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Synthesis of Triangular Metallodendrimers via Coordination-Driven Self-Assembly

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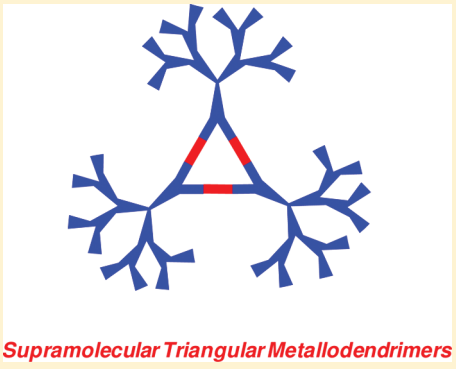
Supporting Information

ABSTRACT: A new family of 60° dendritic di-Pt(II) acceptor tectons have been successfully designed and synthesized, from which a series of novel "three-component" triangular metallodendrimers were prepared via [3 + 3] coordination-driven self-assembly. The structures of newly designed triangular metallodendrimers are characterized by multinuclear NMR (^{1}H and ^{31}P), ^{1}H DOSY NMR, mass spectrometry (CSI-TOF-MS), and elemental analysis. The shape and size of all supramolecular dendritic triangles were investigated with PM6 semiempirical molecular orbital methods.



INTRODUCTION

Dendrimers[1] are highly branched, three-dimensional macromolecules comprised of several dendritic wedges extending outward from an internal core. In the past few decades, the design and synthesis of diverse dendrimers[2] has evolved to be one of the most attractive subjects within supramolecular chemistry because of their wide applications in host−guest chemistry,[3] catalysis,[4] materials science,[5] and nanomedicine,[6] etc. In general, two complementary methodologies,[2a] the divergent and the convergent, have been employed in the preparation of dendrimers. However, such covalent synthetic protocols sometimes suffer from time-consuming 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 exhibits considerable synthetic advantages including comparatively fewer steps, fast and facile formation of the final products, and inherent detect-free assembly. In particular, self-assembly provides an efficient approach to the construction of the higher order supramolecular dendrimers. As a consequence, there has been an increasing interest in the studies of self-assembly of dendrimers to provide well-defined nanoscale architectures[7] via a variety of noncovalent interactions[8] such as electrostatic interactions, hydrogen bonding, and metal−ligand coordination.

Coordination-driven self-assembly[9] has proven to be a particularly powerful method for the construction of supramolecular two-dimensional (2-D) and three-dimensional (3-D) structures with well-defined shape and size.[10,11] Among the known artificial metallacycles, triangle[12] has attracted considerable attention since the first example[12a] of a cyclic organogold molecular triangle reported by Vaughan in 1970. However, the formation of supramolecular triangles sometimes suffers from the noticeable equilibrium with other macrocyclic species when flexible building blocks are employed.[13] For example, Fujita and co-workers have reported that the self-assembly of [Pd(en)-$(ONO_2)_2$] with longer and more flexible 180° dipyridine ligands affords equilibrium mixtures of molecular squares and triangles.[13a] According to the directional-bonding methodology,[9a,c] a predesigned supramolecular triangle can be assembled by the reaction of three rigid ditopic 60° tectons, serving as the corners, with three linear sides.[14] For instance, we have realized the formation of supramolecular multiferrocenyl triangles from the combination of 60° ferrocenyl building blocks with different sized linear donor subunits via coordination-driven self-assembly.[11a] With the aim of developing self-assembly of novel supramolecular functionalized

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triangles, the design and synthesis of new 60° tectons is still necessary.

Herein we have successfully synthesized a new family of 60° dendritic metal-containing corners (Figure 1) from which a

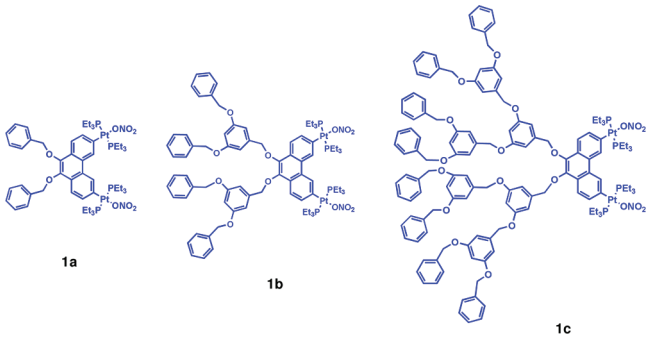


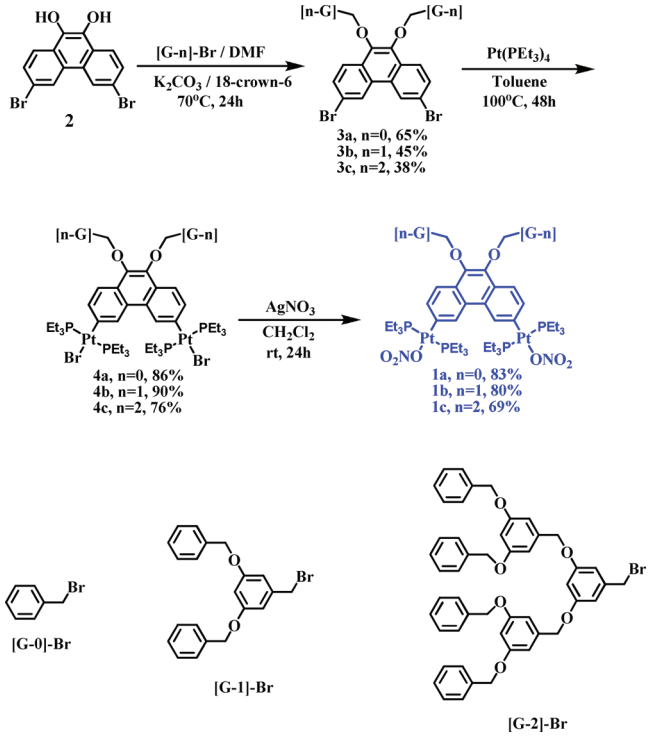
Figure 1. Molecular structures of [G-1]−[G-3] 60° dendritic di-Pt(II) acceptor subunits **1a−c**.

