

## Coordination-Driven Self-Assembly of Metallodendrimers Possessing Well-Defined and Controllable Cavities as Cores

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**Abstract:** The design and self-assembly of novel cavity-cored metallodendrimers via noncovalent interactions are described. By employing [G0]–[G3] 120° ditopic donor linkers substituted with Fréchet-type dendrons and appropriate rigid di-Pt(II) acceptor subunits, [G0]–[G3]-rhomboidal metallodendrimers and [G0]–[G3]-hexagonal, "snowflake-shaped" metallodendrimers with well-defined shape and size were prepared under mild conditions in high yields. The assemblies were characterized with multinuclear NMR (<sup>1</sup>H and <sup>31</sup>P), mass spectrometry (ESI-MS and ESI-FT-ICR-MS), and elemental analysis. Isotopically resolved mass spectrometry data support the existence of the metallodendrimers with rhomboidal and hexagonal cavities, and NMR data are consistent with the formation of all ensembles. The structures of [G0]- and [G1]-rhomboidal metallodendrimers were unambiguously confirmed via single-crystal X-ray crystallography. The shape and size of two [G3]-hexagonal metallodendrimers were investigated with MM2 force-field modeling.

Although modern supramolecular chemistry<sup>1</sup> emerged from the studies of such covalent macrocycles as crown ethers, cyclophanes, calixaranes, cryptands, etc., it is currently dominated by the biomimetic motive of noncovalent interactions such as hydrogen bonding, metal-ligand coordination,  $\pi-\pi$  stacking, electrostatic and van der Waals forces, hydrophobic and hydrophilic interactions, etc. The power and versatility of this bio-derived motive has been illustrated by numerous examples of the use of noncovalent interactions in the synthesis of large supramolecular assemblies in the past few decades. Supramolecular dendrimers are a recent and important subset of such self-assembled structures.

Dendrimers<sup>2</sup> are highly branched, three-dimensional macromolecules comprised of several dendritic wedges extending outward from an internal core. In the past two decades, the design and synthesis of diverse dendrimers has received increasing attention<sup>3</sup> not only because of the aesthetically pleasing structures of these molecules but also as a result of their various applications in host–guest chemistry,<sup>4</sup> material science,<sup>5</sup> and membrane chemistry.<sup>6</sup> Up to now, two complementary methodologies,<sup>3a,7</sup> the divergent and the convergent, have been employed in the preparation of dendrimers. However,

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such covalent synthetic protocols often suffer from timeconsuming procedures and unsatisfactory yields resulting from steric congestions. Compared to the conventional stepwise formation of covalent bonds, the self-assembly process driven by noncovalent interactions that is now universally recognized to be crucial in the proliferation of all biological organisms offers considerable synthetic advantages, including significantly fewer steps, fast and facile formation of the final products, and inherent defect-free assembly. As a consequence, attention has recently turned to the self-assembly of dendrimers to provide welldefined nanoscale architectures<sup>8</sup> via a variety of noncovalent interactions such as electrostatic interactions,<sup>9</sup> hydrogen bonding<sup>10</sup> and metal—ligand coordination.<sup>11,12</sup>

Stimulated by the fact that natural pore-forming proteins play a critical role in the biological process, acting as viral helical coats<sup>13</sup> and transmembrane channels,<sup>14</sup> quite a few attempts have been undertaken to build artificial supramolecular arrays with porous structures by taking advantage of noncovalent interactions.<sup>15</sup> In particular, cavity-cored dendrimers have recently received considerable attention because of their elaborate structures and potential applications in delivery and recognition.<sup>16</sup> For example, dendritic folate rosettes as ion channels in lipid bilayers have been prepared, providing new insights into the mechanism of ion transportation in biological process.<sup>10g</sup> Previously, Percec et al. reported a library of amphiphilic dendritic dipeptides that self-assemble into helical pores both in solution and in bulk.<sup>16h</sup> However, considering nature's simple

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but delicate approach to desirable biomaterials, the design and construction of cavity-cored dendrimers with predefined shape, size, and ultimately function is still extraordinarily challenging.

In the past decade, the formation of discrete supramolecular species by coordination-driven self-assembly has evolved to be a well-established process.<sup>17</sup> This approach offers a variety of opportunities for the preparation of nanoscopic supramolecular ensembles of predetermined shape, size, and symmetry, such as molecular squares,18 rectangles,19 rhomboids,20 triangles,21 and hexagons.<sup>22</sup> Encouraged by the power and versatility of this methodology, we envisioned that the construction of metallodendrimers with well-designed and controlled cavities would be realized by the proper choice of subunits with predefined angles and symmetry. In addition, the possibility to fine-tune the size and shape of the cavities in metallodendrimers would help provide an enhanced understanding of the geometrical requirements necessary for molecular self-assembly. Furthermore, this strategy would likely give rise to the design and synthesis of novel supramolecular species with desired functionality arising from their unique interior cavities and dendritic exteriors.

Recently we reported the self-assembly of the first metallodendrimers exhibiting a nonplanar hexagonal cavity with an internal core radius of approximately 1.6 nm, by the combination

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*Figure 1.* Graphical representation of the self-assembly of rhomboidal and hexagonal, "snowflake-shaped" metallodendrimers.

Scheme 1 . Synthesis of [G0]–[G3] 120° Angular Dendritic Donor Precursors



of 120° dendritic donor subunits (substituted with Fréchet-type dendrons) and 120° di-Pt(II) acceptor angular linkers in a 1:1 stoichiometric ratio.<sup>23</sup> Here we report the results obtained when we extended the investigations to the self-assembly of rhomboidal and "snowflake-shaped" metallodendrimers possessing cavities of various size and shape at the core through the use of coordination-driven self-assembly (Figure 1).

## **Results and Discussion**

Synthesis of 120° Angular Dendritic Donor Subunits. The synthesis of [G0]-[G3] 120° donor building blocks 5a-d commenced with acylation of the commercially available compound 3,5-dibromo-phenol (1) to give 2 (Scheme 1). The 3,5-bis-pyridylethynyl-phenyl ester 3 was prepared by palladium-mediated coupling reaction from ester 2 with 4-ethynylpyridine in reasonable yield (66%). Upon ester hydrolysis and etherification, the [G0]-[G3] 120° precursors 5a-d (Figure 2), substituted with Fréchet-type dendrons, were obtained in good yields.

Synthesis of [G0]–[G3]-Rhomboidal Metallodendrimers 7a-d. With the 120° dendritic precursors in hand, the self-assembly of metallodendrimers with rhomboidal cavities was investigated. In general, the shape of an individual two-



Figure 2. Structures of [G0]-[G3] 120° angular donor precursors 5a-d.

