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Self-Assembly

Finite, Spherical Coordination Networks that Self-Organize from 36 Small Components**

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Highly symmetric structures often appear in nature as revealed by, for example, the capsids of spherical viruses that have icosahedral symmetry consisting of 60*n* identical protein subunits.[1] The reason for the high symmetry lies behind the principle that increasing the number of elements with the same symmetry reduces the amount of independent structural information, which is directly related to the length of DNA. Thus, the self-organization of tiny subunits into a giant biological molecule can be regarded as the process of not only structural growth but of the amplification of molecular information. We show herein that, through metal–ligand interactions,[2,3] simple banana-shaped organic molecules self-organize into finite, spherical coordination networks with a diameter of up to 7 nm, which is in contrast to the formation of two-dimensional (2D) infinite networks that occurs with linear organic ligands. The spherical coordination networks consist of 36 components, 12 equivalent metal centers (M) and 24 equivalent ligands (L), and have cuboctahedron symmetry. By attaching a functional group (e.g., C_{60} or porphyrin) to each ligand, 24 functional groups are aligned equivalently at the periphery of the sphere.

Over the last decade, extensive studies have been made on infinite coordination networks that are formed by the complexation of exo-multidentate ligands with transition-metal ions. A typical and simple example is given by a 2D grid complex that forms from a rodlike ligand and a metal (Figure 1a).[4] We expect that, if the ligand framework is slightly bent, the coordination network will develop with a

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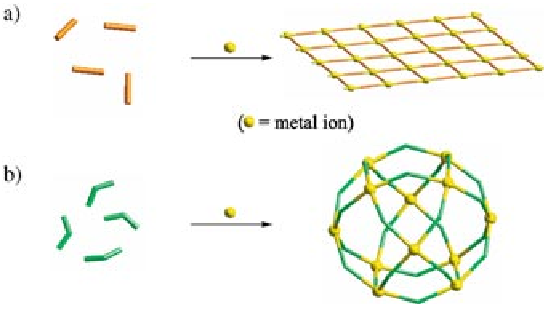
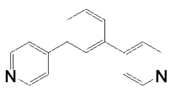
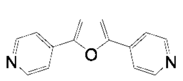


Figure 1. Schematic representation of the self-assembly of coordination networks from metal ions which favor a square-planar coordination geometry and different bridging ligands. a) Linear ligands are expected to self-assemble to give 2D grid complexes. b) Slightly bent ligands are expected to self-assemble to give spherical finite complexes.

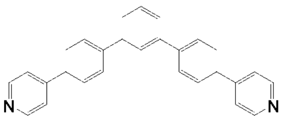
constant radius of curvature and a spherical finite network will be obtained (Figure 1 b), reminiscent of the formation of graphite versus that of fullerene from sp^2 hybridized carbon atoms. Based on this idea, we designed ligands **1a**–**c** and



1a



1b



1c

examined their complexation with naked palladium(II) ions which favor a square-planar coordination environment.[5]

When ligand **1a** (0.02 mmol) was treated with $Pd(NO_3)_2$ (0.01 mmol) in [D$_6$]DMSO (1.0 mL) at 70 °C for 4 h, the quantitative self-assembly of a single product was detected by ^{1}H NMR spectroscopy.[6] Only five signals are observed indicating that all the ligands are located equivalently in the product and have same inherent symmetry (Figure 2). The resonance signals were relatively broad at room temperature but became sharp at higher temperatures, characteristic of very large species whose motion is slow on the NMR time scale. Downfield shift of the signals, particularly for Py$_\alpha$ ($\Delta\delta = 0.79$ ppm; Py = pyridine), was ascribed to the metal–ligand complexation. Diffusion-ordered NMR spectroscopy (DOSY) showed a single band at the diffusion coefficiency of 1.1×10^{-10} m^2 s^{-1}, from which the diameter of the product was roughly estimated to be 3.6 nm.[7] After anion exchange from $[NO_3]^-$ to $[PF_6]^-$ ions, cold-spray ionization mass spectrometry (CSI-MS)[8] clearly indicated an $M_{12}L_{24}$ composition with the molecular weight of 10330 Da by a series of $[M-(PF_6^-)_n]^{n+}$ ($n = 6$–13) peaks (Figure 3).[9] Fragmentation in the MS measurement was hardly observed except the dissociation of counteranions, which demonstrates the remarkable stability of the product in solution. Elemental analysis was also consistent with the $M_{12}L_{24}$ composition.

