Chemistry

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Self-Assembled $M_{24}L_{48}$ Complex and Their Sharp Structural Switch

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Introduction

One of the most challenging targets for chemists to mimic natural super structures is virus capsid assembled from 60*T* protein subunits, 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 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. 1A). We have reported the assemblies for *n* = 6 and 12 but not for larger *n*. Here, we report the self-assembly of the giant $M_{24}L_{48}$ complex **2** (*n* = 24) from Pd^{2+} ions and ligand **1** (Fig. 1B) [1, 2]. 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. 1C). Systematically varying the mean ligand angle 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 $M_{24}L_{48}$ and $M_{12}L_{24}$ spheres.

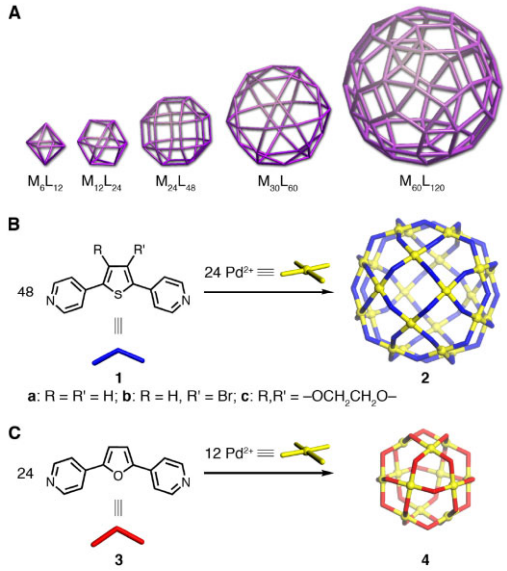
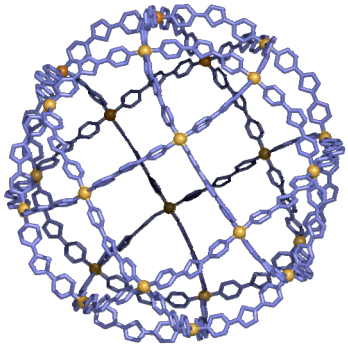


Figure 1 Multicomponent assemblies of M_nL_{2n} polyhedra.

Results and Descussions

When 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 structure was determined by NMR and high resolution MS, giving over 20,000 Da molecular weight. The crystal structure of **2c** was finally revealed to show a 5 nm diameter rhombicuboctahedron (Fig. 2).



crystal data:
space group = $I\bar{4}$
$a = b = 47.527(1)$ Å
$c = 68.663(1)$ Å
$V = 155097(5)$ Å^3
$Z = 2$
$T = 293$ K
$R_1 = 0.2222$
$wR_2 = 0.5427$
$GOF = 1.701$

Figure 2 The crystal structure of **2c**.

The ratio of ligand **1c** and **3** was varied sequentially from 9:1 to 1:9 and surprisingly only pure $M_{12}L_{24}$ or $M_{24}L_{48}$ was observed exclusively (Table 1). This criticality arises from a multiplicity of simple interactions and presicely controls the final structures.

Table 1 Structural switch by ligand geometry.

1c : **3** ratio (mean angle)	product		
		5 : 5 (138.1)	$M_{24}L_{48}$ only
10 : 0 (149.3)	$M_{24}L_{48}$ only	4 : 6 (135.9)	$M_{24}L_{48}$ only
9 : 1 (147.1)	$M_{24}L_{48}$ only	3 : 7 (133.6)	$M_{24}L_{48}$ only
8 : 2 (144.8)	$M_{24}L_{48}$ only	2 : 8 (131.4)	$M_{12}L_{24}$ only
7 : 3 (142.6)	$M_{24}L_{48}$ only	1 : 9 (129.1)	$M_{12}L_{24}$ only
6 : 4 (140.3)	$M_{24}L_{48}$ only	0 : 10 (126.9)	$M_{12}L_{24}$ only

References

[1] Q.-F. Sun et al., Science 328, 1144 (2010).
[2] A. R. Stefankiewicz et al., Science 328, 1115 (2010).

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