Dynamic behavior of double-walled cages in the self-assembly and the guest recognition

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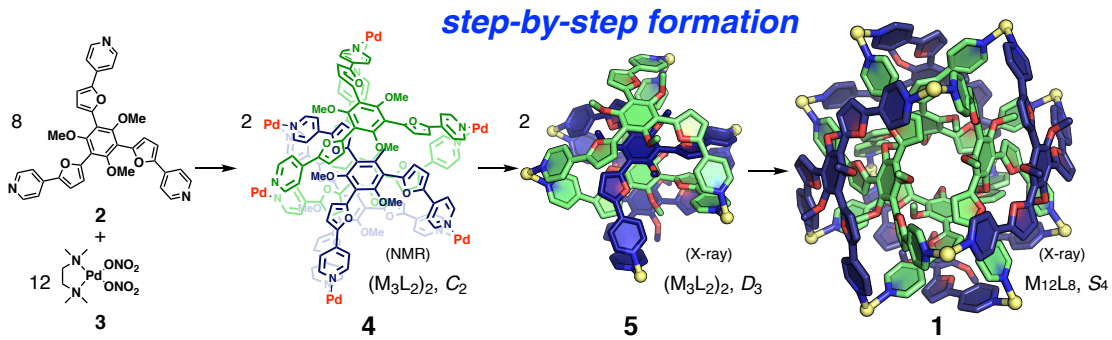
Dynamic behavior in self-assembly and guest recognition processes is vital to develop a complex chemical network. Recently, we have reported that the coordination cage with a double-walled interlocked structure **1** exhibits guest-adaptive molecular recognition and dynamic guest exchange.[1] Here, we validated the guest inclusion through the portal expansion by using a robust Pt analog of the double-walled cage.[2] We also found that the semi-flexible ligand for the cage exhibits dynamic behavior in the self-assembly process and enables step-by-step formations of double-walled interlocked structures.

A Pt analog of double-walled cage **1** was synthesized from a 2:3 mixture of the ligand **2** and a Pt(II) complex by heating at 100 °C for 18 d in the presence of an excess amount of CCl_4 as a template. Kinetic studies in the guest inclusion showed similar kinetics between Pd double-walled cage and the Pt analog, revealing the guest inclusion through adaptive portal expansion.

The dynamic nature in self-assembly of **1** was also investigated. $(M_3L_2)_2$ **4** with C_2 symmetry was formed when a 2:3 mixture of ligand **2** (20 mM) and a Pd(II) complex **3** (30 mM) in CD_3OD was stirred in at room temperature for 5 min. By adding D_2O and CD_3CN to change the solvent system to $CD_3OD/CD_3CN/D_2O$ = 1:1:8 and stirring at 60 ºC for 5 h, **4** was converted to another isomer of $(M_3L_2)_2$ **5** with D_3 symmetry. Both products **4** and **5** have *pseudo*-hexapodal ligands composed of a stacked dimer of tripodal ligand **2**. After stirring at 100 ºC for 25 h, **5** was totally converted to **1**. The results emphasize that the self-recognition of the ligand is essential for the formation of double-walled structures.



1) Y. Tamura, H. Takezawa, M. Fujita, *J. Am. Chem. Soc.* **2020**, *142*, 5504. 2) Y. Tamura, H. Takezawa, M. Fujita, *Chem. Lett.* **2020**, *49*, 912.