JOC Note

Synthesis of Six-Component Metallodendrimers via [3 + 3] Coordination-Driven Self-Assembly

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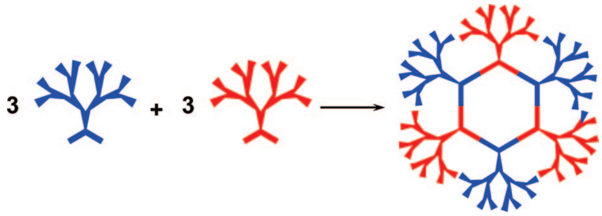

A new class of 120° dendritic di-Pt(II) acceptor subunits has been designed and synthesized, from which six-component hexagonal metallodendrimers were easily formed with 120° dendritic dipyridine donors via [3 + 3] coordination-driven self-assembly. The structures of all metallodendrimers are confirmed by multinuclear NMR, ESI-TOF-MS/ESI-FTMS, and elemental analysis. MMFF force-field simulations indicates that all metallodendrimers have a hexagonal ring with an internal radius of approximately 1.4 nm.

Since the pioneering work by Newkome et al.[1] and Balzani et al.[2] in the early 1990s, metallodendrimers[3] have evolved to be one of the most attractive fields within supramolecular chemistry. Compared to the synthesis of conventional dendrimers that rely heavily on carbon−carbon or carbon−heteroatom bond formation, metal−donor interactions have been shown to function as the key growth steps in the construction of metallodendrimers. The highly efficient formation of coordination bonds offers considerable synthetic advantages such as fewer steps, fast and facile construction of the final products, and inherently self-correcting, defect-free assembly. More importantly, the incorporation of metals endows desirable properties to the resulting metallodendrimers. This new family of dendrimers has been extensively explored as potential functional materials in catalysis,[4] as biological mimetics,[5] and in photo- and electrochemistry.[6] Recently, dendritic metallocycles have received considerable attention because of their potential application in the recognition and delivery of guests incorporated within their cavities.[7] However, the precise control of the size and the shape of the metallodendrimers remains a challenge.

Coordination-driven self-assembly[8] has been demonstrated to be a powerful and facile approach to the construction of polygons and polyhedra[9] with well-designed shapes, sizes, and symmetry. By employing such a strategy, we have previously constructed a series of functionalized metallacycles[10] including well-defined metallodendrimers[11] with various sizes and shapes. For example, by combining predesigned 120° angular dendritic

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organic donors with 180° di-Pt(II) acceptors, "snowflake-shaped" [6 + 6] metallodendrimers[11b] were prepared via coordination-driven self-assembly. More recently, a new family of metallodendritic squares has been synthesized from 4,4′-bipyridines funtionalized with Fréchet-type dendrons and (dppp)Pt(II) or Pd(II) triflate by Schalley et al.[12]

According to the "symmetry interaction" model,[8a,e] 120° anglular building units are required for hexagonal assemblies whereas 108° anglar units lead to the production of pentagonal structures. As supramolecular structures increase in size they also tend toward increasing flexibility. For large, complex supramolecular hexagons, small distortions away from 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. Although no evidence for any other species, such as pentagonal assemblies, was found in multinuclear NMR or mass spectroscopy studies during the formation of [6 + 6] hexagonal metallodendrimers,[11b] it is necessary to find alternative means to prepare six-component hexagonal metallodendrimers that rule out the possibility of forming pentagonal structures entirely.

In general, the shape of an individual two-dimensional polygon is determined by the value of the turning angle within its angular components. According to the "directional bonding" and "symmetry interaction" models,[8a,e] discrete hexagonal entities can be self-assembled via the combination of two complementary ditopic building blocks A^2 and X^2, each incorporating 120° angles between their coordination sites, allowing for the formation of hexagonal structures of type $A^2_3X^2_3$.[13] This strategy, in contrast to the use of six 120° angular units and six 180° linear units that results in larger and more flexible hexagonal assemblies, is able to rule out the possibility of the formation of alternative, nonhexagonal species. Herein, we report the synthesis, via [3 + 3] coordination-driven self-assembly, of six-component hexagonal metallodendrimers from the newly designed 120° di-Pt(II) acceptor **1** and 120° dipyridine donor **2** (Figure 1), both of which are substituted with Fréchet-type dendrons.