Scheme 2. Self-Assembly of [G0]–[G3] 120° Angular Dendritic Linkers 5a–d with 60° Di-platinum Acceptor 6 To Afford Rhomboidal Metallodendrimers 7a–d



dimensional polygon is determined by the value of the turning angle within its angular components. Thus, the combination of  $60^{\circ}$  units with 120° linking components will yield a molecular rhomboid. Stirring the [G0]–[G3] 120° angular donors **5a**–**d** with an equimolar amount of the known 60° angular acceptor, 2,9-(*trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>NO<sub>3</sub>)<sub>2</sub>-phenanthrene (**6**), in CD<sub>2</sub>Cl<sub>2</sub> for 14 h resulted in [2+2] rhomboidal metallodendrimers **7a**–**d**, respectively, in excellent yields (Scheme 2). Multinuclear NMR (<sup>1</sup>H and <sup>31</sup>P) analysis of [G0]–[G3] assemblies **7a**–**d** exhibited

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Figure 3. Calculated (top) and experimental (bottom) ESI-MS spectra of [G0]-[G2]-rhomboidal metallodendrimers 7a (A), 7b (B), and 7c (C).

very similar characteristics, which all suggested the formation of discrete, highly symmetric metallodendrimers with rhomboidal cavities. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the [G0]-[G3] assemblies 7a-d displayed a sharp singlet (ca. 14.6 ppm) shifted upfield from the signal of the starting platinum acceptor 6 by approximately 6.4 ppm. This change, as well as the decrease in coupling of the flanking <sup>195</sup>Pt satellites (ca.  $\Delta J = -177$  Hz), is consistent with back-donation from the platinum atoms. In the <sup>1</sup>H NMR spectrum of each assembly, the  $\alpha$ -hydrogen nuclei of the pyridine rings exhibited 0.75-0.78 ppm downfield shifts, and the  $\beta$ -hydrogen nuclei showed about 0.2 ppm downfield shifts, due to the loss of electron density that occurs upon coordination of the pyridine N atom with the Pt(II) metal center. It is noteworthy that two doublets were observed for these  $\alpha$ -hydrogen nuclei, as this might be attributed to hindered rotation about the Pt-N(pyridyl) bond, which has been previously reported.24

The structures of the rhomboidal metallodendrimers 7a-dhave also been confirmed by mass spectrometry (ESI-MS and ESI-FT-ICR-MS). In the ESI mass spectra of the [G0]-[G2] assemblies 7a-c, peaks attributable to the loss of nitrate counterions,  $[M - 2NO_3]^{2+}$  (m/z = 1486.9 for 7a, m/z = 1699.0 for **7b**, and m/z = 2123.8 for **7c**) and  $[M - 3NO_3]^{3+}$  (m/z =970.5 for **7a**, m/z = 1112.0 for **7b**, and m/z = 1394.8 for **7c**), where M represents the intact assemblies, were observed. These peaks were isotopically resolved, and they agree very well with their respective theoretical distribution (Figure 3). The ESI-FT-ICR mass spectrum of the [G3] assembly 7d showed two charged states at m/z = 1961.4 and 1455.5, corresponding to the  $[M - 3NO_3]^{3+}$  and  $[M - 4NO_3]^{4+}$  species, respectively, and their isotopic resolution is in excellent agreement with the theoretical distribution (Figure 4). The analysis of the signals observed in the full mass spectra confirmed that there was no other assembled species formed (see Supporting Information).

X-ray crystallographic analysis unambiguously established the structures of **7a** and **7b** to be both discrete [G0]- and [G1]rhomboidal metallodendritic assembles (Figures 5 and 6). Crystals suitable for single-crystal X-ray analysis were grown by vapor diffusion of *n*-pentane into a  $CH_2Cl_2/CH_3COCH_3$  (v/v



Figure 4. Calculated (top) and experimental (bottom) ESI-FT-ICR-MS spectra of [G3]-rhomboidal metallodendrimer 7d.

1/1) solution of **7a** and **7b** respectively at ambient temperatures for 3 days. Both **7a** and **7b** crystallize in the triclinic space group  $P\bar{1}$  but are not isomorphous to each other, as revealed by their different unit cell geometries and dimensions. Table 1 summarizes the data collection, structure solution, and refinement for **7a** and **7b**.

The asymmetric unit of each structure contains a half molecule situated around the center of inversion in the unit cell. The entire supramolecular assembly is thus generated by inversion. At the molecular level, both structures feature a welldefined rhombus with an approximately  $2.3 \times 1.3$  nm cavity that embodies the porosity of the crystal. In both structures, this cavity is partially filled with disordered nitrate anions and solvent molecules. No attempt was made to completely model such multiple disorders inside the cavity because these nitrate anions and solvent molecules appear to occupy different positions with fractional occupancies. The rhomboidal structure of 7a has external dimensions of ca. 3.3 nm long and 2.8 nm wide, while **7b** spreads out over an area of ca.  $4.2 \times 2.8 \text{ nm}^2$ . Except for a slight difference in their conformation, the two molecules 7a and 7b can almost be superimposed with each other in their rhomboidal parts (Figure 7).

Synthesis of Hexagonal, "Snowflake-Shaped" Metallodendrimers 10a-d with Smaller Cavities. According to the

<sup>(24) (</sup>a) Tarkanyi, G.; Jude, H.; Palinkas, G.; Stang, P. J. Org. Lett. 2005, 7, 4971–4973. (b) Yang, H.-B.; Das, N.; Huang, F.; Hawkridge, A. M.; Diaz, D. D.; Arif, A. M.; Finn, M. G.; Muddiman, D. C.; Stang, P. J. J. Org. Chem. 2006, 71, 6644–6647.



*Figure 5.* Crystal structure of [G0]-rhomboidal metallodendrimer **7a**. The  $NO_3^-$  anions and solvent molecules have been omitted for clarity.



*Figure 6.* Crystal structure of [G1]-rhomboidal metallodendrimer **7b**. The  $NO_3^-$  anions and solvent molecules have been omitted for clarity.

"directional bonding" model<sup>25</sup> and the "symmetry interaction" model,<sup>26</sup> discrete hexagonal entities of the type  $A_6^2L_6^2$  can be rationally assembled via the combination of six shape-defining and directing corner units  $A^2$  (offering two coordination sites

| Table 1. Crystal Data and Structure Refinement for 7a and |
|---|
|---|

|  | 7a                             | 7b                           |
|--|--------------------------------|------------------------------|
| empirical formula                          | C130H172N8O6P8Pt4              | C158H196N8O10P8Pt4           |
| formula weight                             | 2968.99                        | 3393.16                      |
| temp (K)                                   | $173 \pm 2$                    | $173 \pm 2$                  |
| crystal system                             | triclinic                      | triclinic                    |
| space group                                | $P\overline{1}$                | $P\overline{1}$              |
| unit cell dimensions                       | a = 10.050(2) Å                | a = 14.111(3)  Å             |
|  | b = 18.319(4)  Å               | b = 14.348(3)  Å             |
|  | c = 21.396(5)  Å               | c = 26.476(5)  Å             |
|  | $\alpha = 76.932(4)^{\circ}$   | $\alpha = 79.705(3)^{\circ}$ |
|  | $\beta = 80.904(4)^{\circ}$    | $\beta = 78.901(3)^{\circ}$  |
|  | $\gamma = 78.553(4)^{\circ}$   | $\gamma = 76.468(3)^{\circ}$ |
|  | $V = 3734.0(15) \text{ Å}^3$   | $V = 5063.8(18) \text{ Å}^3$ |
|  | Z = 1                          | Z = 1                        |
| density (calcd, g/cm <sup>3</sup> )        | 1.268                          | 1.179                        |
| abs coeff (mm <sup><math>-1</math></sup> ) | 3.862                          | 2.893                        |
| F(000)                                     | 1428                           | 1810                         |
| crystal size                               | $0.04 \times 0.09 \times 0.13$ | $0.07\times0.12\times0.17$   |
| $\theta$ range for data collection         | 1.96-50.1                      | 1.86-60.3                    |
| reflns collected/unique                    | 30035/13186                    | 56271/28106                  |
|  | [R(int) = 0.0424]              | [R(int) = 0.0740]            |
| refinement method                          | full-matrix least-             | full-matrix least-           |
|  | squares on $F^2$               | squares on $F^2$             |
| data/restraints/params                     | 9071/0/753                     | 14701/0/947                  |
| GOF on $F^2$                               | 1.508                          | 1.034                        |
| final R indices                            | R1 = 0.0722,                   | R1 = 0.0805,                 |
| $[F_{\rm o}^2 > 2\sigma(F_{\rm o}^2)]$     | wR2 = 0.2095                   | wR2 = 0.2211                 |
| largest peak, hole (e/Å <sup>3</sup> )     | 5.846, -0.915                  | 4.546, -1.797                |



