

Single crystal structure determination using synchrotron X-ray of molecular spheres synthesized by temporary labilization of the metal-ligand association

We have developed synthetic methods for multicomponent metal-organic complexes using the self-assembly of transition metal ions (M) and bidentate ligands (L). Typically, square planar coordinative Pd (II) ions and bidentate, organic ligands bearing two pyridyl groups as coordination sites are mixed in an organic solvent, and all the coordination bonds are formed between the Pd (II) ions and pyridyl groups to form hollow, spherical complexes with well-defined numbers of components M and L in quantitative yield. We have found that the bend coordination angles between two pyridyl groups control the product compositions, such as M_6L_4 , $M_{12}L_{24}$, $M_{18}L_{24}$, $M_{24}L_{24}$, and $M_{24}L_{48}$. One of the most important key points in these successful syntheses is the appropriate strength of coordination bonds between M and L that realizes reversible bond formation and cleavage where the destruction of unstable, intermediary structures proceeds and self-assembly affords the most thermodynamically stable final product. When we attempted to replace Pd (II) ions with the same square planar coordinative Pt (II) ions in the self-assembly reaction, we only obtained a complex mixture of oligomers owing to the stronger coordination bonds between Pt (II) ions and pyridyl groups. Here, we report a novel, practical method to accelerate the self-assembly of well-defined $Pt_{12}L_{24}$ spheres by the addition of 2,2,2-trifluoroethanol (TFE) to weaken the Pt(II)-L interaction and to obtain a thermodynamically controlled, desired product (Fig. 1) [1]. In this method, the kinetically inert M-L interaction is switched to a labile one by external stimuli (TFE as an additive), which is termed “temporary labilization.” Once the $Pt_{12}L_{24}$ complex was formed, volatile TFE (bp

78°C) was easily removed in vacuo to switch the bond again into an inert one and to afford an acid-durable complex.

TFE is known to be a weak acid and to donate a hydrogen bond, comparable to that of phenol, and a 1:1 complex of TFE and pyridine as an acid-base pair is reported. Therefore, we expected that the dissociated pyridyl moiety from the metal ion center would be stabilized by the strong hydrogen bond of a TFE to achieve the self-assembly of the desired product. We focused on ligand 1 shown in Fig. 2 as a simple bidentate ligand, which forms a $Pd_{12}L_{24}$ complex by the self-assembly with Pd(II) ions. Ligand 1 (7.0 μmol) and $Pt(\text{NO}_3)_2$ (5.6 μmol) were dissolved in TFE/dimethyl sulfoxide (DMSO) (60/40 v/v%) mixed solvent (700 μL) and heated at 100°C (Fig. 2). The time-dependent NMR monitoring of the reaction solution revealed that the self-assembly completed after 24 h. The formation of a giant product was first indicated by the broadness of the ^1H NMR signals due to the slow tumbling motion of the product in a solution. The diffusion coefficient D is the swimming speed of a molecule in a solution, which is useful for evaluating the size of the product: a large molecule shows a small D . DOSY NMR measurement is simple and reliable way to determine D for NMR signals. All the ^1H signals of the product showed the same D value of 6.31×10^{-11} (m^2/s), which indicated a single product formation of $Pt_{12}L_{24}$ sphere 2 shown in Fig. 2 and was comparable to that of the $Pd_{12}L_{24}$ counterpart. The control experiment for the reaction without TFE, i.e., in DMSO only, showed no convergence to a single product: the unassignable mixture of unstable intermediates, which are kinetic products, remained unchanged in 24 h, because the strong Pt-pyridyl group bonds were not effectively cleaved under the reaction conditions. Another additive-like protic solvents, such as EtOH and acetic acid, were effective for the self-assembly.

