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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

Abstract

The coordination-driven self-assembly of supramolecular hexagonal prisms has been achieved upon mixing hexa(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(PET₃)₂(OTf)₂ in a 1:3:6 ratio. Four assembled hexagonal prisms have been characterized by ³¹P and ¹H multinuclear NMR spectroscopy as well as electrospray ionization mass spectrometry (ESI-MS). 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 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 (3-D) metallo-supramolecular assemblies i.e. cubes,⁹ double squares,¹⁰ cuboctahedra,¹¹ adamantanoids,¹² dodecahedra,¹³ and a sphere.¹⁴ Such 3-D species are capable of functions such as reaction catalysis, guest encapsulation, and act as a micro-reaction vessel.¹⁵ However, until now the construction of 3-D hexagonal prisms via multicomponent coordination-driven transition-metal-mediated self-assembly is rarely reported.¹⁶ Herein, we report the multicomponent template-free synthesis of discrete hexagonal prisms upon 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–d** are designed as pillars, whereas hexa-(4-(4-pyridyl)phenyl) benzene **1**

*To whom correspondence should be addressed. Stang@chem.utah.edu.

Supporting Information Available: General procedure of self-assembly experiment, detailed characterization of assemblies **4a–d**, 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>.

containing six pyridyl groups and *cis*-Pt(PEt₃)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 ³¹P and ¹H multinuclear NMR 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 D₂O (*v/v* 9:1) yielded a clear solution. The ³¹P{¹H}NMR spectrum displayed two coupled doublets at 0.68 and 0.37 ppm with concomitant ¹⁹⁵Pt satellites. The signals are upfield shifted by about 12 ppm compared to that of the starting Pt(II) acceptor **2** due to formation of the Pt-N coordination bond. The two different doublets in the ³¹P{¹H}NMR demonstrate that the phosphorus nuclei connected to the platinum atom in **4a** are chemically nonequivalent, which can only be rationalized by the coordination of donor **1** and **3a** with each platinum center in the hexagonal prism structure **4a**.¹⁷ In the corresponding ¹H NMR spectrum of supramolecule **4a**, 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 hexagonal prism structure **4a** is further confirmed by ESI-MS. As listed in Figure 2 and Figure S3 in the Supporting Information, the isotopically resolved peaks corresponding to the hexagonal prism with loss of PF₆⁻ anions are found at $m/z = 2751.2$ [**4a**-4PF₆]⁴⁺ and 2171.5 [**4a**-5PF₆]⁵⁺.

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

Hexapyridyl donor **1** and carboxylate ligands **3b**, **3c**, or **3d**, respectively, were mixed with acceptor *cis*-Pt(PEt₃)₂(OTf)₂ **2** in a 1:3:6 ratio and heated at 50–56 °C for 6 h in aqueous acetone. Upon ion exchange with KPF₆, hexagonal prisms **4b-d** were obtained in high yields (91%-96%). The ³¹P{¹H}NMR spectra (Figure 3a and Figure S1A and Figure S2A in the Supporting Information) of prisms **4b-d** showed two coupled doublets 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 ¹⁹⁵Pt satellites, and these signals were upfield shifted for **4b**: 6.31 and 11.44 ppm; **4c**: 5.77 and 11.22 ppm; **4d**: 5.34 and 10.19 ppm, compared with the 90° Pt(II) acceptor **2** ($\delta = 12.50$ ppm) upon coordination with the pyridine and carboxylate groups. This result agrees with the heteroleptic coordination motif of **4b-d**.¹⁸ In the ¹H NMR spectra (Figure 3b and Figure S1B and Figure S2B in the Supporting Information) of **4b-d**, 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 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-d** was obtained by ESI-MS (Figure 2b-c and Figure S3 in the Supporting Information). The ESI-MS of peaks for [**4b** exhibited peaks for [**4b**-4PF₆]⁴⁺ and [**4b**-5PF₆]⁵⁺ at $m/z = 2328.3$ and 1834.1 , respectively. Likewise, peaks attributable to **4c** were found at $m/z = 1924.7$ [**4c**-5PF₆]⁵⁺, as were those corresponding to **4d**: $m/z = 1958.4$ [**4d**-5PF₆]⁵⁺ and $m/z = 1607.9$ [**4d**-6PF₆]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–d**. A 1.0 ns molecular dynamics simulation (MMFF force field, 300K, gas phase) was used to equilibrate each supramolecule, and the output of the simulation was then minimized to full convergence. As shown in Figure 4 and Figure S4 (see Supporting Information), models of assemblies **4a–d** are in the shape of hexagonal prism with a diameter 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 dipyriddy and different size carboxylate donors **3a–d** in appropriate stoichiometric ratio, we have successfully constructed discrete, nanoscopic 3-D hexagonal prism of variable size via multicomponent coordination-driven self-assembly without 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 micro-reactors.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