*Figure 7.* Wireframe representation of the crystal structures of **7a** and **7b** as they are superimposed with each other. The  $NO_3^-$  anions, solvent molecules, and hydrogen atoms have been omitted for clarity.

which enclose a 120° angle) with six appropriate linear linker units L<sup>2</sup> (offering two coordination sites oriented 180° from each other). When the [G0]–[G3] 120° angular donor subunits **5a–d** were reacted with the linear di-Pt(II) acceptor 1,4-bis((PMe<sub>3</sub>)<sub>2</sub>-Pt(OTf))<sub>2</sub>-benzene (**8**) in CD<sub>2</sub>Cl<sub>2</sub> at room temperature, the [6+6] "snowflake-shaped" metallodendrimers **10a–d**, respectively, were formed (Scheme 3). <sup>31</sup>P{<sup>1</sup>H} NMR analysis of the reaction mixtures is consistent with the formation of a single, highly symmetric species, as indicated by the appearance of a sharp singlet (ca. –12.8 ppm) with concomitant <sup>195</sup>Pt satellites, shifted upfield by ca. 6.5 ppm as compared to **8** (Figure 9A). As expected, a decrease in coupling of the flanking <sup>195</sup>Pt satellites was also observed (ca.  $\Delta^{1}J_{PPt} = -131$  Hz), lending further

 <sup>(25) (</sup>a) Stang, P. J.; Olenyuk, B. Acc. Chem. Res. 1997, 30, 502–518. (b) Olenyuk, B.; Fechtenkötter, A.; Stang, P. J. J. Chem. Soc., Dalton. Trans. 1998, 1707.

 <sup>(26) (</sup>a) Caulder, D. L.; Raymond, K. N. J. Chem. Soc., Dalton Trans. 1999, 1185.
 (b) Caulder, D. L.; Raymond, K. N. Acc. Chem. Res. 1999, 32, 975–982.

Scheme 3. Self-Assembly of [G0]–[G3] 120° Angular Dendritic Linkers 5a-d with Linear Di-platinum Acceptors 8 and 9 To Afford Hexagonal, "Snowflake-Shaped" Metallodendrimers 10a-d and 11a-d



11a-d m = 2. R = Et. n = 0 - 3

support to the formation of the complexes. In the <sup>1</sup>H NMR spectra of metallodendrimers **10a**–**d**, the  $\alpha$ -H and  $\beta$ -H of the pyridine rings exhibited 0.21–0.27 ppm and ca. 0.28–0.32 ppm downfield shifts, respectively, relative to uncoordinated **5a**–**d** (Figure 8B). The sharp NMR signals in both the <sup>31</sup>P and <sup>1</sup>H NMR spectra along with the solubility of these species ruled out the formation of oligomers.

Mass spectrometric studies of the hexagonal metallodendrimers 10a-d were performed using the ESI-FT-ICR technique, which kept the assembly intact during the ionization process while obtaining the high resolution required for unambiguous determination of individual charge states. In fact, it is very challenging to determine accurate masses for these charged metallodendrimers because of the large molecular weight and isotopic shift. In the ESI-FT-ICR mass spectra of [G0] and [G1] assemblies 10a and 10b, the peaks at m/z = 1597.1 (10a) and m/z = 1851.8 (10b), corresponding to  $[M - 50Tf]^{5+}$  respectively were observed, and their isotopic resolutions are in excellent agreement with the theoretical distributions (Figure 10A,B). The charged state at m/z = 1644.0 was observed in the ESI-FT-ICR mass spectrum of [G2] assembly 10c, which corresponds to [M - 7OTf]<sup>7+</sup>. It was isotopically resolved (Figure 10C), and it agrees very well with the theoretical distribution.



*Figure 8.* Partial <sup>1</sup>H NMR spectra of free [G3]-donor subunit **5d** (A), [G3]-hexagonal metallodendrimer **10d** (B), and [G3]-hexagonal metallodendrimer **11d** (C).



*Figure 9.* <sup>31</sup>P NMR spectra of [G3]-hexagonal metallodendrimer **10d** (A) and [G3]-hexagonal metallodendrimer **11d** (B).

According to the "symmetry interaction" model,<sup>26</sup> the discrepancy between the 120° angle needed for the hexagons and the 108° angle needed for the analogous pentagons can easily be accounted for once one considers the size of the macrocyclic assembly. Since the building blocks are relatively large and therefore quite flexible, small distortions of the ideal bond angles of the subunits can occur and make up for the necessary 12° difference per corner between a hexagon and a pentagon. Therefore, it is necessary to discuss all the peaks exhibited in the full ESI-FT-ICR mass spectra of the assemblies to exclude the formation of a pentagon or a heptagon. By way of an example, the full ESI-FT-ICR mass spectrum of [G1] assembly **10b** displayed 10 multiple-charged molecular peaks (Figure 11). The reasonable fragments attributable to these peaks are



Figure 10. Calculated (top) and experimental (bottom) ESI-FT-ICR-MS spectra of [G0]–[G2]-hexagonal metallodendrimers 10a (A), 10b (B), and 10c (C).



*Figure 11.* Full ESI-FT-ICR mass spectrum of [G1]-hexagonal metallodendrimer **10b**. The letters correspond to the fragments listed in Table 2.

 Table 2.
 Theoretical and Experimental ESI-FT-ICR Mass

 Fragments from [G1]-Hexagonal Metallodendrimer 10b

|   |                                      | m/z      |          |
|---|--------------------------------------|----------|----------|
|   | fragment <sup>a</sup>                | calcd    | found    |
| А | $[2(8) + 2(5b) - 3OTf]^{3+}$         | 961.897  | 962.592  |
| В | $[8 + 2(5b) - 2OTf]^{2+}$            | 983.300  | 983.833  |
| С | $[2(8) + 3(5b) - 3OTf]^{3+}$         | 1161.297 | 1161.711 |
| D | $[2(8) + 5b - 2OTf]^{2+}$            | 1218.190 | 1218.797 |
| Е | $[3(8) + 4(5b) - 4OTf]^{4+}$         | 1250.310 | 1251.159 |
| F | $[8 + \mathbf{5b} - \mathrm{OTf}]^+$ | 1517.320 | 1518.497 |
| G | $[4(8) + 5(5b) - 4OTf]^{4+}$         | 1666.878 | 1668.138 |
| Н | $[3(8) + 4(5b) - 3OTf]^{3+}$         | 1716.730 | 1717.994 |
| Ι | $[2(8) + 3(5b) - 2OTf]^{2+}$         | 1816.420 | 1817.765 |
| J | $[10b - 5OTf]^{5+}$                  | 1851.770 | 1851.742 |

<sup>a</sup> The letters correspond to the peak labeling in Figure 11.

summarized in Table 2. No evidence for any other species, such as a [5+5] pentagonal assembly, was found. Similar results were observed in the full mass spectra of [G0]- and [G2]-metallo-dendrimers **10a** and **10c** (see Supporting Information).

