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Coordination-Driven Self-Assembly of Three-Dimensional Supramolecular Dendrimers

Yao-Rong Zheng,[†] Koushik Ghosh,[†] Hai-Bo Yang,*[,‡] and Peter J. Stang*[,†]

[†]*Department of Chemistry, University of Utah, 315 South 1400 East, Room 2020, Salt Lake City, Utah 84112, and* [‡]*Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 N. Zhongshan Road, Shanghai, China 200062*

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The design and synthesis of novel three-dimensional (3-D) supramolecular dendrimers is described. The coordination-driven self-assembly of a 120° diplatinum acceptor and tritopic pyridyl donors bearing [G-0]−[G-3] Fréchet-type dendrons results in a series of supramolecular dendrimers under mild conditions, possessing a robust adamantanoid core of well-defined shape and size. The assemblies were identified using multinuclear (^{31}P and ^{1}H) NMR spectroscopy and electrospray ionization mass spectrometry, as well as pulsed-field-gradient spin−echo (PGSE) NMR measurement together with computational simulations. Isotopically resolved mass spectral data support the existence of the [6 + 4] assembly of adamantanoid dendrimers, and the NMR results are consistent with the formation of these symmetrical assemblies. PGSE NMR measurements together with MMFF force-field modeling clearly reveal the structural feature of the 3-D supramolecular dendrimers with varying sizes.

Dendrimers of high structural complexity have emerged as one of the most important structures of significant interest in chemistry, biology, and medical research.[1,2] While merging with self-assembly, complicated dendritic structures can be synthesized in a simple manner. One-dimensional (1-D) helical supramolecular dendrimers, for example, that vividly mimic natural pore-forming proteins can be efficiently self-assembled by a library of amphiphilic dendritic peptides.[2a−c] Recently, via coordination-driven self-assembly, a variety of two-dimensional (2-D), such as rhomboid, square, and hexagon, supramolecular dendrimers have been prepared.[3,4] Most reported systems are limited to utilizing helical and 2-D structures. As compared with 1-D and 2-D structures, three-dimensional (3-D) assemblies exhibit a finite cavity of well-defined shape and size and can be valuable in applications such as guest encapsulation, gas storage, catalysis, and drug delivery.[5] However, 3-D supramolecular dendrimers are still rare,[2d] mainly because of the design constraint of rigid well-defined 3-D structures.

Coordination-driven self-assembly represents a successful methodology for constructing 3-D supramolecules, as indicated by a variety of elaborate supramolecular cages, prisms, and polydedra of well-defined shape and size.[6] The self-assembled 3-D supramolecules have proven useful for capturing guest molecules, in supramolecular catalysis, and opening access to unusual reactions by virtue of 3-D nanocavities.[7] Covalent modifications of molecular subunits

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

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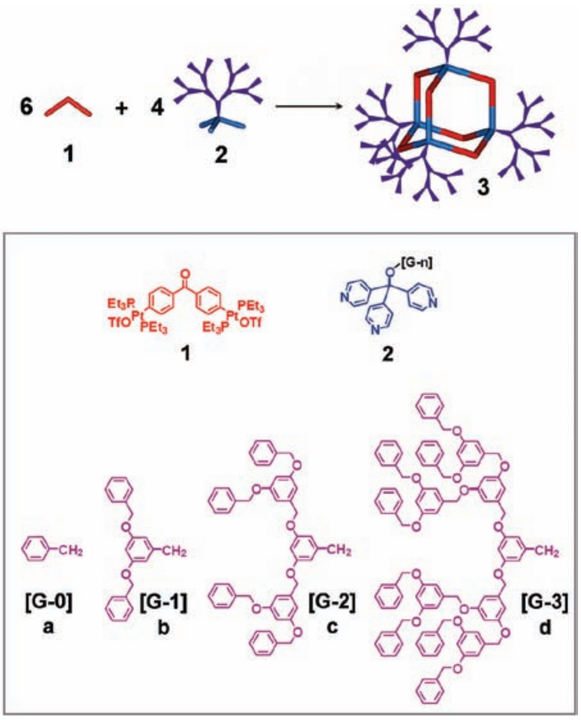
Scheme 1. Representation of the [6 + 4] Self-Assembly of Adamantanoid Supramolecular [G-0]−[G-3] Dendrimers **3a**−**3d**



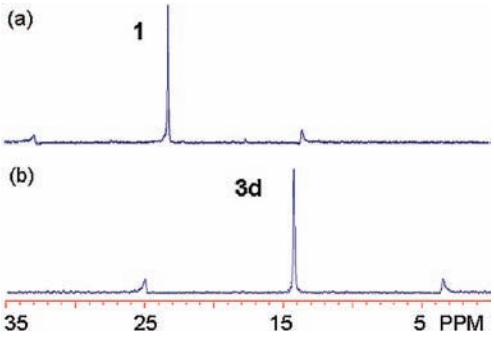


Figure 1. $^{31}P\{^1H\}$ NMR (300 MHz, 1/1 acetone-d_6/CD_2Cl_2) spectra of (a) 120° organoplatinum acceptor **1** and (b) [G-3] supramolecular dendrimer **3d**.