The composition of the product was clearly determined to be $Pt_{12}L_{24}$ by high-resolution cold-spray ionization time-of-flight mass spectrometry (CSI TOF MS) from a series of $[\text{M} - (\text{counter anion})_n]^{n+}$ peaks ($n = 10\text{--}15$), each of which is further resolved into an isotopic distribution pattern consistent with the theoretical simulation result. The MS studies revealed the solution-state structure of the product to be $Pd_{12}L_{24}$, and a consistent solid-state structure was determined by X-ray single-crystal diffraction studies. Single crystals suitable for crystallographic study were obtained by the slow diffusion of isopropyl acetate

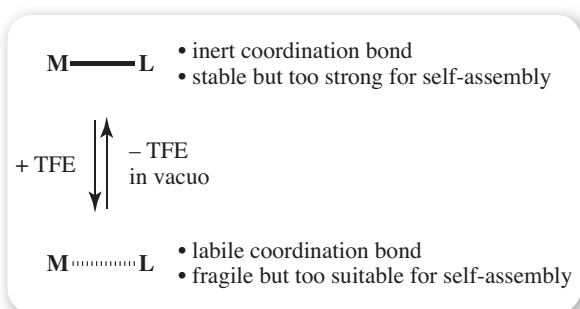


Fig. 1. Illustration of temporary labilization of coordination for self-assembly and stabilization of the product structure.

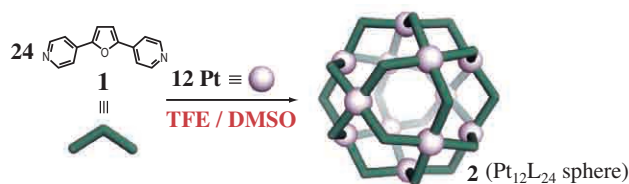


Fig. 2. Self-assembly of Pt(II)₁₂L₂₄ complex 2 in DMSO with a weakly acidic, H-bond-donating TFE solvent.

vapor into a DMSO solution of the product 2. Owing to a severe disorder of solvents and counter ions in the large void of the crystals, the diffraction intensities obtained on an in-house X-ray diffractometer were very low and limited at a too low resolution to solve the molecular structure. We improved the method of treating the fragile crystals containing a volatile solvent and the method of mounting the crystal on the diffractometer. Finally, a high-flux and low-divergence synchrotron X-ray beam with an efficient and high-resolution CCD detector afforded high-quality data from which the Pt₁₂L₂₄ spherical shell 2 was confirmed (Fig. 3). Mapping the 24 ligands to edges and 12 metal ions to vertices, the framework Pt₁₂L₂₄ 2 forms a cuboctahedron. Reasonable bond lengths and angles, especially, the almost perfect square planar orientation of the four pyridyl groups around Pt(II) centers, were confirmed. Importantly, these structural features of the product were essentially the same as those of previously reported Pd₁₂L₂₄ spheres with the same shell frameworks.

The preliminary synchrotron X-ray diffraction

studies were carried out at NE3A beamline in the PF-AR using a diffractometer equipped with an ADSC Quantum 270 CCD detector. The final synchrotron X-ray diffraction studies were carried out at **BL38B1** beamline in SPring-8 using a diffractometer equipped with an ADSC Quantum 315 CCD detector ($\lambda = 0.75000 \text{ \AA}$, 293 K).

The stronger Pt-L bond length should result in a more stable property of the product complex; accordingly, we determined the durability of complexes for nitric acid. When even a large excess amount of nitric acid (480 eq.) was added to the DMSO solution of Pt₁₂L₂₄ complex 2, the NMR spectrum hardly changed, confirming the rigid complex structure. In contrast, the counterpart Pd₁₂L₂₄ complex was not tolerant to the same acidic conditions and immediately decomposed into an unassignable mixture of oligomers owing to the labile nature of the Pd(II)-pyridine coordination. The high stability of the Pt complex is suitable for applications in a wide variety of media firmly retaining the well-defined three-dimensional spherical structures.

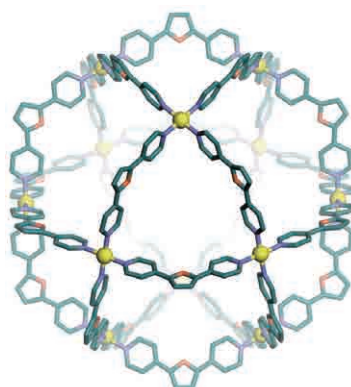


Fig. 3. Crystal structure of Pt₁₂L₂₄ sphere 2. Hydrogen atoms and the two counter ions at the apical positions of each Pt²⁺ are omitted for clarity.

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References

[1] D. Fujita, A. Takahashi, S. Sato and M. Fujita: *J. Am. Chem. Soc.* **133** (2011) 13317.