The combination of a linear ditopic unit with a 120° angular unit in a 1:1 ratio may yield pentagons as well as hexagons, since small distortions in the bond angles of the building blocks are energetically not very costly.<sup>17a</sup> In the case of [G0]–[G2]metallodendrimers **10a**–**c**, only hexagons are found. This may be the result of a particular conformational rigidity of the system (favoring the ideal geometry to a greater extent than usual) or other factors (e.g., the highly charged nature of the assembled structures and/or the interplay between entropic and enthalpic contributions<sup>27</sup>) that are not yet fully understood.

Synthesis of Hexagonal, "Snowflake-Shaped" Metallodendrimers 11a-d with Larger Cavities. Another type of "snowflake-shaped" metallodendrimers 11a-d, with larger hexagonal cavities compared to those of metallodendrimers 10a-d, were synthesized by using a longer linear di-Pt(II) acceptor, 4,4'-bis((PEt<sub>3</sub>)<sub>2</sub>Pt(OTf))<sub>2</sub>-biphenyl (9). Multinuclear NMR (<sup>1</sup>H and <sup>31</sup>P) analysis of the [G0]–[G3] assemblies 11a-d demonstrated the existence of discrete, highly symmetric species. A sharp peak with platinum satellites at ca. 16.0 ppm was observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the [G0]-[G3] assemblies, shifted upfield from the peak of the starting platinum acceptor 9 by approximately 6.2 ppm (Figure 9B). The  $J_{Pt-P}$ decreased by about 150 Hz for all assemblies upon pyridyl coordination. As expected, in the <sup>1</sup>H NMR spectra, the  $\alpha$ -H of the pyridine rings shifted slightly from 8.6 ppm in the free donors to 8.7 ppm in the assemblies, and  $\beta$ -H exhibited approximately 0.4 ppm downfield shifts (Figure 8). In contrast to the results for rhomboidal metallodendrimers 7a-d, the <sup>1</sup>H NMR spectra of **10a-d** and **11a-d** showed only one doublet for the  $\alpha$ -H protons of the pyridine ring linked to the Pt(II) center.

Compared to the hexagonal metallodendrimers 10a-d, it is more difficult to get strong mass signals for the charged ensembles 11a-d, even under the ESI-FT-ICR-MS conditions, on account of their larger molecular weight. For instance, the [G3]-hexagonal metallodendrimer 11d has a molecular weight of 19 097.9 Da. With considerable effort, the peak attributable to  $[M - 70Tf]^{7+}$  was observed in the ESI-FT-ICR-MS spectra of the [G0]-[G2]-hexagonal assemblies 11a-c, which, along with the isotopic resolution (i.e., direct charge state determination), allow for the molecularity of hexagonal metallodendrimers to be unambiguously established (Figure 12).

Unfortunately, all attempts to grow X-ray-quality single crystals of the hexagonal metallodendrimers **10a**-**d** and **11a**-**d** failed. MM2 force-field simulations were employed to optimize the geometry of the [G3]-metallodendrimers **10d** and **11d** 

 <sup>(27) (</sup>a) Yamamoto, T.; Arif, A. M.; Stang, P. J. J. Am. Chem. Soc. 2003, 125, 12309–12317. (b) Das, N.; Ghosh, A.; Arif, A. M.; Stang, P. J. Inorg. Chem. 2005, 44, 7130–7137.



Figure 12. Calculated (top) and experimental (bottom) ESI-FT-ICR-MS spectra of [G0]-[G2]-hexagonal metallodendrimers 11a (A), 11b (B), and 11c (C).



*Figure 13.* Space-filling models of hexagonal metallodendrimers **10d** (A) and **11d** (B) optimized with the MM2 force-field simulation. Trimethyl and triethyl groups have been removed after the optimization for clarity.

(Figure 13). Simple space-filling models of the simulated structures indicate that **10d** and **11d** have a very similar nonplanar hexagonal cavity at their cores. In the case of **10d**, the cored-cavity metallodendrimer has an internal radius of approximately 2.5 nm, while the outer radius is about 4.5 nm. Likewise, the metallodendrimer **11d** has an even larger cavity

as a core, with an internal radius of approximately 2.9 nm and an outer radius of about 5.2 nm.

## Conclusions

The work presented here provides a very simple yet effective approach to the construction of well-defined charged metallodendrimers possessing cavities with various size and shape within their cores via coordination-driven self-assembly. By combination of the predesigned 120° angular dendritic donors and di-Pt(II) acceptors with appropriate angles (60° and 120°), [G0]-[G3]-rhomboidal metallodendrimers and two types of "snowflake-shaped" metallodendrimers were prepared under mild conditions. Multinuclear NMR (<sup>1</sup>H and <sup>31</sup>P) analysis of all assemblies revealed very similar characteristics that are suggestive of the formation of discrete, highly symmetric species. The sharp NMR signals in both the <sup>31</sup>P and <sup>1</sup>H NMR, along with the solubility of these species, ruled out the formation of oligomers. The structures of all the metallodendrimers were further established by mass spectrometry (ESI-MS and ESI-FT-ICR-MS) and elemental analysis. The structures of [G0]and [G1]-rhomboidal dendrimers 7a and 7b were unambiguously confirmed via X-ray crystallography.

Hence, we have demonstrated that highly convergent synthetic protocols based on the simultaneous assembly of appropriate predetermined building blocks allow the rapid construction of novel cavity-cored metallodendrimers. In particular, this approach makes it possible to prepare a variety of metallodendrimers with well-defined and controlled cavities as cores through the proper choice of subunits with predefined angles and symmetry, which enriches the library of different-shaped cavity-cored metallodendrimers. For instance, metallodendrimers having nonplanar hexagonal cavities with different internal radii of approximately 1.6,<sup>23</sup> 2.5, and 2.9 nm have been obtained by this methodology. Furthermore, the shape of the cavities of the supramolecular dendrimers can be rationally designed to be either a rhomboid or a hexagon. Extending this idea further to additional two-dimensional structures, such as squares, rectangles, and triangles, and even three-dimensional architectures like trigonal prisms and trigonal bipyramids, is currently under investigation.

## **Experimental Section**

Triethylamine was distilled from sodium hydroxide, and tetrahydrofuran (THF) was distilled from K(s)/benzophenone. Dendritic bromide [Gn]-Br,<sup>7a</sup> 2,9-(*trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>NO<sub>3</sub>)<sub>2</sub>-phenanthrene (**6**),<sup>21e</sup> 1,4bis((PMe<sub>3</sub>)<sub>2</sub>Pt(OTf))<sub>2</sub>-benzene (8),<sup>28</sup> and 4,4'-bis((PEt<sub>3</sub>)<sub>2</sub>Pt(OTf))<sub>2</sub>-biphenyl  $(9)^{28}$  were prepared according to literature procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). All other reagents were purchased (Aldrich or Acros) and used without further purification. NMR spectra were recorded on a Varian Unity 300 or a Varian XL-300 spectrometer. The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported relative to residual solvent signals, and <sup>31</sup>P NMR resonances are referenced to an external unlocked sample of 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta$  0.0). Element analysis was performed by Atlantic Microlab (Norcross, GA). Mass spectra for 7a-c were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. Mass spectra for 7d, 10a-d, and 11a-d were recorded on a modified ESI-FT-ICR mass spectrometer (Varian, Inc., Lake Forest, CA) equipped with an actively shielded 9.4 T superconducting magnet (Cryomagnetics, Oak Ridge, TN).