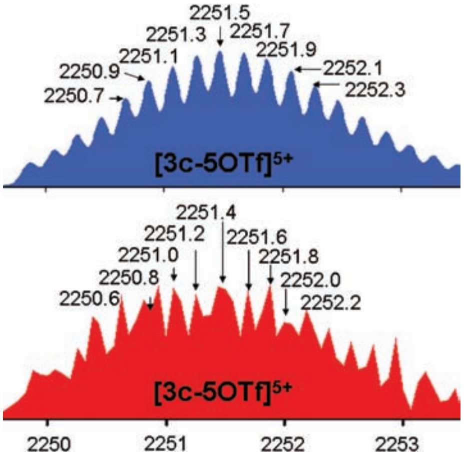


Figure 2. Calculated (blue, top) and experimental (red, bottom) ESI mass spectra of [G-2] supramolecular dendrimer **3c**.

can endow assemblies with a wide variety of fascinating structural and functional properties.[8] Recent examples reported by Fujita et al. demonstrated that functionalization of the interior and/or exterior of a $M_{12}L_{24}$ palladium-based supramolecular sphere can result in saccharide clusters, nanoscale fluorodroplets, and confined polymerization.[9] Because of the robust structure, unique confined space, and designable framework, the coordination-driven self-assembled 3-D metallosupramolecule is a promising candidate for constructing 3-D supramolecular dendrimers.

We have recently prepared 2-D hexagonal and 3-D cuboctahedral multifunctional scaffolds with a precise number, position, and orientation of functional groups by chemical tailoring of molecular subunits.[10] Encouraged by the power and versatility of this methodology, we extend it to the construction of 3-D supramolecular dendrimers and hereby present the self-assembly of 120° diplatinum acceptors **1** with tritopic donors **2a**−**2d**, substituted with Fréchet-type dendrons from [G-0] to [G-3].[10] As shown in Scheme 1, coordination-driven self-assembly allows for the quantitative generation of a series of supramolecular dendrimers **3a**−**3d** possessing a rigid 3-D adamantanoid core. These structures have been identified by multinuclear (^{31}P and ^1H) NMR spectroscopy and electrospray ionization (ESI) mass spectrometry, as well as pulsed-field-gradient spin−echo (PGSE) NMR measurement together with computational simulations.

[G-0]−[G-3] tripyridyl donors **2a**−**2d** were prepared by substituting tripyridin-4-ylmethanol with Fréchet-type dendrons. The CD_2Cl_2 solution of tripyridyl donors **2** was slowly added into an acetone-d_6 solution of 120° organoplatinum acceptor **1** in a 2:3 ratio, and after stirring for 15 min at room temperature, [6 + 4] self-assembly of adamantanoid dendrimers **3** of different sizes was quantitatively obtained. In the $^{31}P\{^1H\}$ NMR spectra (Figure 1a,b and the Supporting Information) of these mixtures, only a sharp singlet (**3a**, 14.06 ppm; **3b**, 14.06 ppm; **3c**, 14.05 ppm; **3d**, 14.01 ppm) with concomitant ^{195}Pt satellites can be found. Because of the formation of the Pt−N coordination bond, the signals are shifted upfield from that of the organoplatinum acceptor **1** by approximately 9.0 ppm. Likewise, the ^1H NMR spectra (see the Supporting Information) exhibit sharp signals for the pyridyl protons with small shifts downfield ($\Delta\delta_{Py\alpha-H}$, 0.30 ppm; $\Delta\delta_{Py\beta-H}$, 0.75 ppm) due to the loss of electron density that occurs upon coordination. The well-assigned sharp NMR signals in both the ^{31}P and ^1H NMR spectra agree with the high symmetry of **3** and rule out the formation of oligomers.