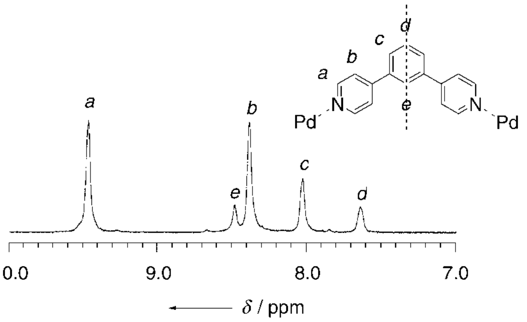


Figure 2. The ^{1}H NMR spectrum (aromatic region) of the product assembled from $Pd(NO_3)_2$ and ligand **1a** (2 equiv; 500 MHz, [D$_6$]DMSO, 25 °C, TMS).

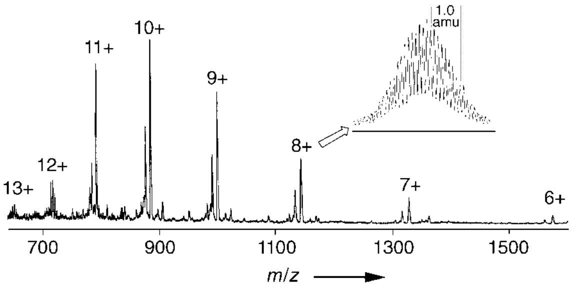
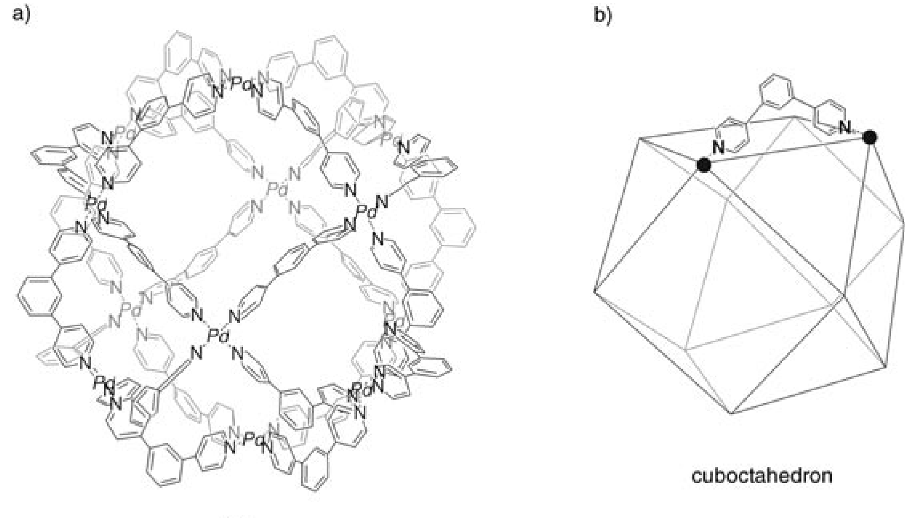


Figure 3. CSI-MS spectrum showing the formation of $M_{12}L_{24}$ product (PF_6^- salt).

From the detailed NMR and mass spectroscopic measurements, the formation of the roughly spherical giant molecule **2a** was deduced because of good agreements with the $M_{12}L_{24}$ composition and the equivalence of all the ligands (Figure 4 a). The symmetry of **2a** is dictated by a cuboctahedron, which is formed by truncating each of the eight vertices of a cube to generate eight triangular faces. The 12 equivalent vertices and 24 equivalent edges of the cuboctahedron can be superimposed on the 12 palladium(II) centers and 24 bridging ligands, respectively (Figure 4 b). Related cuboctahedral complexes with Cotton-type copper(II) dinuclear tetracarboxylate junctions have been reported,[10] but no solution behavior is reported probably because of their poor solubility in common polar solvents. Since these copper(II) species are generated by inert dinuclear tetracarboxylate formation, instead of self-assembly, oligomeric products are produced as well and the yields are moderate or not well determined. In contrast, spherical complex **2a** immediately assembles from 36 components in a quantitative yield thanks to moderately labile palladium(II)–pyridine interactions.

A scanning tunneling microscopy (STM) study revealed the structural integrity of **2a** (Figure 5 a) even under STM conditions. More significantly, the image obtained on a graphite surface demonstrates that the spheres **2a** behaves as "molecular particles" with precise chemical structure and uniformed dimension (height) of 3.5 nm (Figure 5 b), which is consistent with the DOSY measurement and molecular model prediction.



2a

Figure 4. a) Molecular structure **2a** assembled from 24 bidentate ligands **1a** and 12 metal ions. b) Schematic representation of the cuboctahedral frameworks of **2a**.