Successful X-ray crystallographic data collections for **7a** and **7b** were carried out at -100 °C using a Bruker-AXS APEX2 diffractometer. Crystals of **7c** are mechanically too fragile to be handled at low temperatures. The selected single crystals of **7a** and **7b** were each coated with Fluorolube along with the mother liquor and frozen in a cold nitrogen stream to form an amorphous protective matrix.

Synthesis of Acetic Acid 3,5-Dibromo-phenyl Ester 2. A mixture of 3,5-dibromophenol (0.85 g, 3.37 mmol) and acetic anhydride (1.03 g, 10.09 mmol) was heated at 70 °C for 2 h. The mixture was poured onto ice, neutralized with K<sub>2</sub>CO<sub>3</sub>, and extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with water (2 × 25 mL) and brine (25 mL) and dried (Mg<sub>2</sub>SO<sub>4</sub>). The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel (acetone/hexane 1/10) to give **2** as a pale pink solid. Yield: 0.90 g, 95%. *R*<sub>f</sub> = 0.4 (acetone/hexane 1/10). Mp: 56–57 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta$  7.57 (t, *J* = 1.5 Hz, 1H, Ar*H*), 7.27 (d, 2H, Ar*H*), 2.28 (s, 3H, OCC*H*<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz):  $\delta$  168.8, 151.9, 131.9, 124.5, 21.1. MS (CI): m/z 294.9 (M + 1)<sup>+</sup>.

Synthesis of 3,5-Bis-pyridylethynyl-phenyl Ester 3. A 100 mL Schlenk flask was charged with 2 (0.96 g, 3.41 mmol), 4-bromopyridine hydrochloride (1.14 g, 8.17 mmol), tetrakis(triphenylphosphine)-palladium(II) (470 mg, 5 mol %), and CuI (31 mg, 2 mol %), degassed, and back-filled three times with N<sub>2</sub>. Triethylamine (2.5 mL) and dried THF (40 mL) were introduced into the reaction flask by syringe. The reaction was stirred under an inert atmosphere at 60 °C for 16 h. The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel (acetone/hexane 1/1) to give 3 as a pale yellow solid. Yield: 0.76 g, 66%.  $R_{\rm f} = 0.2$  (acetone/hexane 1/1). Mp: 152–153 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta$  8.61 (br, 4H, H<sub>\alpha</sub>-Py), 7.63 (t, J = 1.5 Hz, 1H, ArH), 7.40 (d, J = 5.1 Hz, 4H, H<sub>\beta</sub>-Py), 7.34 (d, 2H, ArH), 2.32 (s, 3H, OCCH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz):  $\delta$  169.1, 150.9, 150.1, 132.6, 130.6, 126.0, 125.7, 124.1, 91.5, 88.3, 21.1. MS (CI): m/z 339.2 (M + 1)<sup>+</sup>.

Synthesis of 3,5-Bis-pyridylethynyl-phenol 4. To a stirred solution of 3 (0.75 g, 2.22 mmol) in methanol (20 mL) was added 1 M NaHCO<sub>3</sub> (25 mL). The reaction was stirred until TLC indicated complete consumption of 3. The solvent volume was reduced to half, and a large amount of brown precipitate appeared. The brown solid was collected by filtration, washed with water (3 × 20 mL), and dried under vacuum. Yield: 0.59 g, 99%. Mp: >250 °C dec. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz):  $\delta$  8.65 (br, 4H, H<sub>\alpha</sub>-Py), 7.54 (br, 4H, H<sub>\beta</sub>-Py), 7.28 (s, 1H, Ar*H*), 7.05 (s, 2H, Ar*H*). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz):  $\delta$  157.8, 150.0, 129.8, 125.7, 122.9, 119.5, 92.3, 87.0. MS (CI): *m/z* 297.2 (M + 1)<sup>+</sup>.

General Procedure for the Preparation of [G0]–[G3] Dendritic Precursors 5a–d. Compound 4 (for the reaction with [G0]-Br and [G1]-Br, 60.5 mg, 0.203 mmol; for the reaction with [G2]-Br and [G3]-Br, 30 mg, 0.115 mmol) and appropriate NaH were placed in a 25 mL Schlenk flask followed by 2–3 mL of anhydrous DMF. The mixture was stirred for 30 min. The appropriate [Gn]-Br was then added under nitrogen. The reaction was continued at 65 °C for another 2 h and then quenched by 10 mL of water, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL), and dried (MgSO<sub>4</sub>). The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel (acetone/hexane ~1/1) to give compounds **5a**–**d**.

**5a.** Yield: 66.7 mg (white solid), 85%.  $R_{\rm f} = 0.40$  (acetone/hexane 2/1). Mp: 170–171 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta$  8.60 (dd, J = 5.2 Hz and J = 1.5 Hz, 4H, H<sub>α</sub>-Py), 7.39–7.45 (m, 10H, H<sub>β</sub>-Py, ArH and PhH), 7.21 (d, 2H, ArH), 5.12 (s, 2H, PhCH<sub>2</sub>O). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz):  $\delta$  159.0, 150.2, 136.6, 131.0, 129.0, 128.6, 128.2, 127.9, 125.9, 124.1, 119.3, 92.5, 87.5, 70.7. MS (FAB): m/z 387.1 (M + 1)<sup>+</sup>. Anal. Calcd for C<sub>27</sub>H<sub>18</sub>N<sub>2</sub>O: C, 83.92; H, 4.69; N, 7.25. Found: C, 83.66; H, 4.67; N, 6.99.

**5b.** Yield: 108.2 mg (white solid), 89%.  $R_{\rm f} = 0.38$  (acetone/hexane 2/1). Mp: 183–184 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta$  8.60 (dd, J = 5.0 Hz and J = 1.5 Hz, 4H, H<sub>α</sub>-Py), 7.33–7.44 (m, 15H, H<sub>β</sub>-Py, ArH and PhH), 7.19 (d, 2H, ArH), 6.69 (d, J = 2.1 Hz, 2H, ArH), 6.59 (t, J = 2.1 Hz, 1H, ArH), 5.07 (s, 2H, ArCH<sub>2</sub>O), 5.06 (s, 4H, PhCH<sub>2</sub>O). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz):  $\delta$  160.6, 158.9, 150.2, 139.1, 137.2, 130.9, 128.9, 128.4, 128.3, 127.9, 126.0, 124.1, 119.3, 106.6, 101.8, 92.6, 87.6, 70.4. MS (FAB): m/z 599.1 (M + 1)<sup>+</sup>. Anal. Calcd for C<sub>41</sub>H<sub>30</sub>N<sub>2</sub>O<sub>3</sub>: C, 82.25; H, 5.05; N, 4.68. Found: C, 82.13; H, 5.15; N, 4.65.