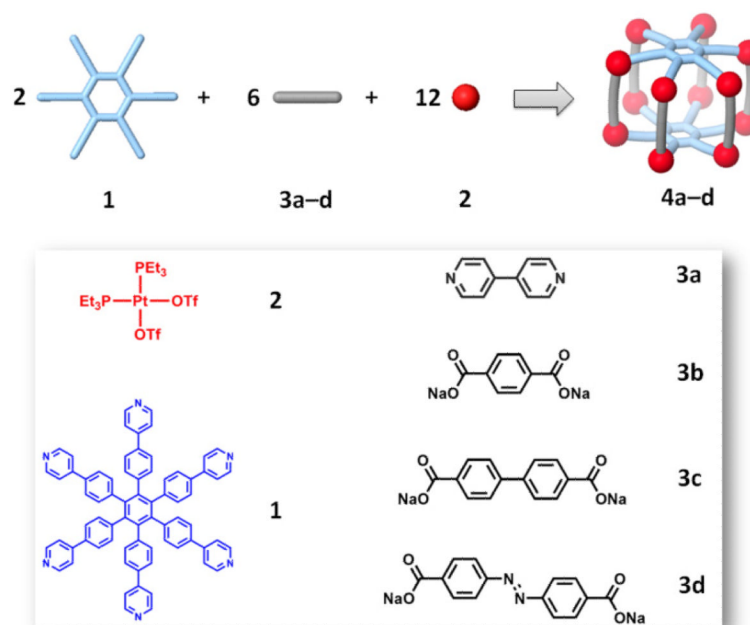
Acknowledgments

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

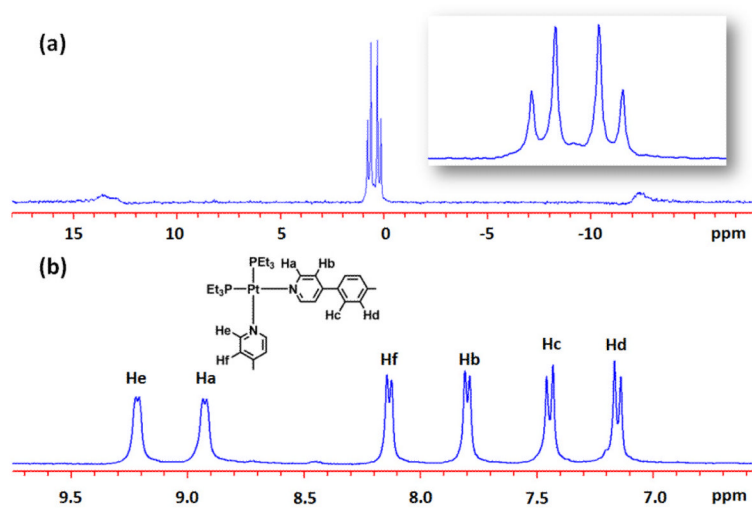


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ (a) and partial ^1H NMR (b) spectra of hexagonal prism **4a**.

