

## Face-Driven Corner-Linked Octahedral Nanocages: $M_6L_8$ Cages Formed by $C_3$ -Symmetric Triangular Facial Ligands Linked via $C_4$ -Symmetric Square Tetratopic $Pd^{II}$ Ions at Truncated Octahedron Corners

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Self-assembled high symmetry polyhedral cages are common in biological systems. The coats of many viruses have icosahedral structures with 60 facial protein subunits,<sup>1</sup> and the iron storage protein, apoferritin, has an octahedral structure with 24 facial protein subunits.<sup>2</sup> Following the lead of nature, attempts to prepare synthetic cages<sup>3</sup> for potential applications, such as storage,<sup>4</sup> recognition,<sup>5</sup> delivery,<sup>6</sup> and catalysis,<sup>7</sup> are very popular among scientists. There is a great deal of interest in metal-induced self-assembled supramolecular cages using the ability of a coordination bond to direct orientation of the desired components.<sup>3c,8</sup> Several coordination-inspired high symmetry cages of trigonal pyramid,<sup>9</sup> square pyramid,<sup>9</sup> trigonal bipyramid,<sup>10</sup> trigonal prism,<sup>11</sup> trigonal antiprism,<sup>12</sup> square prism,<sup>11</sup> tetrahedron,<sup>13</sup> cuboctahedron,<sup>14</sup> and octahedron<sup>15–17</sup> geometries have been reported. Self-assembly of high symmetry cages via coordination with a directional bond utilizes two different approaches.<sup>8b</sup> The first is edge-directed self-assembly of the linear components linked at the corner.<sup>13b,d,14</sup> The other is face-directed self-assembly of the facial components linked either at the edges<sup>9–11,13a</sup> or at the corners.<sup>12,13c</sup>

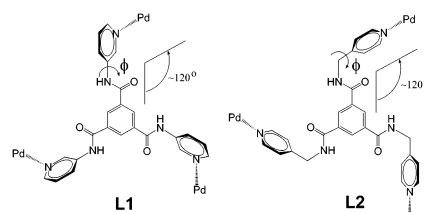
Here we report the use of suitably designed  $C_3$ -symmetric facial ligands (Scheme 1) and  $C_4$ -symmetric metal ions as a general strategy for the preparation of face-driven corner-linked truncated octahedral nanocages (Scheme 2).

The cage,  $[Pd_6L_8]^{12+}$  ( $L1 = N,N',N''$ -tris(3-pyridinyl)-1,3,5-benzenetricarboxamide) **1**, was prepared with eight  $C_3$ -symmetric tridentate ligands. The combination of the nitrogen donor atom at the *meta* position of the carboxamido pyridinyl group and the tilted pyridyl versus the facial plane of the ligand can provide the needed curvature for the formation of an octahedral cage. The nitrogen atoms can coordinate to the square planar palladium(II) ions to form kinks with approximately  $120^\circ$  angles at the  $C_4$ -symmetric square planar corners of the truncated octahedron.

When 4 equiv of ligand **1** was treated with 3 equiv of  $Pd(NO_3)_2$  in  $DMSO-d_6$  (0.5 mL) for 30 min, the quantitative self-assembly of a single product was detected by  $^1H$  NMR spectroscopy (Figure S1a). The six proton signals observed indicate that all the ligands are located equivalently in the product and are in a  $C_3$ -symmetry environment. The coordination of the ligand to the metal ions could be recognized by the relatively broadened and overall downfield shifted resonance signals. Support for the formation of the proposed octahedral cage  $[Pd_6L_8](NO_3)_{12}$ , **1**, with a molecular weight of 4884 Da was obtained by electrospray ionization mass spectra (ESI-MS) (Figure S1b).