The 120° dendritic di-Pt(II) acceptors **2a−c** can be easily synthesized as shown in Scheme 1. The Fréchet-type dendrons ([G-1]−[G-3]) were introduced by a coupling reaction of **3** with the different generation dendritic carboxylic acids.[14] Compounds **4a−c** were then reacted with 4 equiv of *trans*-$PtI_2(PEt_3)_2$ to give diiodo metal complexes **5a−c**. Subsequent halogen abstraction with AgOTf resulted in the isolation of bistriflate salts **2a−c** in reasonable yield. The $^{31}P\{^1H\}$ NMR spectra of diplatinum acceptors **2a−c** displayed singlets at 22.19, 22.65, and 22.56 ppm, respectively, each accompanied by flanking ^{195}Pt satellites.

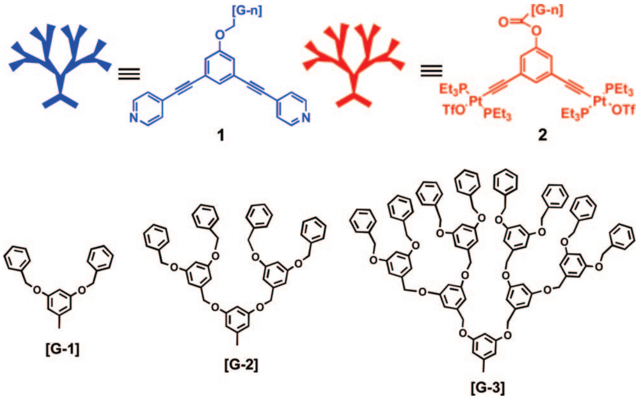
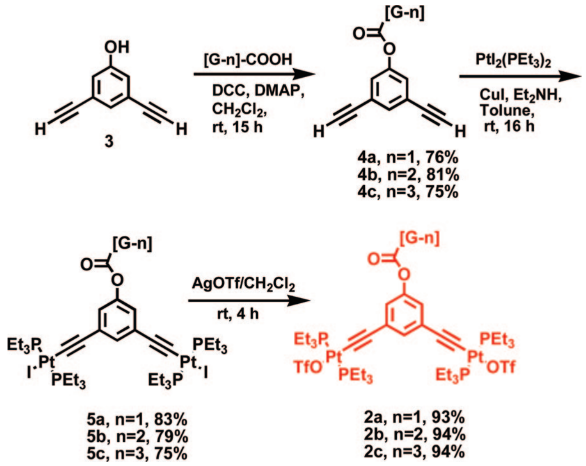


FIGURE 1. Schematic and molecular structure of 120° dendritic donor subunit **1** and 120° dendritic acceptor subunit **2**.

SCHEME 1. Synthesis of 120° Dendritic Di-Pt(II) Acceptor Subunits 2a−c



Single crystals of [G-1] di-Pt(II) diiodide complex **5a**, suitable for X-ray diffraction studies, were grown by slow evaporation of a dichloromethane/methanol solution (1/1) at ambient temperature for 2−3 days. An ORTEP representation of the structure of **5a** (Figure 2) shows that it is indeed a suitable candidate for a 120° building unit, with the angle between the two platinum coordination planes being approximately 124°. The distance between the two Pt centers in **5a** is ~1.0 nm.

When [G-1]−[G-3] 120° dendritic donor subunits **1a−c** were reacted with 120° dendritic di-Pt(II) acceptors **2a−c** in CD_2Cl_2 at room temperature, the [3 + 3] six-component hexagonal

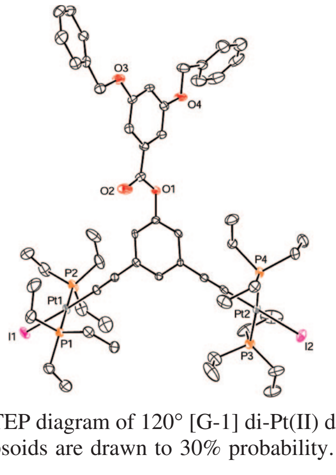


FIGURE 2. ORTEP diagram of 120° [G-1] di-Pt(II) diiodide complex **5a**. Thermal ellipsoids are drawn to 30% probability.

