intermediates needs intermolecular ligand exchanges with **[PtPy^*_2]$^{2+}$**.

Next we conducted the $n-k$ analysis to analyze the intermediates of the ring formation (Figure 3). The ($\langle n \rangle$, $\langle k \rangle$) value stayed at around (1.0, 0.5) from the beginning to the end of the assembly. The fact that the ring formation took place without any changes of the ($\langle n \rangle$, $\langle k \rangle$) value unambiguously
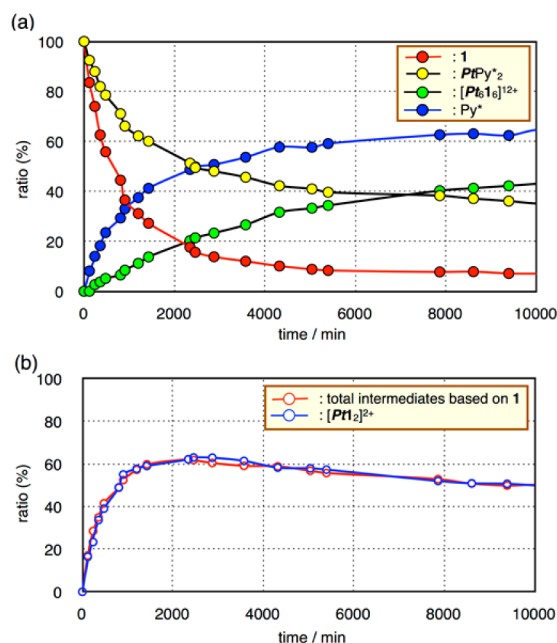
Figure 5. Time variation of (a) each species in the reaction mixture of the $[Pt_6 1_6]^{12+}$ assembly and (b) $[Pt 1_2]^{2+}$ and the abundance ratio of total intermediates based on **1**.

indicates that the species with (n, k) value of $(1.0, 0.5)$, that is $[Pt 1_2]^{2+}$, exists as a dominant intermediate and that the reaction of the intermediate, $[Pt 1_2]^{2+}$, should be the rate-determining step of the assembly of the cyclic hexagon. As $[Pt 1_2]^{2+}$, which was deduced from the $n-k$ analysis, is a simple 1:2 complex of Pt^{2+} and **1**, the intermediate was expected to be directly observable by ^1H NMR. We found several ^1H NMR signals for the ditopic ligand **1** that cannot be assigned to neither **1** nor the hexagon $[Pt_6 1_6]^{12+}$ (the signals colored in purple in Figure 4e–h). The most prominent feature is two chemically inequivalent pyridyl groups, which is well consistent with the symmetry of $[Pt 1_2]^{2+}$. We prepared $[Pt 1_2]^{2+}$ predominantly from a mixture of $[PtPy*_2]^{2+}$ and **1** in a 1:4 ratio (Figure 4d) and thoroughly investigated the species thus obtained. The existence of $[Pt 1_2]^{2+}$ was confirmed by ESI-TOF mass measurement (m/z at 749.24 assignable to $[Pt 1_2]^{2+}$) (Figure S2). DOSY measurement indicated that the species assigned to $[Pt 1_2]^{2+}$ has a log D value of -9.52, which is smaller than those of $[PtPy*_2]^{2+}$ (-9.31), **1** (-9.10), and Py* (-8.80) and is larger than that of $[Pt_6 1_6]^{12+}$ (-10.1) (Figures S3–S5). With the ^1H NMR signals of $[Pt 1_2]^{2+}$, we then evaluated the quantity of $[Pt 1_2]^{2+}$ during the self-assembly and found that it was the same as the total amount of the intermediates calculated from the differences between the consumption of **1** and the formation of the $[Pt_6 1_6]^{12+}$ ring (Figure 5b). These results indicate that $[Pt 1_2]^{2+}$ is the only intermediate with a certain lifetime for the self-assembly of the cyclic hexagon.

The self-assembly of the ring formation using $[Pt(CH_3CN)_2]^{2+}$ with a very weak monodentate ligand, CH_3CN, as the metal source was also investigated. Because the partial detachment of CH_3CN from $[Pt(CH_3CN)_2]^{2+}$ took place in CD_3NO_2, the accurate quantification of $[Pt(CH_3CN)_2]^{2+}$ is impossible so that we monitored the time variation of only **1** and the $[Pt_6 1_6]^{12+}$ ring. The yield of the ring reached 60% and the self-assembly finished within 17 h, much faster than the case using $[PtPy*_2]^{2+}$. In this case, we also found the signals assignable to $[Pt 1_2]^{2+}$ in the ^1H NMR spectra

(Figure S6). We compared the amount of $[Pt 1_2]^{2+}$ with the total amount of the intermediates evaluated based on **1**. Both were the same throughout the self-assembly (Figure S7), indicating that $[Pt 1_2]^{2+}$ is the only intermediate for a certain lifetime for the ring assembly from **1** and $[Pt(CH_3CN)_2]^{2+}$ and that monodentate ligand does not affect the self-assembly process of the ring.

It is worth noting that considering the fact that no other intermediates besides $[Pt 1_2]^{2+}$ were found during the self-assembly, it is certain that once $[Pt 1_2]^{2+}$ reacts with $[PtPy*_2]^{2+}$ or another $[Pt 1_2]^{2+}$, the following step(s) to the ring should take place quickly. Although it is not clear how the cyclic hexagon is formed from $[Pt 1_2]^{2+}$ and $[PtPy*_2]^{2+}$, two scenarios are envisaged. One is a stepwise mechanism that once $[Pt 1_2]^{2+}$ reacts with $[PtPy*_2]^{2+}$ or another $[Pt 1_2]^{2+}$ to form $[Pt_2 1_2 Py*]^{4+}$ or $[Pt_2 1_3]^{4+}$, respectively, either the pyridyl group of **1** or Py* in $[Pt_2 1_2 Py*]^{4+}$ or $[Pt_2 1_3]^{4+}$ becomes more reactive due to electric reasons to accelerate the following ligand exchanges. The other is a concerted mechanism that the cyclic hexagon is produced from a 3:3 reaction of $[Pt 1_2]^{2+}$ and $[PtPy*_2]^{2+}$.

In conclusion, we successfully investigated the self-assembly process of the coordination ring by the $n-k$ analysis, NMR, and ESI-TOF mass measurements and found that a 1:2 complex, $[Pt 1_2]^{2+}$, was the only intermediate that exists for a certain lifetime during the self-assembly. As was observed in the synthesis of covalent macrocycles, it has been expected that a long oligomeric chains are produced during the self-assembly but that these wrong intermediates should be converted efficiently into the macrocycle through intra- or intermolecular process. However, the present results indicate a completely different formation mechanism without the formation of any long oligomers.[11] It is uncertain whether the mechanism revealed in this research is the general case for the formation of coordination macrocycles or not, but the mechanism would be affected by the chemical structure and the electric property of the components and the environment of the self-assembly. A systematic study of the self-assembly process for the supramolecular macrocycles will make the matter clearer.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Full experimental procedures, NMR and ESI-TOF mass spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b04852.

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Notes
The authors declare no competing financial interest.

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(6) Here we assume that the cyclic structures larger than the hexagon are not produced. If these large macrocycles are contained in the intermediates, the length of the acyclic oligomers should be shorter than that evaluated from the maximum $\langle n \rangle$ and/or $\langle k \rangle$ values.

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(11) Our findings cannot absolutely exclude the possibility that longer acyclic oligomers than $[Pt_6 1_6 Py*]^{12+}$ do not form during the self-assembly if we assume that these oligomers may have an extremely short lifetime.