ESI mass spectrometry further confirmed the [6 + 4] structures (Supporting Information). In the ESI mass spectrum of the [G-0] adamantanoid dendrimer **3a**, peaks corresponding to $[M - 4OTf]^{4+}$ and $[M - 5OTf]^{5+}$ can be found at

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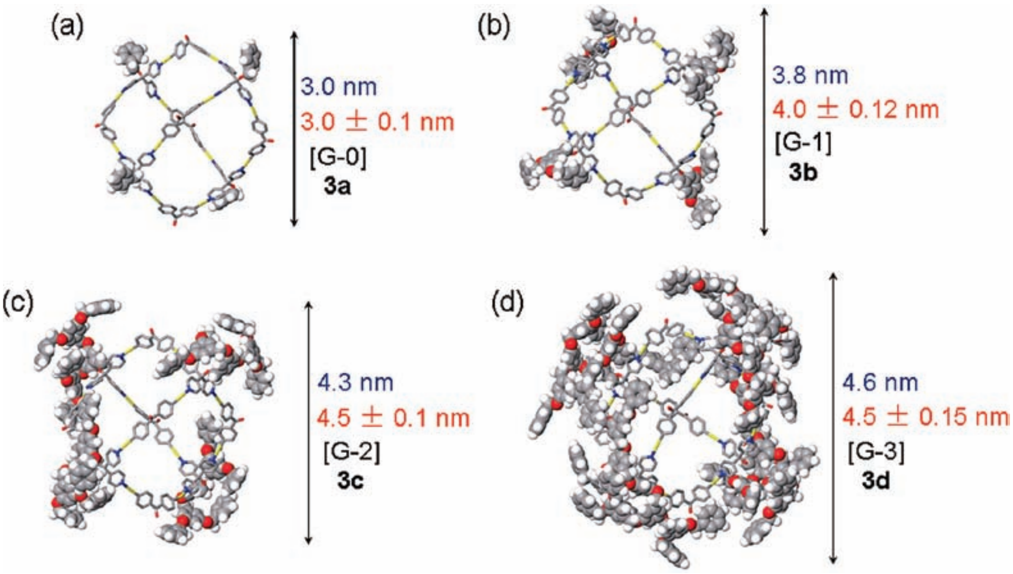

Figure 3. Computational simulations (MMFF) of 3-D dendrimers **3a**−**3d** (protons and triethylphosphrous moieties of the adamantanoid core omitted for clarity) and their calculated (blue) sizes as well as experimental (red) values from PGSE NMR measurements.

m/*z* 1742.4 and 1427.3. The ESI mass peak for loss of triflate anions from [G-1] adamantanoid dendrimer **3b** at *m*/*z* 1912.2 ([M − 5OTf]$^{5+}$) is observed, likewise for the [G-2] adamantanoid dendrimer **3c** at *m*/*z* 2251.6 ([M − 5OTf]$^{5+}$; Figure 2). All ESI mass peaks are isotopically resolved and agree with their theoretical distributions. However, for the [G-3] adamantanoid dendrimer **3d**, because of its high molecular weight, an isotopically resolved ESI mass signal was not obtained.

Because suitable X-ray-quality crystals could not be obtained, a computational study was carried out to gain insight into the structural characteristics of these assemblies. A 1.0 ns molecular dynamics simulation [molecular mechanics force field (MMFF), 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 Figure 3, each assembly has a 3.0 nm adamantanoid core with T_d symmetry, and the size of the overall structure is increased from 3.0 nm (for [G-0] **3a**) to 4.6 nm (for [G-3] **3d**). In **3d**, the adamantanoid core is partially covered by a dendritic shell.

PGSE NMR measurements were used to characterize these structures by determination of the translational self-diffusion coefficient, and in conjunction with the Stokes−Einstein equation, the "effective size" of the overall assembly in solution was obtained.[11] The ^{1}H NMR PGSE measurements for all assemblies in acetone-d_6 (see the Supporting Information) were determined: **3a**, 3.0 ± 0.1 nm; **3b**, 4.0 ± 0.12 nm; **3c**, 4.5 ± 0.1 nm; **3d**, 4.5 ± 0.15 nm. As indicated in Figure 3, they are in good agreement with the computational values (**3a**, 3.0 nm; **3b**, 3.8 nm; **3c**, 4.3 nm; **3d**, 4.6 nm) from the MMFF modeling. Because the dendrons on the exterior are spreading around the adamantanoid core instead of spreading out, the size increase from **3c** to **3d** is minor, resulting in a similar size in the PGSE NMR measurement.

In conclusion, we have developed a convergent synthesis of 3-D metallosupramolecular dendrimers via coordination-driven self-assembly, where the exterior dendrons were introduced by premodification of the molecular subunits. These supramolecular dendrimers show a unique 3-D adamantanoid core, which is partially covered by the dendritic exterior, and exploration of the interior environment would be interesting and valuable. Furthermore, functionalization of the dendrons and/or the supramolecular core should allow access to 3-D hollow supramolecular functional systems with potential applications such as guest encapsulation, nanoreactor, and drug delivery.[1]

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Supporting Information Available: General detailed experimental procedures for the synthesis and characterization of dendritic tripyridyl donors **2a**−**2d** and supramolecular dendrimers **3a**−**3d** (http://pubs.acs.org/paragonplus/submission/jacsat/). This material is available free of charge via the Internet at http://pubs.acs.org.

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