Self-Assembly Behavior in Artificial 36- and 72- Component Systems

A huge self-assembled coordination sphere from 24 metal ions (M) and 48 curved (bent) ligands (L) was synthesized. The $M_{24}L_{48}$ structure with a diameter of 5 nm and molecular weight of over 20,000 Da was clearly determined by nuclear magnetic resonance (NMR), high resolution mass spectrometry (MS), and single crystal X-ray diffraction studies. With the thus obtained 72-component assembly and previously reported 36-component assembly, we identified the fundamental self-assembly behavior, where a tiny difference in the starting component strictly governs the structure of the product: the phenomenon is a key mark of emergent behavior.

One of the most challenging targets for chemists to mimic natural superstructures is a virus capsid assembled from 60T protein subunits without structural distribution, where T = 1, 3, 4, 7, 13, and 16. The possible capsid polyhedral structures are limited by simple geometrical constraints, and similar constraints have been found in artificial multicomponent assemblies. The formation of spherical polyhedra with a formula of M_nL_{2n} is predicted when metal ions (M) with a square planar coordination sphere and bent bidentate ligands (L) are mapped onto the vertices and edges, respectively, of the polyhedra, where n = 6, 12, 24, 30, and 60 [Fig. 1(a)]. We have reported the assemblies for n = 6 and 12 but not for larger n, and found that the multicomponent

system is quite stable to firmly maintain the coordination bonds [1]. Here, we report the self-assembly of the giant $M_{24}L_{48}$ complex 2 (n = 24) from 24 Pd^{2+} ions and 48 ligand 1 [Fig. 1(b)] [2, 3]. The formation of this 72-component system is highly sensitive to the ligand geometry. The smaller 36-component $M_{12}L_{24}$ sphere 4 (n = 12) forms when the analogous ligand 3 is employed [Fig. 1(c)]. Systematically varying the mean coordination angle defined by the directions of two coordinating pyridyl groups by mixing 1 and 3 in various ratios revealed that even a slight change in the mean bend angle critically switches the final structure between the $M_{24}L_{48}$ and $M_{12}L_{24}$ spheres.
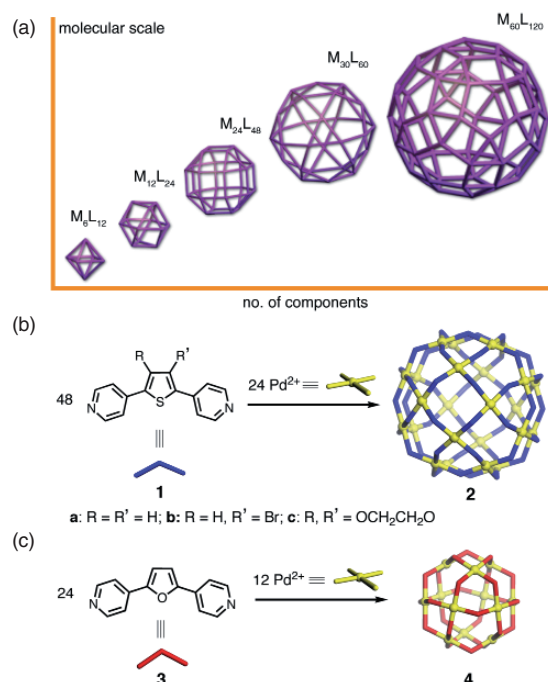

(a) molecular scale

M_6L_{12} $M_{12}L_{24}$ $M_{24}L_{48}$ $M_{30}L_{60}$ $M_{60}L_{120}$

no. of components

(b)

48 [R, R' ring with thiophene S, pyridyl N] + 24 Pd^{2+} → 2

1

a: R = R' = H; b: R = H, R' = Br; c: R, R' = OCH_2CH_2O

(c)

24 [furan O ring, pyridyl N] + 12 Pd^{2+} → 4

3

Figure 1
Multicomponent assemblies of M_nL_{2n} polyhedra: (a) The M_nL_{2n} polyhedras where M and L are mapped onto the vertices and edges, respectively, of the polyhedra. (b) Self-assembly of $M_{24}L_{48}$ 2. (c) Self-assembly of $M_{12}L_{24}$ 4.
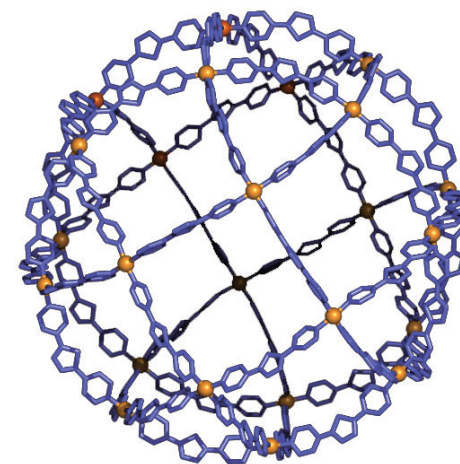

Figure 2
The crystal structure of 2c.

When stoichiometric amounts of ligand 1a (10 µmol) and $Pd(NO_3)_2$ (5.0 µmol) were heated in dimethyl sulfoxide-d_6 (DMSO-d_6) (0.7 ml) at 70°C for 17 h, the $M_{24}L_{48}$ sphere 2a was obtained quantitatively. The symmetric structure and the formation of coordination bonds were determined by 1D NMR, and the hydrodynamic radius was estimated by the diffusion ordered spectroscopy (DOSY) NMR technique. MS analyses on an ultrahigh resolution cryo-spray ionization time-of-flight (CSI TOF) mass spectrometer gave the series of multivalent signals corresponding to the removal of counter anions, giving a molecular weight of over 20,000 Da. Single crystals suitable for X-ray diffraction study were obtained, and, with many optimizations of the measurement conditions on synchrotron beamlines, the crystal structure of 2c was finally revealed to be a 5-nm diameter rhombicuboctahedron (Fig. 2).

We noticed that the small angular difference in the bent coordination direction of ligands 1 and 3 changed the structures of resultant assembled systems, $M_{24}L_{48}$ or $M_{12}L_{24}$, from 1 or 3, respectively. The bend angle of ligand 1 is 149.3°, which is larger than that of ligand 3 (126.9°), because the C-S bond length is longer than the C-O bond length. We wanted to change the angle continuously and used the ligands together, regarding the mixed system as an imaginary ligand bearing the

mean bend angle. The ratio of ligand 1c to ligand 3 was varied sequentially from 9:1 to 1:9 and surprisingly only pure $M_{24}L_{48}$ or $M_{12}L_{24}$ was observed exclusively: $M_{24}L_{48}$ was obtained from 1c:3 = 10:0 to 3:7, and $M_{12}L_{24}$ was obtained from 1c:3 = 2:8 to 0:10. The products contained both of the ligands according to the used mixing ratio, which was clearly determined by CSI TOF MS. This criticality arises from a multiplicity of simple interactions and precisely controls the final structures, which can be regarded as an artificial emergent behavior in multicomponent systems.

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