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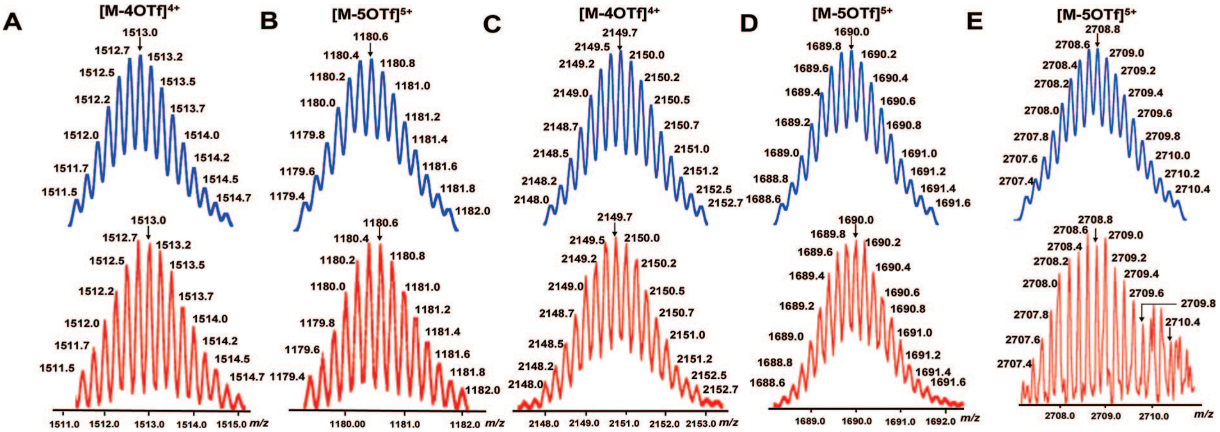
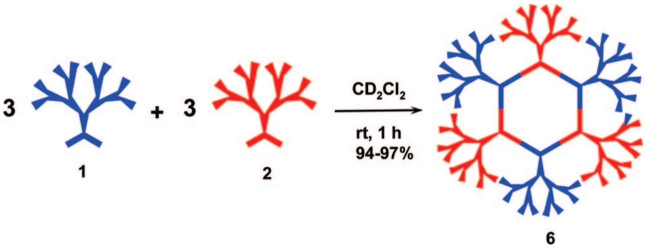


FIGURE 3. Calculated (top) and experimental (bottom) ESI-TOF-MS spectra of metallodendrimers **6a** (A and B) and **6b** (C and D) and ESI-FTMS spectra of metallodendrimer **6c** (E).

SCHEME 2. Self-Assembly of Six-Component Hexagonal Metallodendrimers via [3 + 3] Coordination-Driven Self-Assembly



metallodendrimers **6a**−**c**, respectively, were formed (Scheme 2). $^{31}P\{^1H\}$ NMR analysis of the reaction mixtures is consistent with the formation of single, highly symmetric species as indicated by the appearance of a sharp singlet (ca. 16.2 ppm) with concomitant ^{195}Pt satellites, shifted upfield by ca. 6.4 ppm as compared to **2a**−**c**. This change, as well as the decrease in coupling of the flanking ^{195}Pt satellites (ca. $\Delta^1J_{PPt} = -62$ Hz for **6a**; $\Delta^1J_{PPt} = -64$ Hz for **6b**; $\Delta^1J_{PPt} = -67$ Hz for **6c**), is consistent with back-donation from the platinum atom, lending further support to the formation of the supramolecular complexes. In the ^{1}H NMR spectra of metallodendrimers **6a**−**c**, the β-H of the pyridine rings exhibited ca. 0.40−0.51 ppm downfield shifts relative to uncoordinated **5a**−**d** due to the loss of electron density that occurs upon coordination of the pyridine-N atom with the Pt(II) metal center. Upon stirring at 298 K for 72 h, the $^{31}P\{^1H\}$ and ^{1}H NMR of assemblies **6a**−**c** do not show any significant change, demonstrating the stability of these novel supramolecular assemblies. The sharp NMR signals in both the $^{31}P\{^1H\}$ and ^{1}H NMR spectra (see the Supporting Information) along with the solubility of these species ruled out the formation of oligomers.

Mass-spectrometric studies of metallodendrimers **6a**−**d** were performed by ESI-TOF-MS and ESI-FTMS spectrometry, which allows the assemblies to remain intact during the ionization process in order to obtain the high resolution required for unambiguous determination of individual charge states. The high molecular weight and complex isotope splitting of such charged multiplatinum species necessitates high-resolution mass spectral analysis in order to determine their absolute molecular weight and their molecularity, which reveals the absolute stoichiometry of constituent subunits and can definitively rule out the possibility of supramolecular pentagon assembly.

