Mathematical Control in the Self-assembly of Giant M_nL_{2n} Polyhedral Clusters

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Self-assembly of giant structures from a large number of small components is one of the most exciting challenges in current chemistry for the bottom-up control of chemical structures on the nano-scale. Metal-ligand self-assembly provides highly efficient and powerful approach to discrete giant structures, and several groups have been intensively studying the self-assembly of coordination polyhedra whose framework topologies are described by Platonic or Archimedian solids. From four-coordinated metals (M) and divalent bridging ligands (L), a series of M_nL_{2n} regular/semi-regular polyhedra, in which four edges meet at ever vertex, can be formed with geometrically restricted *n* values of 6, 12, 24, 30, and 60.[1] The most important structure parameter that determines the n value is the bend angle (θ) of the ligand component and we have previously shown that θ values below 127° give $M_{12}L_{24}$ (n = 12) while those above 135° does $M_{24}L_{48}$ (n = 24) both exclusively.[2] Here we report that, by further expanding the θ value (up to 149°), we succeeded in the self-assembly of $M_{30}L_{60}$ and $M_{48}L_{96}$ complexes. Interestingly, the $M_{48}L_{96}$ polyhedron does not belong to Platonic or Archimedian solids, but to a new family of pseudo Archimedian solids in which component square is not completely planar.

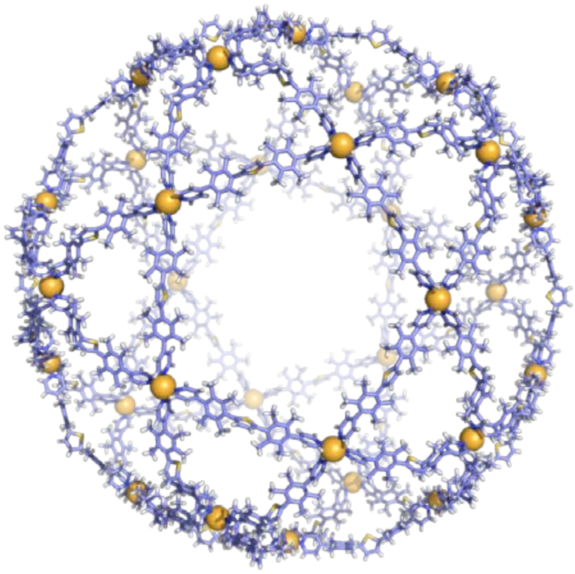

Figure 1. X-ray crystal structure of the self-assembled $M_{30}L_{60}$ complex (d = 8.2 nm).

Reference:

(1) A review: K. Harris, D. Fujita, and M. Fujita Chem. Commun. **2013**, 49, 6703-6712.
(2) Q.-F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi, and M. Fujita *Science* **2010**, *328*, 1144-1147.