

## Self-Assembly of Nanoscopic Dodecahedra from 50 Pre-designed Components

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Rapid growth in the field of supramolecular chemistry<sup>1</sup> has resulted in a new generation of conformationally rigid polyhedral structures of controlled shape and size which can be built from the spontaneous assembly of complementary subunits. The structural and functional features of the self-assembled product may be entirely encoded in its components without the use of templates.<sup>2</sup> The resulting ensemble possesses a central void that makes it potentially useful for the development of molecular sensors, new types of catalysts, and various other materials with useful properties.<sup>3</sup> Here we report the preparation of dodecahedra with outer dimensions of  $\sim 5$  and  $\sim 8$  Å. The actual process of self-assembly of a single dodecahedron molecule involves formation of 60 metal–ligand bonds and participation of 50 individual molecules. As the size of these self-assembled metallocyclic structures increases, the rigidity of the individual building blocks becomes essential for transmission of directing effects over larger distances. Flexible linear connectors cause the formation of oligomers instead of discrete molecules with defined shape presumably due to the formation of defects which cannot self-correct.

The most complex of the five Platonic polyhedra, the dodecahedron, contains 12 fused five-membered rings that comprise the highest symmetry group  $I_h$ . Its 12 pentagonal faces are formed from 20 vertexes and 30 edges; hence it can be prepared via edge-directed assembly from 20 tridentate angular subunits with approximately  $108^\circ$  directing angles combined with 30 bidentate linear subunits (Figure 1). A suitable angular subunit, tri(4'-pyridyl)methanol (**1**), was prepared from the known di(4'-pyridyl)ketone<sup>4</sup> in good yield. X-ray crystallographic analysis established the structure of compound **1** (Figure 2),<sup>5</sup> demonstrating that the tetrahedral directing angles in **1** are near the optimal  $108^\circ$ . The linear bidentate units bis[4,4'-(*trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>OTf)]benzene (**2**), bis[4,4'-(*trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>OTf)]biphenyl (**3**), and bis[4,4'-(*trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>OTf)]biphenyl (**4**) were prepared according to procedures previously described.<sup>6</sup> Bis[1,4-(*trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>OTf)]ethynylbenzene (**5**) was obtained via a base-catalyzed coupling of 1,4-diethynyl-

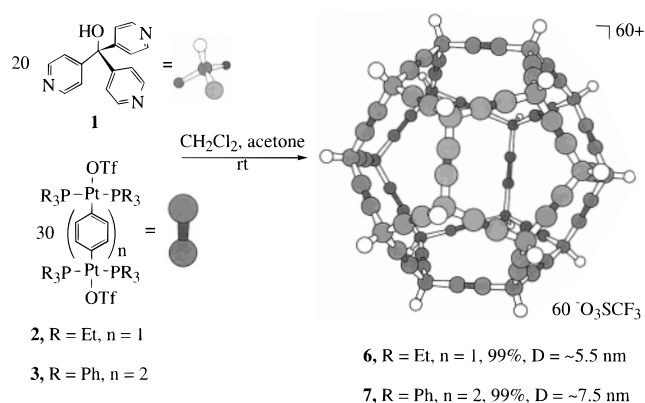


Figure 1. Self-assembly of the nanoscopic dodecahedra **6** and **7**.

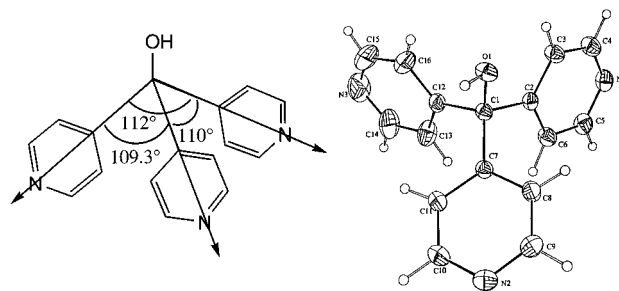
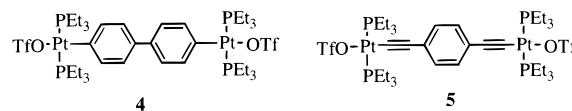


Figure 2. Summary of important geometric features and an ORTEP diagram of tri(4'-pyridyl)methanol (**1**).

benzene with *trans*-diiodobis(triethylphosphine)platinum(II) and subsequent treatment with AgOTf.



When a solution of the angular component **1** in acetone was added to the linear unit **2** in dichloromethane, under careful monitoring of the stoichiometry by <sup>1</sup>H and <sup>31</sup>P NMR, a self-assembled dodecahedron **6** was formed in 99% isolated yield. The observed <sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C NMR spectra<sup>5</sup> are all consistent with the formation of a single, highly symmetrical molecule. This molecule has 60 positive charges and contains 60 triflate counterions. Its estimated diameter along the 3-fold axis is about 5.5 nm and it has a molecular weight of 41656.0 Da, making it comparable in size and molecular weight to small proteins. Despite the large size and molecular weight, it is remarkably soluble in polar organic solvents, presumably due to extensive solvation of its charged spherical surface.

To further test this methodology, we tried to assemble even larger dodecahedra by utilizing longer linear connectors. The reaction of **1** with **3** produced the desired dodecahedron **7**. The estimated diameter of this assembly is 7.5 nm along the 3-fold axis and it has a molecular weight of 61955.4 Da.

