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Metallosupramolecular Tetragonal Prisms via Multicomponent Coordination-Driven Template-Free Self-Assembly

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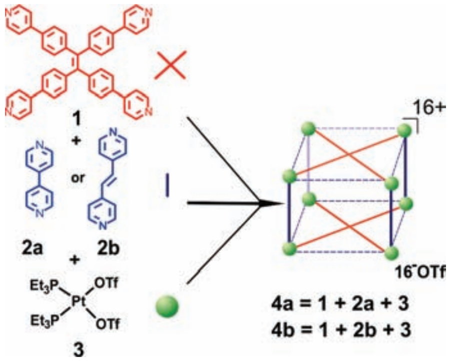
Nature has developed the construction of functional biological systems via the assembly of multiple distinct molecular subunits. For example, the proteasome of yeast *Saccharomyces cerevisiae* is assembled from pairs of seven different proteins.[1] In the past two decades, coordination-driven self-assembly has emerged as a powerful new tool simulating nature's own complexity to construct abiological supramolecular architectures with well-defined shape and size.[2] Remarkable progress has been made in the self-assembly of two elaborately designed building blocks encoded with specific information such as coordination geometry and directionality in proper stoichiometric ratios to give preprogrammed supramolecular structures.[3] However, for multicomponent coordination-driven self-assembly with more than one metal center or individual donors, an equilibrium between numerous supramolecular structures generally exists,[4] resulting in a self-organized mixture via self-recognition and self-selection.[5] Thus, the preparation of a single and discrete supramolecular architecture capable of mimicking the natural systems via multicomponent coordination-driven self-assembly remains challenging.[6]

Until now, the efficient preparation of metallosupramolecules via multicomponent abiological self-assembly has been largely limited to 2-D structures.[6−9] We recently demonstrated the formation of 2-D fused metallacyclic polygons via the combination of properly designed multiple different tectons in specific stoichiometric ratios;[7] Schmittel et al. also reported the formation of a five-component supramolecular trapezoid through integrative self-sorting.[8,9] However, self-assembled 3-D structures are more prevalent and important in nature and biology. For example, polypeptides have to fold into a 3-D structure to ensure their function, and the viral coats of many viruses have structures with icosahedral symmetry.[10] Furthermore, functional 3-D supramolecules play significant roles in a wide range of applications such as host−guest chemistry[11] and supramolecular catalysis[12] and as micro-reaction vessels.[13] Although two-component coordination-driven self-assembly is an efficient method to prepare 3-D metallosupramolecules, construction of 3-D supramolecular structures by multicomponent self-assembly remains limited.[14] For example, trigonal prisms could be prepared via three-component self-assembly, but only in the presence of aromatic templates.[15] Herein, we present the multicomponent coordination-driven self-assembly of 3-D tetragonal prisms by the reaction of two different donors and one metal acceptor in proper stoichiometric ratios without the use of any templates.

The design rationale for multicomponent coordination-driven self-assembly of a tetragonal prism is illustrated in Scheme 1. Tetra(4-pyridylphenyl)ethylene compound **1** is designed incorporating four pyridine groups that can act as the faces of a tetragonal prism during the self-assembly, while the linear donor 4,4′-bipyridine (**2a**) or *trans*-1,2-di(4-pyridyl)ethylene (**2b**) and 90° platinum triflate **3** are selected as pillars and corners of the tetragonal prism, respectively, under the combined interaction of edge-directed and face-directed self-assembly.[2d] When the three building blocks **1**, **2**, and **3** are reacted in a stoichiometric ratio of 1:2:4, the formation of tetragonal prism can be expected as shown in Scheme 1.

Scheme 1. Multicomponent Coordination-Driven Self-Assembly of Tetragonal Prisms



The self-assembly behavior of the three-component system composed of coplanar tetratopic donor **1**, linear donor **2**, and acceptor **3** was investigated by addition of the CD_2Cl_2 solution of donors **1** and **2** into the CD_3NO_2 solution of acceptor **3** in the ratio of 1:2:4, followed by a further 12 h of reaction at room temperature. ^{31}P and ^{1}H NMR multinuclear analysis of the reaction mixture indicated the formation of single and discrete assemblies with high symmetry. The $^{31}P\{^{1}H\}$ NMR spectra of self-assembly products **4a**,**b** show two different doublets at −0.7 and −0.6 ppm with concomitant ^{195}Pt satellites, upfield-shifted about 13.5 ppm compared to the signal of the staring acceptor **3** due to coordination with the pyridine rings (Figure 1 and Figure S2 in the Supporting Information (SI)); the two doublets were confirmed by different field strength and variable-temperature $^{31}P\{^{1}H\}$ NMR spectra (Figures S3 and S4, SI). The two different doublets in the $^{31}P\{^{1}H\}$ NMR indicates that the phosphorus nuclei connected to the platinum atom in **4** are magnetically nonequivalent. These results could only be explained by considering that each platinum center is coordinating with two different pyridines belonging to donors **1** and **2**, respectively, in the tetragonal prism structure **4** (Scheme 1). In the

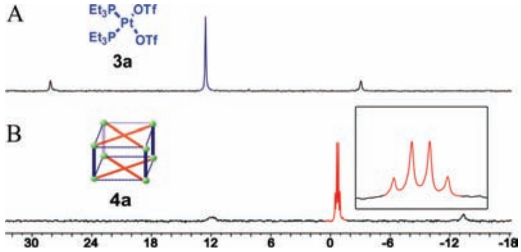


Figure 1. $^{31}P\{^{1}H\}$ NMR spectra (121.4 MHz, 298 K, CD_2Cl_2/CD_3NO_2 v:v = 2:1) of acceptor **3** (A) and tetragonal prism **4a** (B).

