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Construction of Hexagonal Prisms of Variable Size via Coordination-Driven Multicomponent Self-Assembly

Zhigang Zhao, Yao-Rong Zheng, Ming Wang, J. Bryant Pollock, and Peter J. Stang*

Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84112

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The coordination-driven self-assembly of supramolecular hexagonal prisms has been achieved upon mixing a hexakis[4-(4-pyridyl)-phenyl]benzene donor ligand and carboxylate donor ligands such as sodium terephthalate, sodium (1,1′-biphenyl)-4,4′-dicarboxylate, sodium 4,4′-(diazene-1,2-diyl)dibenzoate, and 4,4′-dipyridyl with *cis*-$Pt(PEt_3)_2(OTf)_2$ in a 1:3:6 ratio. Four assembled hexagonal prisms have been characterized by ^{31}P and ^{1}H NMR multinuclear spectroscopy as well as electrospray ionization mass spectrometry. Molecular force-field simulations provide the possible conformation and size of each structure.

During the past two decades, coordination-driven metal-mediated self-assembly has attracted considerable attention and proven to be a powerful tool in the synthesis of well-defined multimetallic architectures with increasing structural complexity.[1−6] This was often accomplished by the combination of an organic donor with a metal acceptor, where both reagents possessed well-defined bonding directionality, leading to a discrete, highly symmetrical product. A more complex situation in self-assembly arises when more than two starting materials are mixed together in one vessel. Will an ordered discrete supramolecule or an oligomeric product mixture be the result? In fact, the successful achievement of the self-assembly of multiple components into discrete structures is less documented because of the increased number of numerous reaction pathways and products.[7] In general, a template molecule or an ion is often necessary to control such a multicomponent coordination self-assembly outcome.[8]

Furthermore, in an attempt to emulate nature's own complexity, synthetic chemists have become more adept at the construction of three-dimensional (3D) metallosupramolecular assemblies, i.e., cubes,[9] double squares,[10] cuboctahedra,[11]

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*To whom correspondence should be addressed. E-mail: Stang@chem.utah.edu.

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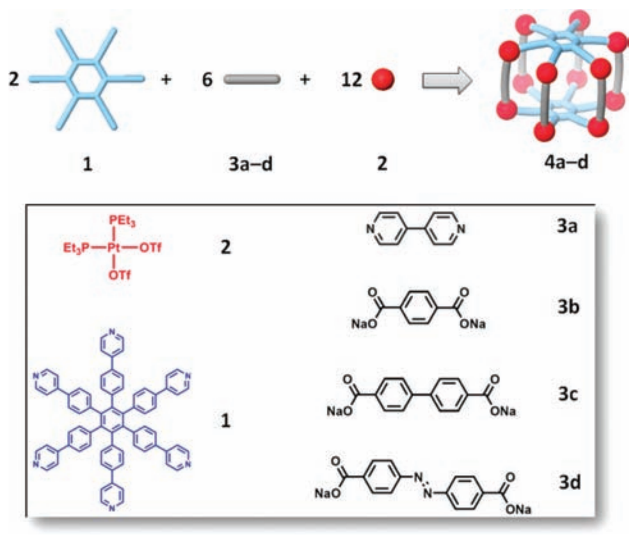
Scheme 1. Graphical Representation of the [2 + 6 + 12] Multicomponent Self-Assembly of Hexagonal Prisms **4a**−**4d**



adamantanoids,[12] dodecahedra,[13] and a sphere.[14] Such 3D species are capable of functions such as reaction catalysis and guest encapsulation and act as a microreaction vessel.[15] However, until now the construction of 3D hexagonal prisms via multicomponent coordination-driven transition-metal-mediated self-assembly has rarely been reported.[16] Herein, we report the multicomponent template-free synthesis of discrete hexagonal prisms upon the self-assembly of a 90° platinum acceptor with a hexapyridyl donor and a carboxylate or dipyridyl ligand. Despite the possibility of forming a myriad of oligomeric structures, discrete supramolecular hexagonal prisms are generated as the predominant products.