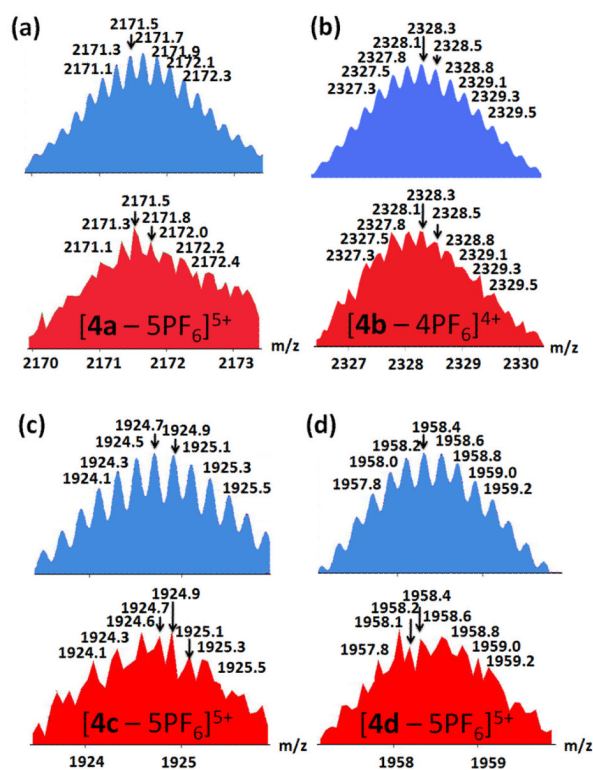


Figure 2. Theoretical (top, blue) and experimental (bottom, red) ESIMS results for **4a–d** hexagonal prisms.

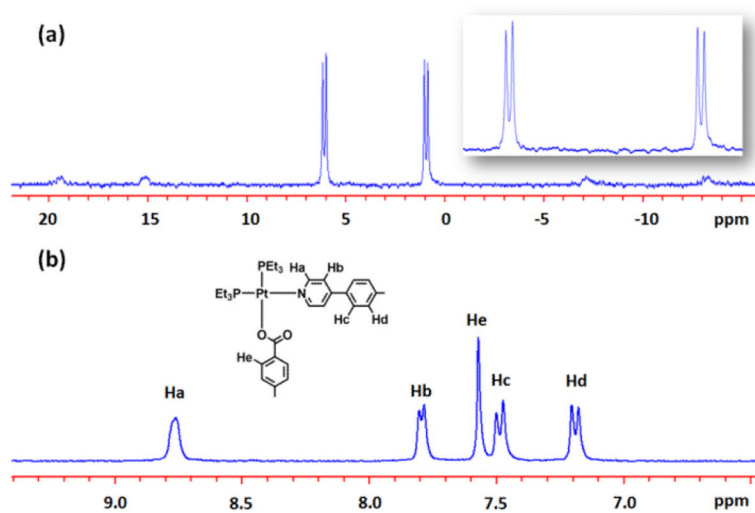


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ (a) and partial ^1H NMR (b) spectra of hexagonal prism **4b**.

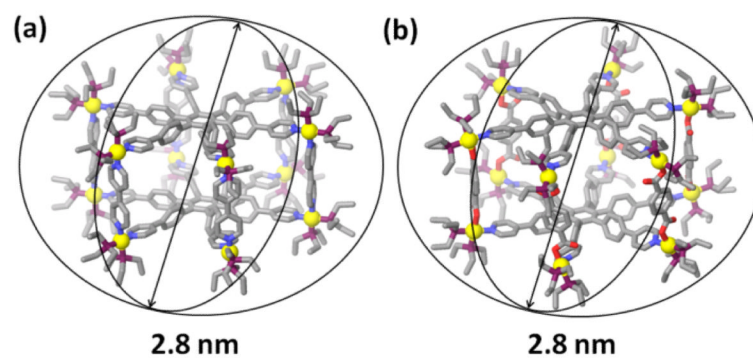


Figure 4. Molecular modeling of supramolecular hexagonal prisms **4a** (a) and **4b** (b) and their computational sizes.