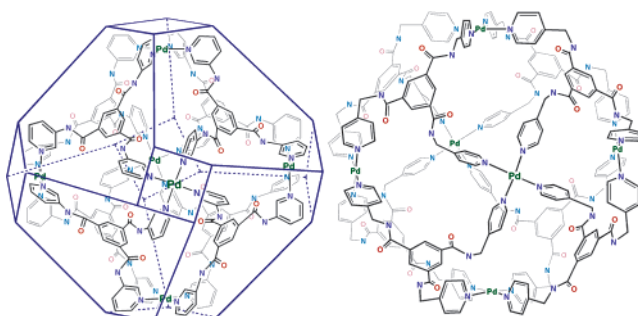
The crystal structure unambiguously demonstrates that **1** has a  $[Pd_6L_8]^{12+}$  cage of truncated octahedral geometry (Figure 1). Eight  $C_3$ -symmetric facial **1** ligands are connected at six truncated

### Scheme 1<sup>a</sup>

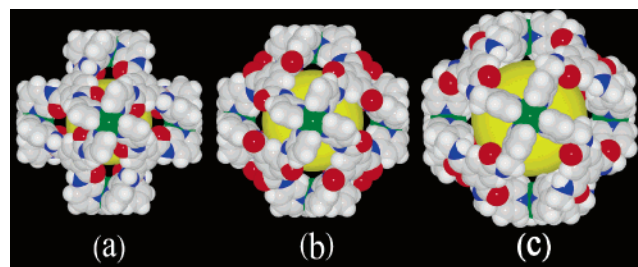


<sup>a</sup> The combination of the nitrogen donor atom of **L1** and **L2** in  $\sim 120^\circ$  kink from the amide group and the tilted pyridyl group (tilting angle  $\phi$ ) provides the needed curvature for out-of-plane coordination from the plane of the  $C_3$ -symmetric facial ligands.

### Scheme 2<sup>a</sup>



<sup>a</sup> (a) Cage **1**: Eight  $C_3$ -symmetric facial **L1** ligands are connected at six truncated octahedral corners via  $C_4$ -symmetric square planar palladium(II) ions. (b) Cage **2**: Addition of a methylene group and the *para* positioning of the pyridyl nitrogen in **L2** ligands give similar kinds of curvature for cage formation.



**Figure 1.** CPK model for the crystal structure along the  $C_4$ -symmetric axis. The major form of cage **1** (a), minor form of cage **1** (b), a dummy ball diameter of  $\sim 12.0$  Å inside (a) and  $\sim 13.6$  Å in (b). (c) Cage **2**. A dummy ball diameter of  $\sim 14.4$  Å. Color code: green, palladium; red, oxygen; blue, nitrogen; gray, carbon; white, hydrogen; yellow, dummy atom. octahedral corners via  $C_4$ -symmetric square planar palladium(II) ions. The pyridyl donor atom of **L1** is at a  $\sim 120^\circ$  kink from the amide group, and the tilting angle,  $\sim 57^\circ$ , between the central benzene and the pyridyl group gives the curvature needed for cage formation for the pyridyl donors in the out-of-plane direction from

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the plane of the  $C_3$ -symmetric facial ligand. Each Pd<sup>II</sup> has a square planar geometry with Pd $\cdots$ N<sub>Pyridyl</sub> distance of 2.033(4) Å, and N<sub>Pyridyl</sub>–Pd–N<sub>Pyridyl</sub> angles of 89.992(3) and 178.7(2)°. Two conformational isomers in a ratio of approximately 3:2 were observed as statically disordered structures. Depending on the conformation of the ligands,<sup>16</sup> two different truncated octahedral cages of around 2.4 nm in diameters were formed (Figure 1a and 1b). The major form of **1** with a syn-conformational ligand has a cavity volume of ~1600 Å<sup>3</sup> (Figure 1a). The cage has 12 ports ( $3.4 \times 3.5$  Å<sup>2</sup>) at all edges of the octahedron. The minor form of cage **1** with anti-conformational ligands has a slightly increased cavity volume (~1900 Å<sup>3</sup>) and port size ( $3.3 \times 8.0$  Å<sup>2</sup>) (Figure 1b). However, the ROESY spectrum of cage **1** indicates that the major form with the ligand in the syn-conformation is the only species in solution (Figure S3).