The formation of 3D hexagonal prisms is shown in Scheme 1. The linear carboxylate and dipyridyl donors **3a**−**3d** are designed as pillars, whereas hexakis[4-(4-pyridyl)phenyl]benzene (**1**) containing six pyridyl groups and *cis*-Pt$(PEt_3)_2(OTf)_2$ (**2**) are selected as faces and corners of the hexagonal prisms, respectively. When the three building blocks are mixed and reacted in a ratio of 1:3:6, discrete supramolecular hexagonal prisms can be formed. Their structures were characterized by ^{31}P and ^{1}H NMR multinuclear spectroscopy and electrospray ionization mass spectrometry (ESI-MS).

After heating at 50−56 °C for 6 h, the 1:3:6 mixture of **1**, **3a**, and **2** in acetone-d_6 and D_2O (9:1, v/v) yielded a clear solution. The $^{31}P\{^{1}H\}$NMR spectrum displayed two coupled doublets at 0.68 and 0.37 ppm with concomitant ^{195}Pt satellites. The signals are upfield-shifted by about 12 ppm compared to that of the starting platinum(II) acceptor **2** because of formation of the Pt−N coordination bond. The two different doublets in the $^{31}P\{^{1}H\}$NMR spectrum demonstrate that the phosphorus nuclei connected to the platinum atom in **4a** are chemically nonequivalent, which can only be rationalized by the coordination of donors **1** and **3a** with each platinum center in the hexagonal prism structure **4a**.[17] In the corresponding ^{1}H NMR spectrum of supramolecule **4a** (Figure 1), the α- and β-pyridyl protons of donors **1** and **3a** experience downfield shifts ($H_{\alpha\text{-Py}}$, 0.41−0.48 ppm; $H_{\beta\text{-Py}}$, 0.46−0.59 ppm) because of the loss of electron density that occurs upon coordination. The formation of the hexagonal prism structure **4a** is further confirmed by ESI-MS. As listed in Figures 2 and S3 in the Supporting Information, the isotopically resolved peaks corresponding to the hexagonal prism with the loss of PF_6^- anions are found at *m*/*z* 2751.2 $[\mathbf{4a} - 4PF_6]^{4+}$ and 2171.5 $[\mathbf{4a} - 5PF_6]^{5+}$.

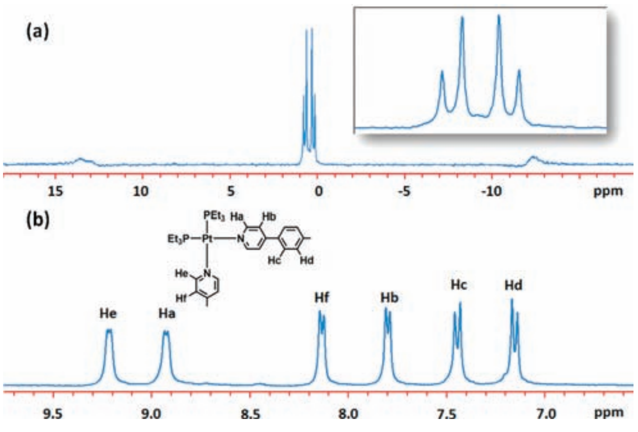


Figure 1. $^{31}P\{^{1}H\}$ (a) and partial ^{1}H (b) NMR spectra of hexagonal prism **4a**.

To further extend the variety of supramolecular hexagonal prisms constructed, we next utilized carboxylate ligands **3b**−**3d** as pillars to react with the hexapyridyl donor **1** and the 90° platinum(II) acceptor **2**.