All results of mass studies of assemblies **6a**−**c** have provided strong support for the formation of hexagonal metallodendrimers. In the ESI-TOF-MS spectra of [G-1] and [G-2] assemblies **6a** and **6b**, peaks at $m/z = 1513.0$ and 1180.6 for **6a** and $m/z = 2149.7$ and 1690.0 for **6b**, corresponding to the charge states $[M - 4OTf]^{4+}$ and $[M - 5OTf]^{5+}$, respectively, were observed, and their isotopic resolutions are in excellent agreement with the theoretical distributions (Figure 3A−D). Given the significantly larger molecular weight (14278.7 Da) of the [G-3] hexagonal metallodendrimer, it is more difficult to get strong mass signals even under the ESI-TOF-MS conditions. With considerable effort, a peak at $m/z = 2708.8$ was observed in the ESI-FTMS spectrum of [G-3]-assembly **6c**, which corresponds to the $[M - 5OTf]^{5+}$ charge state. The peak was isotopically resolved (Figure 3E) and agrees well with the theoretical distribution, although overlap with the signal of a minor unknown fragment, which could not be attributed to any alternative polygonal supramolecules, was also observed.

We have demonstrated that [3 + 3] hexagonal structures can be self-assembled by combining three 120° pyridyl donor building blocks and three 120° diplatinum acceptors.[13] Furthermore, recent studies have indicated that the addition of functional groups at the vertices of individual building units, such as ferrocene and crown ether moieties, does not hinder the formation of [3 + 3] self-assembled metallosupramolecules.[13] Close examination of the ESI mass spectra of **6a**−**c** revealed no peaks indicating the formation or existence of [2 + 2] rhomboidal or [4 + 4] octagonal structures. It should again be noted that it is not possible to form polygons with an odd number of sides (i.e., pentagon, heptagon, etc.) by combining 120° donors with 120° acceptors as they would require the direct connection of either two acceptor or two donor moieties. The lack of mass spectral peaks corresponding to other polygon architectures and the singularity of each ^{31}P NMR signal ensures that only [3 + 3] hexagonal metallodendrimers are formed in each self-assembly.

Large supramolecular coordination-compounds and flexible, high-generation dendrimers often prove difficult to crystallize. Likewise, all attempts to grow X-ray-quality single crystals of hexagonal metallodendrimers **6a**−**c** have proven to be unsuccessful to date. MMFF force-field simulations were employed to optimize the geometry of all metallodendrimers **6a**−**c** (For [G-1] and [G-2], see the Supporting Information). Simple space-filling models of the simulated structures indicate that each of **6a**−**c** have a very similar, roughly planar hexagonal ring at their

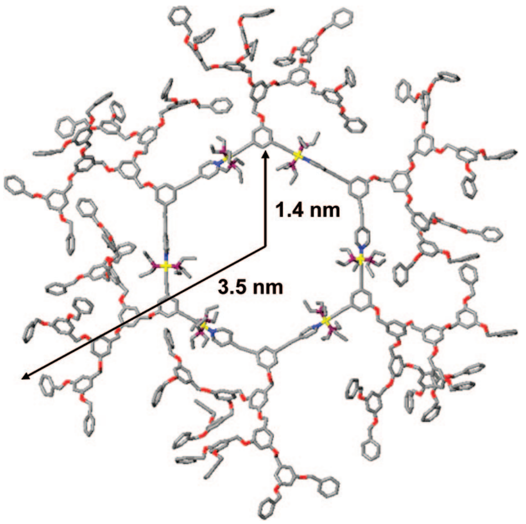


FIGURE 4. Simulated molecular model of [G-3] six-component hexagonal metallodendrimer **6c** (C = gray, O = red, N = blue, P = purple, Pt = yellow; hydrogen atoms have been removed for clarity).

core surrounded by flexible dendrons. In the case of **6c**, the hexagonal ring-shaped metallodendrimer has an internal radius of approximately 1.4 nm while the outer dendron radius averages 3.5 nm (Figure 4).