**5c.** Yield: 102.4 mg (white solid), 87%.  $R_{\rm f} = 0.35$  (acetone/hexane 2/1). Mp: 165–166 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz): δ 8.58 (dd, J = 5.7 Hz and J = 1.5 Hz, 4H, H<sub>α</sub>-Py), 7.31–7.42 (m, 25H, H<sub>β</sub>-Py, ArH and PhH), 7.19 (d, 2H, ArH), 6.68 (d, J = 2.1 Hz, 6H, ArH), 6.56 (m, 3H, ArH), 5.06 (s, 2H, ArCH<sub>2</sub>O), 5.04 (s, 8H, PhCH<sub>2</sub>O), 5.00 (s, 4H, ArCH<sub>2</sub>O). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz): δ 160.5, 158.9, 150.2, 139.7, 139.1, 137.3, 131.0, 128.9, 128.5, 128.3, 127.9, 126.0, 124.1, 119.3, 106.6, 101.8, 101.7, 92.6, 87.6, 70.4, 70.3. MS (FAB): m/z 1023.0 (M + 1)<sup>+</sup>. Anal. Calcd for C<sub>69</sub>H<sub>54</sub>N<sub>2</sub>O<sub>7</sub>: C, 81.00; H, 5.32; N, 2.74. Found: C, 81.07; H, 5.35; N, 2.69.

**5d.** Yield: 151.6 mg (pale yellow glassy solid), 79%.  $R_f = 0.30$  (acetone/hexane 2/1). Mp: 78–79 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz): δ 8.58 (d, J = 5.4 Hz, 4H, H<sub>α</sub>-Py), 7.31–7.42 (m, 45H, H<sub>β</sub>-Py, Ar*H* and Ph*H*), 7.19 (s, 2H, Ar*H*), 6.68 (br, 14H, Ar*H*), 6.55 (m, 7H, Ar*H*), 4.99–5.02 (m, 30H, ArCH<sub>2</sub>O and PhCH<sub>2</sub>O). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz): δ 160.3, 160.2, 158.7, 150.1, 139.6, 139.5, 139.0, 137.1, 130.8, 128.7, 128.6, 128.4, 128.2, 128.0, 127.8, 125.7, 123.9, 119.2, 106.5, 101.7, 101.6, 92.4, 87.5. MS (FAB): m/z 1871.6 (M + 1)<sup>+</sup>. Anal. Calcd for C<sub>125</sub>H<sub>102</sub>N<sub>2</sub>O<sub>15</sub>: C, 80.19; H, 5.49; N, 1.50. Found: C, 80.12; H, 5.64; N,1.41.

General Procedure for the Preparation of [G0]–[G3]-Rhomboidal Metallodendrimers 7a–d. To a 0.5 mL dichloromethane- $d_2$ solution of nitrate 6 (5.2 mg, 0.00447 mmol) was added a 0.5 mL dichloromethane- $d_2$  solution of the appropriate [G0]–[G3] dendric donor precursor 5a–d, drop by drop, with continuous stirring (10 min). The reaction mixture was stirred overnight at room temperature. The solution was evaporated to dryness, and the product was collected.

**[G0]-Rhomboidal Metallodendrimer 7a.** Yield: 6.86 mg (pale yellow solid), 99%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz): δ 9.35 (d, J = 5.4 Hz, 4H, H<sub>α</sub>-Py), 8.84 (s, 4H, H<sub>4</sub>), 8.72 (d, J = 5.4 Hz, 4H, H<sub>α</sub>-Py), 7.95 (d, J = 4.5 Hz, 4H, H<sub>2</sub>), 7.80 (d, J = 5.4 Hz, 4H, H<sub>1</sub>), 7.65 (s, 4H, H<sub>10</sub>), 7.59 (d, J = 6.6 Hz, 8H, H<sub>β</sub>-Py), 7.39–7.52 (m, 16H, Ph*H* and Ar*H*), 5.20 (s, 4H, OCH<sub>2</sub>Ph), 1.36–1.37 (m, 48H, PCH<sub>2</sub>CH<sub>3</sub>), 1.10–1.20 (m, 72H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.4 MHz): δ 14.7 (s, <sup>1</sup>J<sub>Pt-P</sub> = 2708.9 Hz). Anal. Calcd for C<sub>130</sub>H<sub>172</sub>N<sub>8</sub>O<sub>14</sub>P<sub>8</sub>Pt<sub>4</sub>·CH<sub>2</sub>·Cl<sub>2</sub>: C, 49.42; H, 5.51; N, 3.52. Found: C, 49.65; H, 5.63; N, 3.47.

**[G1]-Rhomboidal Metallodendrimer 7b.** Yield: 7.56 mg (pale yellow solid), 96%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz): δ 9.36 (d, J = 5.7 Hz, 4H, H<sub>α</sub>-Py), 8.84 (s, 4H, H<sub>4</sub>), 8.70 (d, J = 6.0 Hz, 4H, H<sub>α</sub>-Py),

<sup>(28) (</sup>a) Manna, J.; Kuehl, C. J.; Whiteford, J. A.; Stang, P. J.; Muddiman, D. C.; Hofstadler, S. A.; Smith, R. D. J. Am. Chem. Soc. **1997**, 119, 11611–11619. (b) Manna, J.; Kuehl, C. J.; Whiteford, J. A.; Stang, P. J. Organometallics **1997**, 16, 1897–1905.

7.95 (d, J = 5.4 Hz, 4H, H<sub>2</sub>), 7.78 (d, J = 5.4 Hz, 4H, H<sub>1</sub>), 7.65 (s, 4H, H<sub>10</sub>), 7.59 (d, J = 5.7 Hz, 8H, H<sub>β</sub>-Py), 7.34–7.47 (m, 26H, PhH and ArH), 6.74 (d, 4H, J = 2.1 Hz, ArH), 6.62 (t, J = 2.1 Hz, 2H, ArH), 5.15 (s, 4H, OCH<sub>2</sub>Ar), 5.07 (s, 8H, OCH<sub>2</sub>Ph), 1.36–1.37 (m, 48H, PCH<sub>2</sub>CH<sub>3</sub>), 1.10–1.20 (m, 72H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>-Cl<sub>2</sub>, 121.4 MHz):  $\delta$  14.6 (s, <sup>1</sup> $J_{Pt-P} = 2707.7$  Hz). Anal. Calcd for C<sub>158</sub>H<sub>196</sub>N<sub>8</sub>O<sub>18</sub>P<sub>8</sub>Pt<sub>4</sub>: C, 53.86; H, 5.61; N, 3.18. Found: C, 53.56; H, 5.96; N, 2.92.

**[G2]-Rhomboidal Metallodendrimer 7c.** Yield: 9.58 mg (pale yellow solid), 98%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta$  9.37 (d, J = 6.0 Hz, 4H, H<sub>a</sub>-Py), 8.85 (s, 4H, H<sub>4</sub>), 8.68 (d, J = 6.0 Hz, 4H, H<sub>a</sub>-Py), 7.94 (d, J = 5.7 Hz, 4H, H<sub>2</sub>), 7.76 (d, J = 5.7 Hz, 4H, H<sub>1</sub>), 7.65 (s, 4H, H<sub>10</sub>), 7.59 (d, J = 4.8 Hz, 8H, H<sub>β</sub>-Py), 7.30–7.44 (m, 46H, Ph*H*), 6.71–6.74 (m, 12H, Ar*H*), 6.57–6.60 (m, 6H, Ar*H*), 5.14 (s, 4H, OCH<sub>2</sub>-Ar), 5.06 (s, 16H, OCH<sub>2</sub>Ph), 5.03 (s, 8H, OCH<sub>2</sub>Ar), 1.36 (m, 48H, PCH<sub>2</sub>CH<sub>3</sub>), 1.09–1.19 (m, 72H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.4 MHz):  $\delta$  14.6 (s, <sup>1</sup>J<sub>Pt-P</sub> = 2707.7 Hz). Anal. Calcd for C<sub>214</sub>H<sub>244</sub>N<sub>8</sub>O<sub>26</sub>P<sub>8</sub>Pt<sub>4</sub>: C, 58.78; H, 5.62; N, 2.56. Found: C, 58.61; H, 6.02; N, 2.22.

