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# Molecular Architecture via Coordination: Self-Assembly of Nanoscale Hexagonal Metallodendrimers with Designed Building Blocks

Hai-Bo Yang,*,† Neeladri Das,† Feihe Huang,† Adam M. Hawkridge,‡ David C. Muddiman,‡ and Peter J. Stang*,†

*Department of Chemistry, University of Utah, 315 South 1400 East, RM 2020, Salt Lake City, Utah 84112, and W. M. Keck FT-ICR Mass Spectrometry Laboratory and Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695*

Received May 15, 2006; E-mail: stang@chem.utah.edu

Dendrimers that have a regularly branched three-dimensional architecture have emerged as one of the most striking topics within supramolecular chemistry since the mid-1980s.[1] Recently, self-assembly of dendrimers to provide well-defined nanoscale architectures has been investigated by employing electrostatic, hydrogen-bonding, metal-ligating, and other noncovalent interactions.[2,3] Among various types of self-assembled dendrimers, metallodendrimers are quite attractive due to their potential applications in catalysis,[4] chiroptical sensing,[5] biological function mimicking,[6] and light harvesting.[7]

Recently, cavity-cored dendrimers have received considerable attention because of their elaborate structures and potential applications in delivery and recognition.[8] For instance, molecular hexagons functionalized with Percec-like first generation dendrons[9] and cavity-cored dendrimers formed via metal nanoparticle (MNP)-cored strategy[8f] have been reported. However, until now there are few examples of metallodendrimers that possess cavities with predesigned shape as their core.[8d,e] Most organometallic dendrimers reported previously employ metal atoms, organic skeletons, or metal nanoparticles as a core.[3b,8a]

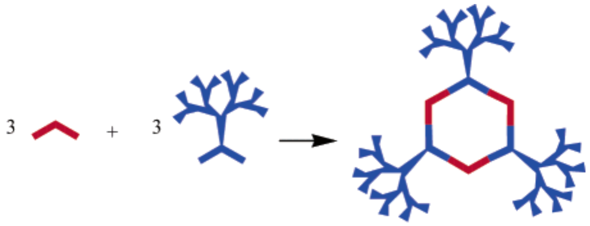
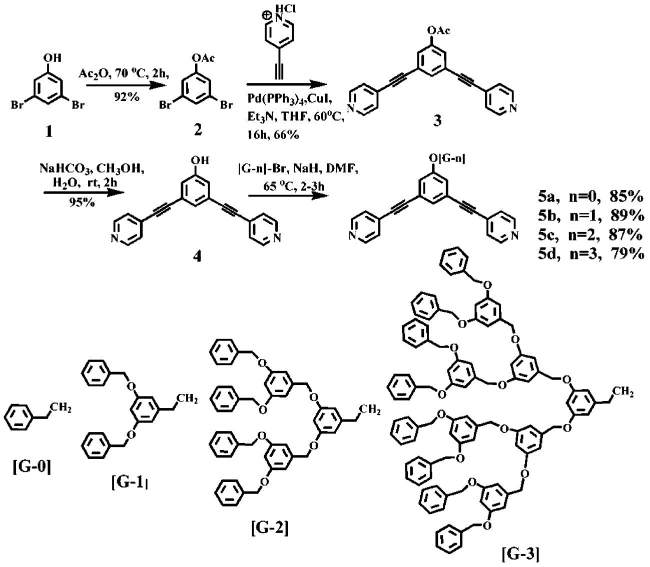


***Figure 1.*** Graphical representation of the self-assembly of hexagonal metallodendrimers.

Highly symmetric supramolecular polygons have been successfully generated via the directional-bonding approach.[10] Metallodendrimers having a cavity with predetermined shape, geometry, and symmetry as a core can be synthesized efficiently by the proper choice of a dendritic donor precursor or Pt-containing acceptor subunit with predefined angles and symmetry. Herein, we report the first self-assembly of nanoscale metallodendrimers that have a hexagonal cavity as a core using the aforementioned strategy (Figure 1). These novel hexagonal metallodendrimers containing a void space have been prepared in excellent yield (>95%) by the combination of 120° dendritic donor subunits (substituted with Fréchet-type dendrons) and 120° di-Pt(II) acceptor angular linkers in 1:1 stoichiometric ratio.