We could apply the same strategy for the preparation of another  $O$ -symmetry truncated octahedral cage with similar a  $C_3$ -symmetric facial ligand, L2 (L2 = *N,N',N''*-tris(4-pyridinylmethyl)-1,3,5-benzenetricarboxamide), with an additional methylene group between the amide and the pyridyl group (Scheme 1). The change in position of the pyridyl nitrogen from the *meta* to the *para* also provides the similar 120° kink needed for cage formation. The cage [Pd<sub>6</sub>L<sub>2</sub>](NO<sub>3</sub>)<sub>12</sub>, **2**, was prepared with eight  $C_3$ -symmetric tridentate ligands with three donor atoms at the *para* position of the pyridyl group (Scheme 2). When 4 equiv of ligand L2 was treated with 3 equiv of Pd(NO<sub>3</sub>)<sub>2</sub> in DMSO-*d*<sub>6</sub> (0.5 mL) for 30 min, the quantitative self-assembly of a single product of high symmetry was observed by <sup>1</sup>H NMR spectroscopy (Figure S4).

The crystal structure demonstrates that **2** has the [Pd<sub>6</sub>L<sub>2</sub>]<sup>12+</sup> cage of truncated octahedral geometry of around 2.6 nm in diameter (Figure 1c). In this instance also, as in the case of cage **1**, eight  $C_3$ -symmetric facial L2 ligands are connected at six truncated octahedral corners via  $C_4$ -symmetric square planar palladium(II) ions as in cage **1**. The combination of a 120° kink and the tilting angle, 70°, between the central benzene and the pyridyl group again provides the curvature needed for cage formation. The coordination environment of the Pd<sup>II</sup> center is very similar to that in cage **1**. However, the orientation of the pyridyl group is slightly different from that in cage **1**. The angle between the square plane of the Pd(II) center and pyridyl plane is closer to orthogonal compared with that in cage **1** (63.4° in cage **1** and 69.7–89.7° range, avg. = 79.0° in cage **2**). The insertion of a methylene group in L2 has not only increased the cavity volume of **2** to ~2200 Å<sup>3</sup> but also enlarged the port size to  $4.1 \times 8.0$  Å<sup>2</sup>. However, an atomic force microscopy (AFM) study of cage **2** showed that the cages had a height of  $1.8 \pm 0.1$  nm (mean  $\pm$  standard deviation,  $N = 100$ ) with narrow height distribution (Figure S5). This value is about 30% smaller than the calculated size of 2.6 nm from the crystal structure. This compression of the cages contrasts with the recent result of Fujita's M<sub>12</sub>L<sub>24</sub> endo-filled nanoball, where the height of the cage measured by AFM matches the estimated size from molecular modeling.<sup>17</sup> We believe that this decrease in height in cage **2** is due to tip-induced compression<sup>18</sup> of the cage, which suggests the nonrigidity of cage **2** contrary to Fujita's rigid endo-filled nanoball.

In summary, we have generalized the preparation of nanosized octahedral cages using suitably designed  $C_3$ -symmetric triangular ligands as facial components and  $C_4$ -symmetric Pd<sup>II</sup> metal ions as corner linkers. The curvature needed for truncation at the octahedral vertices was accomplished using ligands with a tilted pyridyl group and a nitrogen donor atom in a ~120° kink. These face-driven corner-linked nanocages have 12 ports at the edges of the truncated octahedron. Depending on the size of the facial ligands, not only the cavity size but also the port size of the cage could be controlled. This offers potential possibilities of developing suitable nanosized

host systems that can accommodate suitable small molecular guests or chiral catalysts.

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**Supporting Information Available:** Experimental procedures, spectra, and an X-ray crystallographic file in CIF format for the structure determination. This material is available free of charge via Internet at <http://pubs.acs.org>.

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