In summary, we have designed and synthesized a new class of 120° dendritic di-Pt(II) acceptor subunits, from which six-component hexagonal metallodendrimers can be easily formed via [3 + 3] coordination-driven self-assembly, thus enriching the library of dendritic metallocycles. More importantly, compared to previous reports of the synthesis of six-component hexagonal metallodendrimers, this study provides another highly efficient approach to the construction of such species that unambiguously avoids the possible formation of other polygons caused by small distortions of the subunit bond angles. All metallodendrimers are characterized with multinuclear NMR, ESI-TOF-MS/ESI-FTMS, and elemental analysis. Their structural properties have been studied using MMFF force-field simulations, which indicate that all metallodendrimers have hexagonal rings with internal radii of approximately 1.4 nm. This research has once again proven the versatility and modularity of the directional bonding approach to self-assembly, which surely will be employed to the synthesis of other functional dendritic metallocycles in the future.

Experimental Section

General Procedure for the Preparation of Six-Component Hexagonal Metallodendrimers 6a−c. To a 0.5 mL dichloromethane-d_2 solution of triflate **2a−c** (for **2a**, 5.40 mg, 0.00334 mmol; for **2b**, 5.95 mg, 0.00291 mmol; for **2c**, 5.70 mg, 0.00197 mmol) was added a 0.5 mL dichloromethane-d_2 solution of the appropriate [G-1]−[G-3] dendritic donor precursors **1a−c** (for **1a**, 2.0 mg, 0.00334 mmol; for **1b**, 2.98 mg, 0.00291 mmol; for **1c**, 3.69 mg, 0.00197 mmol) drop by drop with continuous stirring (10 min). The reaction mixture was stirred for 1 h at room temperature. The solution was evaporated to dryness, and the product was collected.

6a. Yield: 7.10 mg (pale yellow solid), 96%. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.63 (d, J = 6.3 Hz, 12H), 7.81 (d, J = 6.3 Hz, 12H), 7.59 (s, 3H), 7.31−7.44 (m, 72H), 7.08 (s, 3H), 6.95 (s, 6H), 6.91 (s, 3H), 6.70 (s, 6H), 6.60 (s, 3H), 5.13 (s, 12H), 5.11 (s, 6H), 5.06 (s, 12H), 1.80−1.83 (m, 72H), 1.13−1.24 (m, 108H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 16.12 (s,$^1J_{Pt-P}$ = 2299.8 Hz). Anal. Calcd for $C_{294}H_{330}F_{18}N_6O_{39}P_{12}$ Pt_6S_6: C, 53.11; H, 5.00; N, 1.26. Found: C, 53.45; H, 5.23; N, 1.52.

6b. Yield: 8.42 mg (pale yellow solid), 97%. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.61 (d, J = 6.3 Hz, 12H), 7.80 (d, J = 6.3 Hz, 12H), 7.60 (s, 3H), 7.35−7.43 (m, 132H), 7.07 (s, 3H), 6.95 (s, 6H), 6.88 (s, 3H), 6.69 (s, 30H), 6.58 (s, 15H), 5.01−5.10 (m, 78H), 1.79−1.81 (m, 72H), 1.12−1.23 (m, 108H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 16.18 (s,$^1J_{Pt-P}$ = 2310.1 Hz). Anal. Calcd for $C_{462}H_{474}F_{18}N_6O_{63}P_{12}Pt_6S_6$: C, 60.35; H, 5.20; N, 0.91. Found: C, 60.18; H, 5.46; N, 0.98.

6c. Yield: 8.83 mg (pale yellow glassy solid), 94%. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.58 (s, 12H), 7.78 (d, J = 6.3 Hz, 12H), 7.61 (s, 3H), 7.32−7.40 (m, 252H), 7.06 (s, 3H), 6.94 (s, 6H), 6.87 (s, 3H), 6.69 (br, 78H), 6.58 (br, 39H), 4.97−5.00 (m, 174H), 1.79−1.81 (m, 72H), 1.12−1.23 (m, 108H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 16.15 (s,$^1J_{Pt-P}$ = 2305.8 Hz). Anal. Calcd for $C_{798}H_{762}F_{18}N_6O_{111}P_{12}Pt_6S_6$: C, 67.08; H, 5.38; N, 0.59. Found: C, 66.78; H, 5.51; N, 0.61.

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Supporting Information Available: Experimental procedures, characterization data, copies of spectra for compounds (**2a−c**, **4a−c**, **5a−c**, and **6a−c**), simulated molecular model of **6a** and **6b**, and crystallographic file (CIF) of **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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