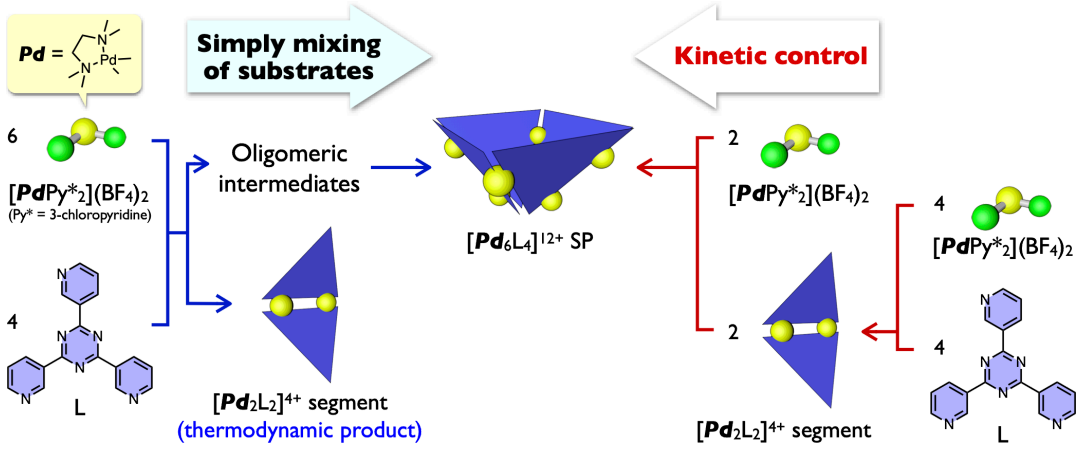
Kinetic control over the self-assembly of a Pd_6L_4 square-based pyramid

([1]*Graduate School of Arts and Sciences, The University of Tokyo*)
○Tomoki Tateishi,[1] Satoshi Takahashi,[1] Keisuke Aratsu,[1] Shuichi Hiraoka[1]
Keywords: self-assembly; kinetic control; Pd(II) complex; selectivity; reaction design

The self-assembly of the $[\boldsymbol{Pd}'_6L_4]^{12+}$ square-based pyramid (**SP**), where ***Pd'*** indicates a *cis*-protected Pd(ethylenediamine), in water was reported by Fujita and his coworkers.[1] They proposed that the self-assembly of the **SP** would take place through a $[\boldsymbol{Pd}'_2L_2]^{4+}$ segment, which was supported by the isolation of a $[\boldsymbol{Pd}''_2L_2]^{4+}$ segment, where ***Pd''*** indicates Pd(2,2-bipyridine).

In this work, the time-development of self-assembly process of the $[\boldsymbol{Pd}_6L_4]^{12+}$ **SP**, where ***Pd*** indicates a *cis*-protected Pd(*N*,*N*,*N*',*N*'-tetramethylethylenediamine)[2], was investigated in organic solvent by QASAP[3] and NASAP[2,4]. To our surprise, the $[\boldsymbol{Pd}_2L_2]^{4+}$ segment was produced as a thermodynamically most stable, major product (66%) with the $[\boldsymbol{Pd}_6L_4]^{12+}$ **SP** in only 17% yield. QASAP and NASAP indicate that the $[\boldsymbol{Pd}_6L_4]^{12+}$ **SP** is not produced mainly through the $[\boldsymbol{Pd}_2L_2]^{4+}$ segment but through chain-like oligomers without bridging. It was found that the $[\boldsymbol{Pd}_6L_4]^{12+}$ **SP** was produced in 69% yield by the reaction between the presynthesized $[\boldsymbol{Pd}_2L_2]^{4+}$ segment and $[\boldsymbol{Pd}Py^*_2](BF_4)_2$ under kinetic control.



1) Fujita, M.; Yu, S.-Y.; Kusukawa, T.; Funaki, H.; Ogura, K.; Yamaguchi, K. *Angew. Chem. Int. Ed.* **1998**, *37*, 2082–2085. 2) Komine, S.; Takahashi, S.; Kojima, T.; Sato, H.; Hiraoka, S. *J. Am. Chem. Soc.* **2019**, *141*, 3178–3186. 3) (a) Tsujimoto, Y.; Kojima, T.; Hiraoka, S. *Chem. Sci.* **2014**, *5*, 4167–4172. (b) Hiraoka, S. *Bull. Chem. Soc. Jpn.* **2018**, *91*, 957–978. (c) Hiraoka, S. *Isr. J. Chem.* **2019**, *59*, 151–165. 4) (a) Matsumura, Y.; Hiraoka, S.; Sato, H. *Phys. Chem. Chem. Phys*. **2017**, *19*, 20338–20342. (b) Takahashi, S.; Sasaki, Y.; Hiraoka, S.; Sato, H. *Phys. Chem. Chem. Phys.* **2019**, *21*, 6341–6347. (c) Hiraoka, S.; Takahashi, S.; Sato, H. *Chem. Rec.* **2020**, DOI: 10.1002/tcr.202000124.