Hexapyridyl donor **1** and carboxylate ligand **3b**, **3c**, or **3d**, respectively, were mixed with acceptor **2** in a 1:3:6 ratio and heated at 50−56 °C for 6 h in aqueous acetone. Upon ion exchange with KPF_6, hexagonal prisms **4b**−**4d** were obtained in high yield (91−96%). The $^{31}P\{^{1}H\}$NMR spectra (Figures 3a and S1A and S2A in the Supporting Information) of prisms **4b**−**4d** showed two coupled doublet peaks (**4b**, 6.19 and 1.06 ppm; $^{2}J_{P-P} = 21.30$ Hz; **4c**, 6.56 and 1.10 ppm; $^{2}J_{P-P} = 21.30$ Hz; **4d**, 6.99 and 2.13 ppm; $^{2}J_{P-P} = 21.30$ Hz) of approximately equal intensity with concomitant ^{195}Pt satellites, and these signals were upfield-shifted for **4b** (6.31 and 11.44 ppm), **4c** (5.77 and 11.22 ppm), and **4d** (5.34 and 10.19 ppm), compared with the 90° platinum(II) acceptor **2** (δ = 12.50 ppm) upon coordination with the pyridine and carboxylate groups. This result agrees with the heteroleptic coordination motif of **4b**−**4d**.[18] In the ^{1}H NMR spectra (Figures 3b and S1B and S2B in the Supporting Information) of **4b**−**4d**, the α- and β-pyridyl hydrogen signals both experience downfield shifts (**4b**, 0.25 and 0.46 ppm; **4c**, 0.45 and 0.68 ppm; **4d**, 0.44 and 0.65 ppm) compared with their chemical shifts in the precursor building block **1**, which are

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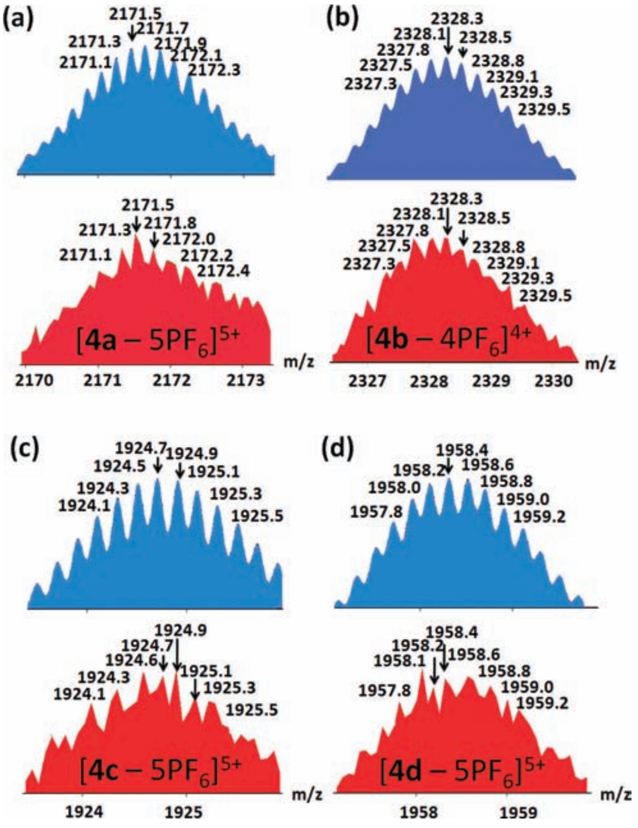

Figure 2. Theoretical (top, blue) and experimental (bottom, red) ESI-MS results for **4a**−**4d** hexagonal prisms.