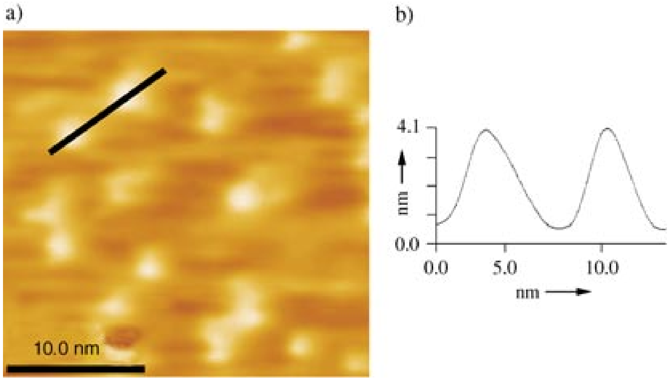


Figure 5. a) STM image of individual spheres **2a** on the graphite at room temperature. b) Height profile of the STM image.

Reliable evidence for the spherical $M_{12}L_{24}$ structure was obtained by X-ray crystallographic analysis of **2b**, which is an analogue of **2a** where ligand **1a** is replaced by **1b**.[11] Single crystals of **2b** were obtained by very slow vapor diffusion of 1,1,2-trichloroethane into a DMSO solution of **2b**. With a CCD detector, MoK_α radiation (55 kV, 30 mA) afforded low resolution data (only 874 unique reflections ($>2\sigma(I)$)), which were insufficient for solving the structure. The poor quality of the data was due to severe disorder of solvent molecules and anions in the extraordinarily large void within the spherical framework of **2b**. However, synchrotron X-ray radiation with high flux and low divergence provided much higher quality of data with 2717 unique reflections ($>2\sigma(I)$), from which the spherical $M_{12}L_{24}$ structure of **2b** was solved with all the heavy atoms being refined anisotropically (Figure 6). The crystal system is cubic and the cell volume is 108456(16) Å^3. Surprisingly, the framework of **2b** occupies only 20% of the cell volume (as estimated by Platon program), remaining 80% being occupied by disordered solvent molecules and counterions. The diameter of a sphere in which **2b** is inscribed is 3.4 nm. The shortest Pd–Pd separation is 1.3 nm while the longest one is 2.6 nm.

In the crystal, the spherical complex **2b** enjoys a cubic close-packed structure. Each molecule of **2b** is linked to twelve neighboring spheres by Pd^{II}-NO_3^--Pd^{II} bridges, which presumably stabilize the crystal of **2b** despite approximately 80% void space.

Ligand **1c** is effectively an expanded version of the framework of **1a**. From $Pd(NO_3)_2$ and ligand **1c** in 1:2 stoichiometry, we again observed the self-assembly of a single and highly symmetric product, **2c** (an analogue of **2a** where ligand **1a** is replaced by **1c**) which was assigned by CSI-MS measurement. The molecular mass of 13982 Da for **2c** was clearly demonstrated (see Supporting Information). Molecular modeling of **2c** by Cerius^2 program predicted a diameter of 5.2 nm.[12]

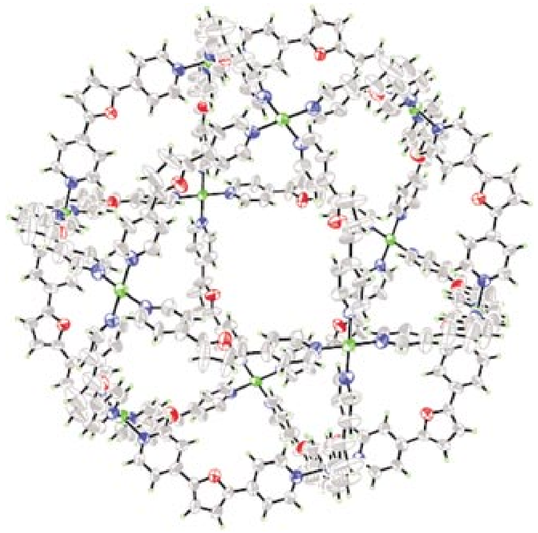
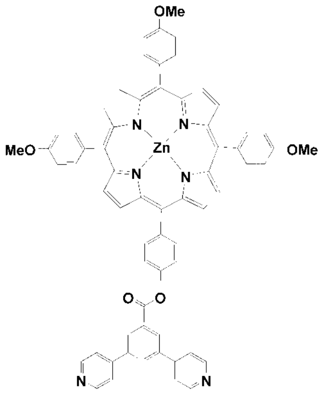
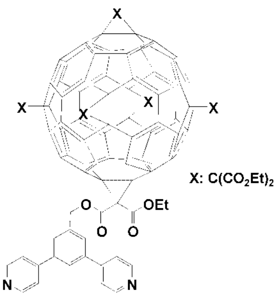


Figure 6. The crystal structure of sphere **2b**. Counterions and solvent molecules are omitted for clarity (green Pd, red O, blue N, gray C).