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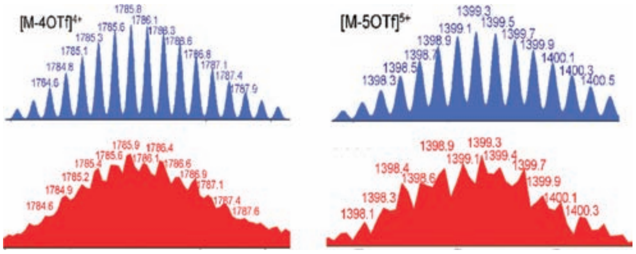

Figure 2. Theoretical (blue) and experimental (red) ESI mass spectra of tetragonal prism **4a**.

corresponding ^{1}H NMR spectra of product **4**, signals for the protons of the pyridine rings in donor ligands **1** and **2** exhibit downfield shifts (H_α−Py, 0.20−0.30 ppm for **4a**,**b**; H_β−Py, 0.40−0.45 ppm for **4a** and 0.20−0.25 ppm for **4b**) resulting from the loss of electron density upon coordination of the pyridine nitrogen atoms with the platinum metal center (Figures S5 and S6, SI). The sharp NMR signals in both of the ^{31}P{^{1}H} and ^{1}H NMR spectra along with the solubility of these species ruled out the formation of oligomers. Moreover, the observed NMR data exclude the formation of either simple prisms or squares between donor **1** and **3**, as well as donor **2** and **3**, respectively.

Electrospray ionization (ESI) mass spectra of **4** were measured to provide evidence for the formation of tetragonal prism structures. In the mass spectrum of assembly **4a**, peaks at $m/z = 1786.1$ and 1399.3 corresponding to the $[M - 4OTf]^{4+}$ and $[M - 5OTf]^{5+}$ were observed, and their isotopic distributions were in good agreement with the theoretical expectation (Figure 2). The mass spectrum of tetragonal prism **4b** shows a $[M - 5OTf]^{5+}$ peak at $m/z = 1420.1$, in good agreement with its theoretical isotopic distribution (Figure S7, SI).

All attempts to get crystal structures of tetragonal prisms **4** were unsuccessful; therefore, molecular force field simulations were used to gain further insight into the structural characteristics of supramolecules **4**. A 1.0 ns molecular dynamics simulation (MMFF force field) was used to equilibrate supramolecules **4a**,**b**, followed by energy minimization of the resulting structures to full convergence. The model structure of **4a** features a well-defined tetragonal prism with length, width, and height of 1.66, 1.55, and 1.14 nm, respectively. The modeling of prism **4a** also indicated a diameter of 3.61 nm (Figure 3). The simulation of **4b** shows a similar tetragonal structure and reveals a diameter of 3.65 nm (Figure S8, SI). We also carried out pulsed-gradient spin−echo (PGSE) NMR measurements and, in conjunction with the Stokes−Einstein equation (see Table S1, SI), determined the approximate sizes of **4**. The results from the PGSE NMR measurements (**4a**, 4.2 ± 0.1 nm; **4b**, 4.3 ± 0.1 nm) are comparable to those obtained by molecular force field modeling for the diameter of **4** (Figure 3).

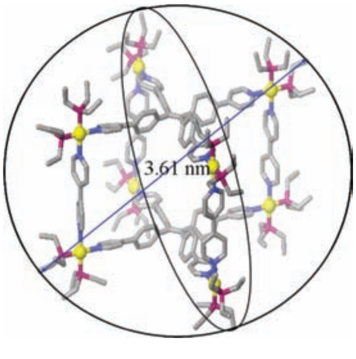

Figure 3. Molecular modeling of tetragonal prism **4a**.

In conclusion, we report herein the construction of discrete 3-D tetragonal prisms via multicomponent coordination-driven self-assembly from combination of a tetraphenylethylene-based tetratopic donor (**1**), a linear dipyridine donor (**2a**,**b**), and a 90° platinum metal complex in appropriate stoichiometric ratios without using any template. Furthermore, the use of linear pillars of different lengths in the assembly allows leads to tetragonal prisms with different cavity size, which may result in applications in host−guest chemistry or as new micro-reactors. We are currently exploring the functionalization of these tetragonal prisms via multicomponent coordination-driven self-assembly.

Acknowledgment. P.J.S. thanks the NIH (Grant GM-057052) for financial support.

Supporting Information Available: Synthesis and analytical data for **1** and **4**; PGSE measurement, strength, and temperature-dependent ^{31}P{^{1}H} NMR for **4**; ESI mass spectra and molecular modeling for **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA100889H