***Scheme 1.*** Synthesis of [G0]−[G3] 120° Dendritic Linkers



The synthesis of [G0]−[G3] 120° donor building blocks **5a**−**d** commenced with acylation of commercially available 2,3-dibromophenol to give **2** (Scheme 1). **3** was made by palladium-mediated coupling of **2** with 4-ethynyl pyridine in reasonable yield (66%). After ester hydrolysis and etherification, the [G0]−[G3] 120° precursors **5a**−**d** substituted with Fréchet-type dendrons were obtained.[11]

Heating the [G0]−[G3] 120° donors **5a**−**d** with an equimolar amount of the 120° di-platinum acceptor **6** in a 10:1 (v/v) acetone-$d_6$/$D_2O$ mixture overnight resulted in the [3+3] hexagonal metallodendrimers in excellent yields, respectively (Scheme 2). Multinuclear NMR ($^1$H and $^{31}$P) analysis of [G0]−[G3] assemblies **7a**−**d** exhibited very similar characteristics, which suggested the formation of discrete, highly symmetric species. The $^{31}$P {$^1$H} NMR spectra of [G0]−[G3] assemblies displayed a sharp singlet (ca. 18.5 ppm) shifted upfield from the starting platinum acceptor **6** by approximately 5.5 ppm. This change, as well as the decrease in coupling of the flanking $^{195}$Pt satellites (ca. $\Delta J = -195$ Hz), is consistent with back-donation from the platinum atoms. In the $^1$H NMR spectrum of each assembly, the hydrogen atoms of the pyridine rings exhibited small shifts downfield (α-H, 0.34−0.41 ppm; $\beta$-H, 0.43−0.50 ppm) due to the loss of electron density that occurs upon coordination of the pyridine−N atom with the Pt(II) metal center. The sharp NMR signals in both the $^{31}$P and $^1$H NMR along with the solubility of these species ruled out the formation of oligomers.

The structures of the hexagonal metallodendrimers have also been confirmed by ESI mass spectrometry and elemental analysis. In the ESI mass spectra of [G0] and [G1] assemblies **7a** and **7b**, peaks

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† University of Utah.
‡ North Carolina State University.

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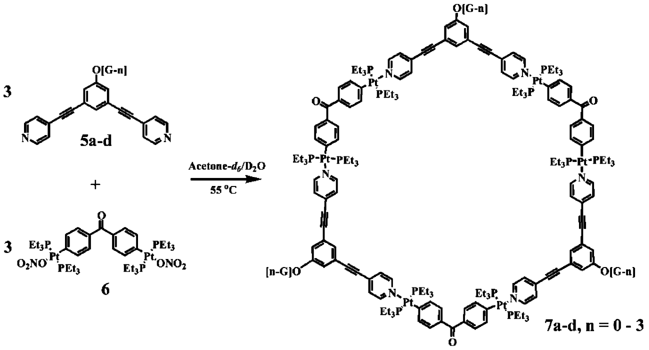
***Scheme 2.*** Self-Assembly of [G0]−[G3] 120° Dendritic Linkers **5a**−**d** with Di-platinum Acceptor **6**



attributable to the loss of nitrate counterions, $[M - 2NO_3]^{2+}$ ($m/z$ = 2267.7 **7a**, $m/z$ = 2586.3 **7b**), where M represents the intact assemblies, were observed. These peaks were isotopically resolved and they agree very well with the theoretical distribution. The ESI mass spectrum of [G2] assembly **7c** showed two charged states at $m/z$ = 1580.6 and 1252.0, corresponding to the $[M - 4NO_3]^{4+}$ and $[M - 5NO_3]^{5+}$ species, respectively, and their isotopic resolution is in good agreement with the theoretical distribution. The isotopic resolution of the peak at $m/z$ = 1761.5 $[M - 5NO_3]^{5+}$ in ESI−FT-ICR mass spectrum of [G3] assembly **7d** is in excellent agreement with the theoretical distribution (Figure 2).

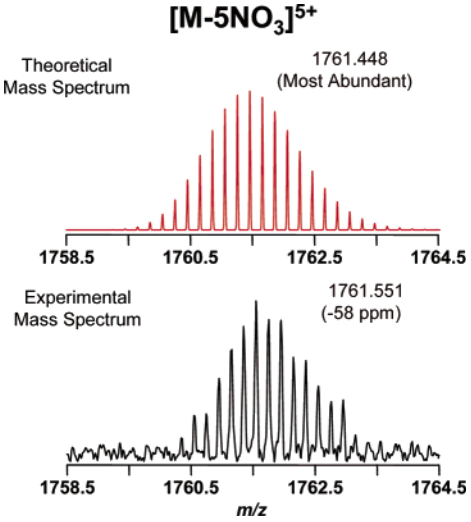


***Figure 2.*** The ESI−FT-ICR mass spectrum of [G3]-metallodendrimer **7d**.

MM2 force-field simulations were employed to optimize the geometry of [G3]-metallodendrimer **7d** (Figure 3). The space filling model of the simulated structure indicates **7d** has a nonplanar hexagonal cavity with an internal radius of approximately 1.6 nm as the core, whereas the outer radius is about 2.8 nm.