We also emphasize that, by attaching a functional group on each ligand, 24 functional groups are aligned equivalently at the periphery of the sphere. Metal–porphyrins are known to collect light energy when they are aggregated as in light-harvesting proteins or chlorophylls. To mimic these aggregates, we synthesized ligand **1d** in which a porphyrin unit is attached on the backbone of **1a**. By simply mixing this ligand with $Pd(NO_3)_2$ in a 2:1 ratio in DMSO, porphyrin nanoball **2d** with regular arrangement of the 24 porphyrin units at the periphery of the sphere was immediately assembled (Figure 7). The NMR spectrum of this complex at 25°C shows the equivalence of the 24 attached porphyrin ligands.



1d



1e

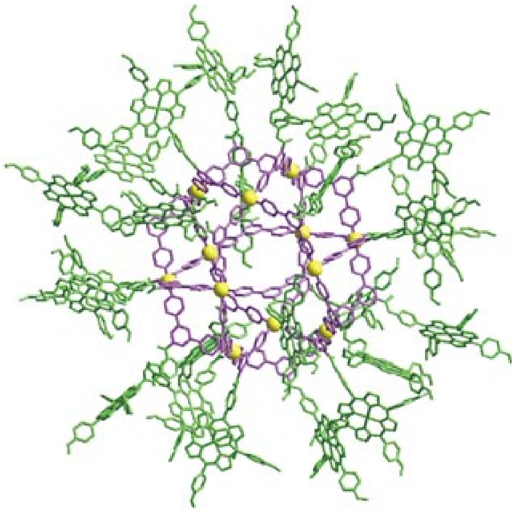


Figure 7. A molecular modeling study of **2d** optimized by a force-field calculation with Cerius^2 3.5 package (Pd yellow, the porphyrin-based and pyridine-based units of ligand **1d** are green and purple, respectively).

The DOSY spectrum showed a single band, which suggests the quantitative formation of **2d** (Figure 8b). Similarly, fullerene nanoball **2e** was assembled from ligand **1e** and Pd(NO$_3$)$_2$ (Figure 8c). The diffusion coefficients of **2b**, **2d**, and **2e** determined by DOSY experiments were 1.20, 0.60, and 0.76×10^{-10} m^{2}s^{-1}, respectively. These values give an estimation of the dimensions of **2b**, **2d**, and **2e** (3.4, 6.7, and 5.3 nm, respectively), which agree quite well with the X-ray structure (3.4 nm for **2b**) and refined structures with Cerius^2 program (3.4, 7.4, and 6.0 nm for **2b**, **2d** and **2e**, respectively).

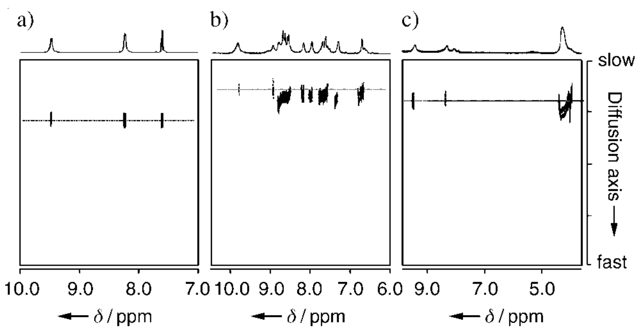


Figure 8. DOSY spectra of the sphere a) **2b**, b) **2d**, and c) **2e** (500 MHz, [D$_6$]DMSO, 25 °C, TMS).

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[9] Spheres **2a**, **2b**, and **2c** were analyzed by CSI-MS. A series of $[M-(\mathrm{PF}_6)_n]^{n+}$ peaks was observed. See the Supporting Information.

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[11] X-ray crystallographic analysis of **2b**: The diffraction data was measured at 120 K ($\lambda = 0.6890$ Å) at PF-AR of the High Energy Accelerator Research Organization (KEK). X-ray data showed no significant crystal decay during data collection. $Pd_{12}(C_{13}N_2O)_{24}(NO_3)_{24}$, $M_r = 7568.80$, cubic, space group $Fm\bar{3}m$, $T = 120(2)$ K, $a = 47.689(4)$ Å, $V = 108456(16)$ Å^3, $Z = 4$. Anisotropic least-squares refinement for the cage atoms and isotropic for the anion and solvent molecules (122 parameters) on 2658 independent merged reflections ($R_{int} = 0.0753$) converged at $wR_2(F^2) = 0.1770$ for all data; $R_1(F) = 0.1518$ for 1718 observed data ($I > 2\sigma(I)$), GOF = 1.708. Because two independent nitrate anions sit on the special positions ((y, 0, y) and (0.25, 0, 0.25)), their models are not fitted for the ideal geometry of D_{3d} symmetry. All the solvent molecules could not be treated properly because of their severely disordered structures. Therefore, all large residual electron density peaks were assigned to chlorine atoms of 1,1,2-trichloroethane molecules (poor solvent of crystallization). CCDC-238399 (**2b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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