**[G3]-Rhomboidal Metallodendrimer 7d.** Yield: 13.03 mg (pale yellow glassy solid), 96%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta$  9.36 (d, *J* = 5.4 Hz, 4H, H<sub>α</sub>-Py), 8.83 (s, 4H, H<sub>4</sub>), 8.65 (d, *J* = 5.4 Hz, 8H, H<sub>α</sub>-Py), 7.95 (d, *J* = 5.7 Hz, 4H, H<sub>2</sub>), 7.74 (d, *J* = 5.4 Hz, 4H, H<sub>1</sub>), 7.66 (s, 4H, H<sub>10</sub>), 7.58 (d, *J* = 4.5 Hz, 8H, H<sub>β</sub>-Py), 7.30–7.42 (m, 86H, Ph*H*), 6.62–6.75 (m, 28H, Ar*H*), 6.55 (br, 14H, Ar*H*), 5.09 (s, 4H, OC*H*<sub>2</sub>Ar), 4.94–5.02 (m, 56H, OC*H*<sub>2</sub>Ph and OC*H*<sub>2</sub>Ar), 1.36 (m, 48H, PC*H*<sub>2</sub>CH<sub>3</sub>), 1.09–1.19 (m, 72H, PCH<sub>2</sub>C*H*<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>-Cl<sub>2</sub>, 121.4 MHz):  $\delta$  14.6 (s, <sup>1</sup>*J*<sub>Pl</sub>–P = 2707.7 Hz). Anal. Calcd for C<sub>326</sub>H<sub>340</sub>N<sub>8</sub>O<sub>42</sub>P<sub>8</sub>Pt<sub>4</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 63.81; H, 5.60; N, 1.82. Found: C, 63.99; H, 5.82; N, 1.68.

General Procedure for the Preparation of [G0]–[G3]-Hexagonal Metallodendrimers 10a–d. To a 0.5 mL acetone- $d_6$  solution of triflate 8 (5.50 mg, 0.00515 mmol) was added a 0.5 mL dichloromethane- $d_2$ solution of the appropriate [G0]–[G3] dendric donor precursor 5a–d, drop by drop, with continuous stirring (10 min). The reaction mixture was stirred overnight at room temperature. The solution was evaporated to dryness, and the product was collected.

**[G0]-Hexagonal Metallodendrimer 10a.** Yield: 7.41 mg (pale yellow solid), 99%. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>/CD<sub>2</sub>Cl<sub>2</sub> 1/1, 300 MHz): δ 8.86 (d, *J* = 5.7 Hz, 24H, H<sub>α</sub>-Py), 7.70 (d, *J* = 6.3 Hz, 24H, H<sub>β</sub>-Py), 7.25–7.41 (m, 48H, Ar*H* and Ph*H*), 6.99 (s, 24H, Ar*H*), 5.10 (s, 12H, OC*H*<sub>2</sub>Ph), 1.05–1.07 (m, 216H, PC*H*<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>/CD<sub>2</sub>Cl<sub>2</sub> 1/1, 121.4 MHz):  $\delta$  –12.8 (s, <sup>1</sup>*J*<sub>Pt-P</sub> = 2734.5 Hz). Anal. Calcd for C<sub>282</sub>H<sub>348</sub>F<sub>36</sub>N<sub>12</sub>O<sub>42</sub>P<sub>24</sub>Pt<sub>12</sub>: C, 38.79; H, 4.02; N, 1.93. Found: C, 38.39; H, 4.40; N, 1.79.

**[G1]-Hexagonal Metallodendrimer 10b.** Yield: 8.32 mg (pale yellow solid), 97%. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>/CD<sub>2</sub>Cl<sub>2</sub> 1/1, 300 MHz): δ 8.87 (d, *J* = 6.3 Hz, 24H, H<sub>α</sub>-Py), 7.70 (d, *J* = 6.3 Hz, 24H, H<sub>β</sub>-Py), 7.23–7.40 (m, 78H, Ar*H* and Ph*H*), 6.99 (s, 24H, Ar*H*), 6.64 (d, *J* = 2.1 Hz, 12H, Ar*H*), 6.54 (t, *J* = 2.1 Hz, 6H, Ar*H*), 5.05 (s, 12H, OC*H*<sub>2</sub>-Ar), 5.00 (s, 24H, OC*H*<sub>2</sub>Ph), 1.05–1.07 (m, 216H, PC*H*<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>/CD<sub>2</sub>Cl<sub>2</sub> 1/1, 121.4 MHz):  $\delta$  –12.8 (s, <sup>1</sup>*J*<sub>Pt-P</sub> = 2730.3 Hz). Anal. Calcd for C<sub>366</sub>H<sub>420</sub>F<sub>36</sub>N<sub>12</sub>O<sub>54</sub>P<sub>24</sub>Pt<sub>12</sub>S<sub>12</sub>: C, 43.94; H, 4.23; N, 1.68. Found: C, 43.64; H, 4.37; N, 1.58.

**[G2]-Hexagonal Metallodendrimer 10c.** Yield: 10.55 mg (pale yellow solid), 98%. <sup>1</sup>H NMR (acetone- $d_6$ /CD<sub>2</sub>Cl<sub>2</sub> 1/1, 300 MHz):  $\delta$  8.82 (br, 24H, H<sub>\alpha</sub>-Py), 7.67 (br, 24H, H<sub>\beta</sub>-Py), 7.23–7.34 (m, 138H, Ar*H* and Ph*H*), 6.99 (s, 24H, Ar*H*), 6.63 (d, J = 2.7 Hz, 36H, Ar*H*), 6.50 (t, J = 2.7 Hz, 12H, Ar*H*), 5.05 (s, 12H, OCH<sub>2</sub>Ar), 4.96–4.98 (m, 72H, OCH<sub>2</sub>Ar and OCH<sub>2</sub>Ph), 1.05–1.07 (m, 216H, PCH<sub>3</sub>). <sup>31</sup>P-{<sup>1</sup>H} NMR (acetone- $d_6$ /CD<sub>2</sub>Cl<sub>2</sub> 1/1, 121.4 MHz):  $\delta$  –12.8 (s, <sup>1</sup>*J*<sub>Pt-P</sub> = 2730.3 Hz). Anal. Calcd for C<sub>534</sub>H<sub>564</sub>F<sub>36</sub>N<sub>12</sub>O<sub>78</sub>P<sub>2</sub>4Pt<sub>12</sub>S<sub>12</sub>·2CH<sub>2</sub>Cl<sub>2</sub>: C, 50.61; H, 4.50; N, 1.32. Found: C, 50.32; H, 4.62; N, 1.16.