In contrast, the interaction of **1** with **4** or **5**, respectively, resulted only in the formation of insoluble oligomers even at early stages of the reaction. We suspect that the reason for the different behavior with the linear connectors **3**, **4**, and **5** is their differing rigidity,<sup>7</sup> even though all three have similar length. Molecular modeling shows that  $\pi$ -stacking of the phosphorus-bound and

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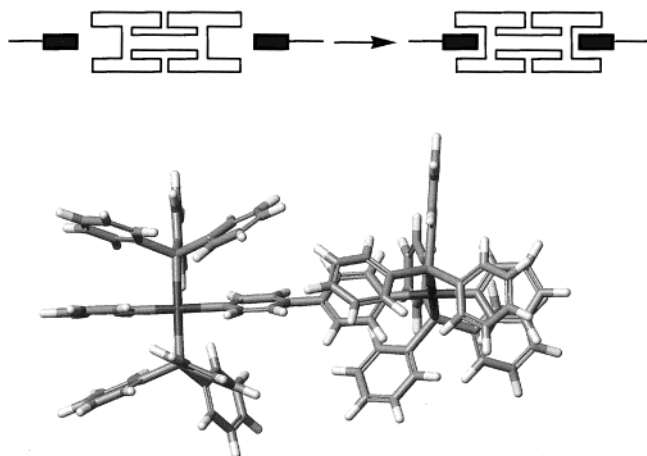
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**Figure 3.** Schematic representation of the steric reinforcement of the linking units via the  $\pi$ -stacking of the aromatic rings. Black rectangles represent pyridine rings. White rectangles represent phenyl rings.

platinum-bound phenyl rings is possible with linker **3**, which provides enhanced rigidity (Figure 3). Furthermore, the pyridine rings coordinated to the platinum atoms upon metal–ligand bond formation can also participate in  $\pi$ -stacking with the phosphorus-bound phenyls. Linkers **4** and **5** lack this mechanism of enhancing rigidity and therefore, presumably, are more flexible than **3**. Flexible linkers are less capable of transmitting the directing effect of the angular precursors over such a large distance. Thus, defects are likely formed in the early stages of the self-assembly that precludes closure to a three-dimensional symmetric structure, instead oligomers are formed and precipitate.

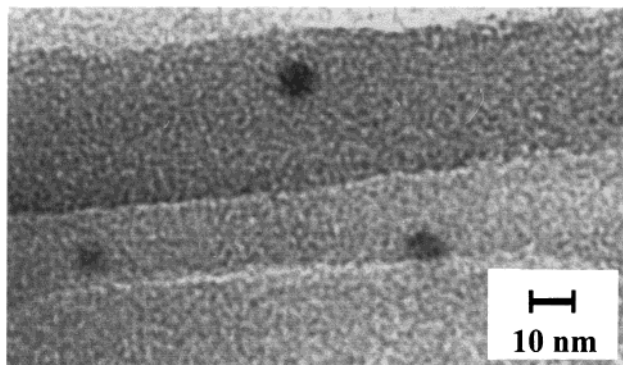
The experimental size of **6** and **7** was assessed by measuring their self-diffusion coefficients with the pulse gradient spin–echo (PGSE) NMR technique.<sup>8</sup> This technique can provide diffusion and aggregation data of various assemblies in solution and has been used extensively to study many chemical and biological systems,<sup>9</sup> including charged polycyclic systems<sup>10</sup> and large biomolecules.<sup>11</sup> The experimental self-diffusion coefficients at 25 °C are  $(1.80 \pm 0.05) \times 10^{-6} \text{ cm}^2/\text{s}$  for **6** and  $(1.32 \pm 0.06) \times 10^{-6} \text{ cm}^2/\text{s}$  for **7** which, after simulation of the motion through a medium with a defined viscosity, gives an experimental hydrodynamic diameter of 5.2 nm for **6** and 7.5 nm for **7**. Additional evidence for the molecular structure of the dodecahedra **6** and **7**

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**Figure 4.** TEM micrograph of individual dodecahedra **7**, deposited on a carbon film at low concentrations and dried at  $-130$  °C.

was obtained from electrospray ionization mass spectrometry (ESMS). Observation of the multiply charged ions of the intact cages as well as identification of the fragments supported the expected molecular masses and compositions.<sup>5</sup>

Transmission electron microscopy (TEM) studies of the larger dodecahedron **7**, deposited at low concentrations on a thin carbon film, showed isolated, nearly-spherical entities  $\sim 8$  nm in diameter (Figure 4). The observed size of the particles is consistent with the estimated molecular size of **7**. Preliminary energy-dispersive X-ray spectroscopy (EDS) studies indicate the presence of Pt in the assemblies. Thus, the spectroscopic and physical properties, ESMS data, along with the experimental size determination from diffusion, obtained via PGSE techniques and TEM, are all consistent with the proposed structures of **6** and **7**.

These self-assembled dodecahedra are significantly larger than the hydrocarbon  $\text{C}_{20}\text{H}_{20}$  with the same symmetry, obtained by classical covalent synthesis in 23 overall linear steps.<sup>12</sup> The cavity inside the self-assembled dodecahedra **6** and **7** should be capable of encapsulating not only small molecules, but also globular oligomers, molecules with solvation shells, and nanocrystals.

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**Supporting Information Available:** Details about pulse gradient spin–echo experiments, electrospray ionization MS, and TEM experiments, physical and spectroscopic data for compounds **6** and **7**, and X-ray crystallographic report for **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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