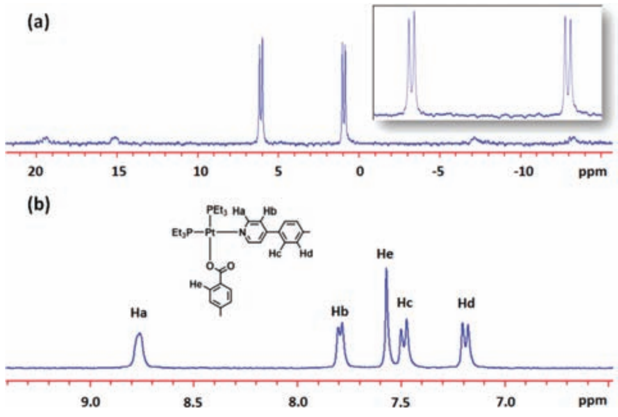

Figure 3. ^{31}P{^{1}H} (a) and partial ^{1}H (b) NMR spectra of hexagonal prism **4b**.

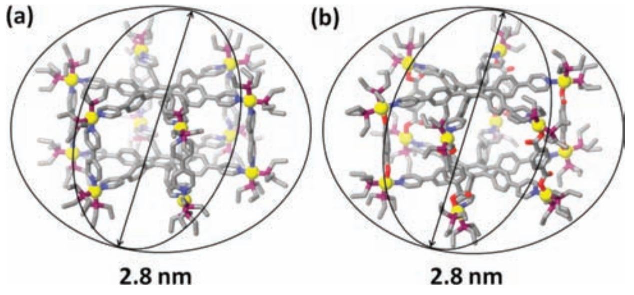

Figure 4. Molecular modeling of supramolecular hexagonal prisms **4a** (a) and **4b** (b) and their computational sizes.

associated with the loss of electron density upon coordination to the platinum metal centers. The sharp NMR spectral signals together with the solubility of the assemblies indicate that a self-assembly of high symmetry was formed predominantly in each reaction, and the formation of homoleptic species and oligomers can be ruled out.

Further evidence for the formation of assemblies **4b**−**4d** was obtained by ESI-MS (Figures 2b−2d and S3 in the Supporting Information). The ESI-MS of **4b** exhibited peaks for $[\mathbf{4b} - 4\mathrm{PF}_6]^{4+}$ and $[\mathbf{4b} - 5\mathrm{PF}_6]^{5+}$ at m/z 2328.3 and 1834.1, respectively. Likewise, peaks attributable to **4c** were found at m/z 1924.7 $[\mathbf{4c} - 5\mathrm{PF}_6]^{5+}$, as were those corresponding to **4d**, m/z 1958.4 $[\mathbf{4d} - 5\mathrm{PF}_6]^{5+}$ and m/z1607.9 $[\mathbf{4d} - 6\mathrm{PF}_6]^{6+}$. All ESI-MS signals are in good agreement with their theoretical distributions.

All attempts to crystallize the above four hexagonal prism structures have so far been unsuccessful. We have therefore used molecular force-field simulation to investigate the structural characteristics of supramolecular architectures **4a**−**4d**. A 1.0 ns molecular dynamics simulation (MMFF force field, 300 K, gas phase) was used to equilibrate each supramolecule, and the output of the simulation was then minimized to full convergence. As shown in Figures 4 and S4 in the Supporting Information, models of assemblies **4a**−**4d** are in the shape of hexagonal prisms with diameters of 2.8 nm (**4a**), 2.8 nm (**4b**), 3.4 nm (**4c**), and 3.8 nm (**4d**), respectively.

In conclusion, by combining hexapyridyl donor **1** and 90° organoplatinum acceptor **2** with dipyridyl and differently sized carboxylate donors **3a**−**3d** in an appropriate stoichiometric ratio, we have successfully constructed a discrete, nanoscopic 3D hexagonal prism of variable size via muticomponent coordination-driven self-assembly without the use of any template or ion. In addition, molecular force-field modeling has shown that these supramolecule hexagonal prisms have different sizes, which may have applications in host−guest chemistry and function as new microreactors.

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Supporting Information Available: General procedure of the self-assembly experiment, detailed characterization of assemblies **4a**−**4d**, and NMR and ESI-MS data as well as computational simulations for assemblies **4c** and **4d**. This material is available free of charge via the Internet at http://pubs.acs.org.