Creation of Coordination Polyhedra by Collaborative Metal–Acetylene π-coordination

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Institute for Molecular Science*) ○Yuya Domoto,[1] Masahiro Abe,[1] Kidai Yamamoto,[1] Makoto Fujita[1,2]

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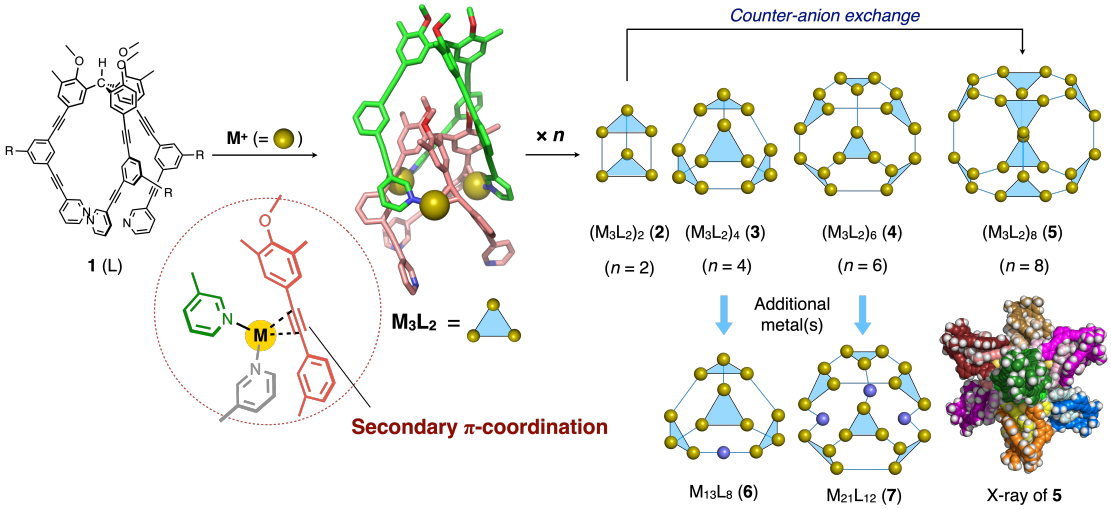
Acetylene π-coordination is a well-known weak interaction working in diverse organometallic transformations, while it has seldom been applied to metal-directed self-assembly in contrast to other coordination bonds such as relatively strong pyridyl or carboxylate coordination. We have recently elucidated that the self-assembly of propeller-shaped ligand **1** (L, R = H) and metal ions (M = Cu^I, Ag^I) afforded highly-entangled coordination polyhedra $(M_3L_2)_n$ (**2**-**4**; n = 2,4,6), based on a key role of the acetylene spacers in **1** as weak secondary coordination sites upon metal binding at the primary pyridyl sites.[1,2] Furthermore, the larger $(M_3L_2)_8$ (**5**) with a truncated cubic framework was also selectively constructed by post-assembly counter-anion exchange (BF_4 to NO_3) of $(M_3L_2)_2$ cage **2**. Flexible nature of acetylene π-coordination with weak directionality would realize the formation of a series of cage structures with high structural complexity, which emerge as a promising strategy for the construction of new classes of nanostructures.

We will also present (i) construction of hybridized cage frameworks ($M_{13}L_8$ (**6**) and $M_{21}L_{12}$ (**7**)) by additional metal insertion to $(M_3L_2)_n$ polyhedra, and (ii) helicity control of the inherently chiral cage structures via accumulation of small chiral functional groups (R = (*S*)-2-alkoxy groups) on the frameworks, which also contain highly entangled substructures.



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