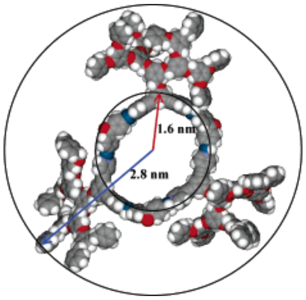


***Figure 3.*** Space-filling model of [G3]-metallodendrimer **7d** optimized with the MM2 force-field simulation.

The coordination-driven self-assembly described here demonstrates the ready formation of discrete nanoscopic metallodendrimers by simple combination of predesigned dendritic donor and di-Pt(II) acceptor building blocks, which enriches the library of metallodendrimers. This strategy provides rapid access to supramolecular metallodendrimers with a hexagonal cavity as a core that may have potential applications in host−guest chemistry. We are currently extending this idea to other two-dimensional structures such as rhomboids, squares, and triangles, and even three-dimensional architectures such as trigonal prisms and trigonal bipyramids.

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**Supporting Information Available:** General detailed experimental procedures and characterizations data for all metallodendrimers, ESI/MS of metallodendrimers **7a**−**d**, and ESI−FTI-ICR/MS of **7d**. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) (a) Fréchet, J. M. J.; Tomalia, D. A. *Dendrimers and Other Dendritic Polymers*; VCH-Wiley: New York, 2000. (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons*; Wiley-VCH: Weinheim, 2001. (c) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819−3868.

(2) (a) Franz, A.; Bauer, W.; Hirsch, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1564−1567. (b) Corbin, P. S.; Lawless, L. J.; Li, Z.; Ma, Y.; Witmer, M. J.; Zimmerman, S. C. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5099. (c) Crespo-Biel, O.; Dordi, B.; Reinhoudt, D. N.; Huskens, J. *J. Am. Chem. Soc.* **2005**, *127*, 7594−7600. (d) Leung, K. C.-F.; Arico, F.; Cantrill, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 5808−5810. (e) Yamaguchi, N.; Hamilton, L. M.; Gibson, H. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 3275−3279.

(3) (a) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681−1712. (b) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689−1746. (c) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665−1688.

(4) (a) Astruc, D.; Blais, J.-C.; Cloutet, E.; Djakovitch, L.; Rigaut, S.; Ruiz, J.; Sartor, V.; Valério, C. *Top. Curr. Chem.* **2000**, *210*, 229−259. (b) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181−190.

(5) Li, W.-S.; Jiang, D.-L.; Suna, Y.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 7700−7702.

(6) (a) Enomoto, M.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 874−875. (b) Percec, V.; Dulcey, A. E.; Peterca, M.; Ilies, M.; Sienkowska, M. J.; Heiney, P. A. *J. Am. Chem. Soc.* **2005**, *127*, 17902−17909.

(7) (a) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701−1710. 10658. (b) Choi, M.-S.; Yamazaki, T.; Yamazaki, I.; Aida, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 150−158. (c) Mo, Y.-J.; Jiang, D.-L.; Uyemura, M.; Aida, T.; Kitagawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 10020−10027.

(8) (a) Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293−346. (b) Wendland, M. S.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 1389−1390. (c) Percec, V.; Dulcey, A. E.; Balagurusamy, V. S. K.; Miura, Y.; Smidrkal, J.; Peterca, M.; Nummelin, S.; Edlund, U.; Hudson, S. D.; Heiney, P. A.; Duan, H.; Magonov, S. N.; Vinogradov, S. A. *Nature.* **2004**, *430*, 764−768. (d) Gorman, C. B.; Smith, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 9342−9343. (e) Wang, P.; Moorefield, C. N.; Newkome, G. R. *Org. Lett.* **2004**, *6*, 1197−1200. (f) Niu, Y.; Crooks, R. M. In *Dendrimers and Nanoscience*; Astruc, D., Ed.; Compte-Rendus Chimie, Elsevier: Paris, 2003; Vol. 6, p 989.

(9) (a) Fischer, M.; Lieser, G.; Rapp, A.; Schnell, I.; Mamdouh, W.; De Feyter, S.; De Schryver, F. C.; Hoger, S. *J. Am. Chem. Soc.* **2004**, *126*, 214−222. (b) Hoger, S.; Bonrad, K.; Moller, M.; Mourran, A.; Beginn, U. *J. Am. Chem. Soc.* **2001**, *123*, 5651−5659.

(10) (a) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369−378. (b) Gianneschi, N. C.; Masar, M. S., III; Mirkin, C. A. *Acc. Chem. Res.* **2005**, *38*, 825−837. (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−908. (d) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502−518. (e) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759−771. (f) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 351−360.

(11) The detailed procedure will be published in the full paper.

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