[G3]-Hexagonal Metallodendrimer 10d. Yield: 14.83 mg (pale yellow glassy solid), 98%. <sup>1</sup>H NMR (acetone- $d_6$ /CD<sub>2</sub>Cl<sub>2</sub> 1/1, 300 MHz): δ 8.79 (br, 24H, H<sub>α</sub>-Py), 7.66 (br, 24H, H<sub>β</sub>-Py), 7.21–7.40

(m, 258H, Ar*H* and Ph*H*), 6.98 (s, 24H, Ar*H*), 6.60–6.63 (m, 84H, Ar*H*), 6.48 (br, 42H, Ar*H*), 4.91–5.05 (m, 180H, OC*H*<sub>2</sub>Ar and OC*H*<sub>2</sub>-Ph), 1.04 (m, 216H, PC*H*<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} MMR (acetone- $d_6$ /CD<sub>2</sub>Cl<sub>2</sub> 1/1, 121.4 MHz):  $\delta$  –12.8 (s, <sup>1</sup>*J*<sub>Pl</sub>–P = 2732.1 Hz). Anal. Calcd for C<sub>870</sub>H<sub>852</sub>F<sub>36</sub>N<sub>12</sub>O<sub>126</sub>P<sub>24</sub>Pt<sub>12</sub>S<sub>12</sub>: C, 59.22; H, 4.87; N, 0.95. Found: C, 58.96; H, 5.21; N, 0.86.

General Procedure for the Preparation of [G0]–[G3]-Hexagonal Metallodendrimers 11a–d. To a 0.5 mL dichloromethane- $d_2$  solution of triflate 9 (6.02 mg, 0.00458 mmol) was added a 0.5 mL dichloromethane- $d_2$  solution of the appropriate [G0]–[G3] dendric donor precursor 5a–d, drop by drop, with continuous stirring (10 min). The reaction mixture was stirred overnight at room temperature. The solution was evaporated to dryness, and the product was collected.

**[G0]-Hexagonal Metallodendrimer 11a.** Yield: 7.40 mg (pale yellow solid), 95%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta$  8.69 (d, J = 5.1 Hz, 24H, H<sub> $\alpha$ </sub>-Py), 7.82 (d, J = 6.0 Hz, 24H, H<sub> $\beta$ </sub>-Py), 7.61 (s, 6H, Ar*H*), 7.34–7.50 (m, 90H, Ar*H* and Ph*H*), 5.17 (s, 12H, OC*H*<sub>2</sub>Ph), 1.35 (m, 144H, PCH<sub>2</sub>CH<sub>3</sub>), 1.09–1.19 (m, 216H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.4 MHz):  $\delta$  16.0 (s, <sup>1</sup>*J*<sub>Pt-P</sub> = 2686.9 Hz). Anal. Calcd for C<sub>390</sub>H<sub>516</sub> F<sub>36</sub>N<sub>12</sub>O<sub>42</sub>P<sub>24</sub>Pt<sub>12</sub>: C, 45.94; H, 5.10; N, 1.65. Found: C, 45.86; H, 5.34; N, 1.62.

**[G1]-Hexagonal Metallodendrimer 11b.** Yield: 8.51 mg (pale yellow solid), 97%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta$  8.69 (d, J = 5.4 Hz, 24H, H<sub>a</sub>-Py), 7.82 (d, J = 5.7 Hz, 24H, H<sub>β</sub>-Py), 7.62 (s, 6H, Ar*H*), 7.32–7.46 (m, 120H, Ar*H* and Ph*H*), 6.72 (s, 12H, Ar*H*), 6.61 (s, 6H, Ar), 5.12 (s, 12H, OCH<sub>2</sub>Ar), 5.08 (s, 24H, OCH<sub>2</sub>Ph), 1.35 (m, 144H, PCH<sub>2</sub>CH<sub>3</sub>), 1.09–1.19 (m, 216H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.4 MHz):  $\delta$  16.0 (s, <sup>1</sup> $J_{Pt-P} = 2687.6$  Hz). Anal. Calcd for C<sub>474</sub>H<sub>588</sub>F<sub>36</sub>N<sub>12</sub>O<sub>54</sub>P<sub>24</sub>Pt<sub>12</sub>S<sub>12</sub>: C, 49.63; H, 5.17; N, 1.47. Found: C, 49.64; H, 5.35; N, 1.42.

[G2]-Hexagonal Metallodendrimer 11c. Yield: 10.28 mg (pale yellow solid), 96%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz): δ 8.67 (br, 24H, H<sub>α</sub>-Py), 7.81 (d, J = 5.1 Hz, 24H, H<sub>β</sub>-Py), 7.62 (s, 6H, Ar*H*), 7.32–7.44 (m, 180H, Ar*H* and Ph*H*), 6.70–6.71 (m, 36H, Ar*H*), 6.57–6.80 (m, 18H, Ar), 5.11 (s, 12H, OCH<sub>2</sub>Ar), 5.05 (s, 48H, OCH<sub>2</sub>Ph), 5.02 (s, 24H, OCH<sub>2</sub>Ar), 1.35 (m, 144H, PCH<sub>2</sub>CH<sub>3</sub>), 1.09–1.20 (m, 216H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.4 MHz): δ 16.0 (s, <sup>1</sup>*J*<sub>Pt-P</sub> = 2689.4 Hz). Anal. Calcd for C<sub>642</sub>H<sub>732</sub> F<sub>36</sub>N<sub>12</sub>O<sub>78</sub>P<sub>24</sub>Pt<sub>12</sub>S<sub>12</sub>: C, 55.01; H, 5.26; N, 1.20. Found: C, 55.21; H, 5.46; N, 1.21.

**[G3]-Hexagonal Metallodendrimer 11d.** Yield: 14.18 mg (pale yellow glassy solid), 97%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz): δ 8.66 (br, 24H, H<sub>α</sub>-Py), 7.79 (br, 24H, H<sub>β</sub>-Py), 7.63 (s, 6H, ArH), 7.30–7.41 (m, 300H, ArH and PhH), 6.62–6.73 (m, 84H, ArH), 6.55 (br, 42H, ArH), 4.99–5.07 (m, 180H, OCH<sub>2</sub>Ar and OCH<sub>2</sub>Ph), 1.33 (m, 144H, PCH<sub>2</sub>-CH<sub>3</sub>), 1.07–1.20 (m, 216H, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.4 MHz): δ 16.0 (s, <sup>1</sup>J<sub>Pt-P</sub> = 2696.1 Hz). Anal. Calcd for C<sub>978</sub>H<sub>1020</sub>F<sub>36</sub>N<sub>12</sub>-O<sub>126</sub>P<sub>24</sub> Pt<sub>12</sub>S<sub>12</sub>·2CH<sub>2</sub>Cl<sub>2</sub>: C, 61.07; H, 5.36; N, 0.87. Found: C, 60.74; H, 5.80; N, 0.81.

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Supporting Information Available: <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds 2–4 and 5a–d, <sup>1</sup>H and <sup>31</sup>P NMR spectra of metallodendrimers 7a–d, 10a–d, and 11a–d, crystallographic files (in CIF format) of [G0]- and [G1]-rhomboidal metallodendrimers 7a and 7b, and full mass spectra of metallodendrimers 7a–d and 10a–c. This material is available free of charge via the Internet at http://pubs.acs.org.

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