series of novel supramolecular metallodendritic triangles were obtained via coordination-driven self-assembly. These triangular metallodendrimers are formed via the directional-bonding approach that is not template directed. It should be noted that supramolecular metallodendrimers are of special interest because of a variety of materials and synthetic applications.[15,16] For example, we have previously reported the self-assembly of a variety of metallodendrimers with cavities of various shapes and sizes such as rhomboids and hexagons.[16a−f] Moreover, a family of new metallodendritic squares has been synthesized from 4,4′-bipyridines funtionalized with Fréchet dendrons and (dppp)-Pt(II) or Pd(II) triflate by Schalley's group.[16g] Very recently, Newkome and co-workers have reported the synthesis and photophysical properties of a series of new dendron-functionalized bis(terpyridine)−iron(II) or −cadmium(II) metallomacrocycles.[16h] Herein we report our results on the self-assembly of triangular metallodendrimers from the newly designed 60° dendritic corners without using a template.

RESULTS AND DISCUSSION

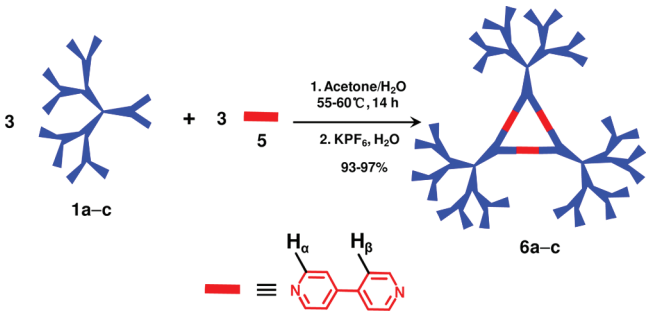
The new 60° dendritic di-Pt(II) acceptors **1a−c** can be easily synthesized in three steps as shown in Scheme 1. The Fréchet-type dendrons were introduced by an etherification reaction of 3,6-dibromophenanthrene-9,10-diol[17] (**2**) with the corresponding dendritic bromides.[16f] Compounds **3a−c** were then reacted with 4 equiv of Pt $(PEt_3)_4$ to give bromide complexes **4a−c**. Subsequent halogen abstraction with $AgNO_3$ resulted in the isolation of bisnitrate salts **1a−c** in reasonable yield. It was found that 60° dendritic diplatinum linkers **1a−c** displayed singlets (19.27 ppm for **1a**; 19.29 ppm for **1b**; 19.00 ppm for **1c**), accompanied by concomitant ^{195}Pt satellites in the $^{31}P\{^1H\}$ NMR spectra. Single crystals of di-Pt(II) dibromide complex **4a**, suitable for X-ray diffraction studies, were grown by slow vapor evaporation of a solution of a solvent mixture (CH_2Cl_2 /CH_3OH: 1/1) at ambient temperature for 2−3 days. An ORTEP representation of the structure of **4a** (Figure S1, see the Supporting Information) shows that it is indeed a suitable candidate for a 60° building unit, with the angle between the two platinum coordination planes being approximately 62°. The distance between the two Pt centers in **4a** is 7.7 Å. All of the atoms (except for the triethylphosphine ligands) lie approximately in the same plane.

Scheme 1. Synthesis of 60° Dendritic Di-Pt(II) Acceptor Subunits 1a−c



For the assembly of supramolecular metallodendritic triangles, 4,4-bipyridyl (**5**) was employed as 180° linear building blocks. The self-assembly of triangular metallodendrimers **6a−c** proceeded essentially quantitatively as outlined in Scheme 2. Heating the mixtures of 4,4-bipyridyl (**5**) and the

Scheme 2. Self-Assembly of Supramolecular Triangular Metallodendrimers 6a−c via [3 + 3] Coordination-Driven Self-Assembly



corresponding 60° dendritic diplatinum acceptors **1a−c** in a 1:1 stoichiometric ratio in aqueous acetone (water/acetone 1/6) overnight resulted in supramolecular metallodendritic triangles **6a−c**, respectively. $^{31}P\{^1H\}$ 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. 11.8 ppm) with concomitant ^{195}Pt satellites, shifted upfield by ca. 7.2 ppm as compared to the precursors **1a−c** (Figure 2). In the ^{1}H NMR spectrum of each assembly (Figure 3), the α-hydrogen nuclei of the pyridine rings exhibited 0.16−0.67 ppm downfield shifts and the β-hydrogen nuclei showed about 0.74−0.92 ppm downfield shifts because of the loss of electron density that occurs upon coordination of the pyridine-

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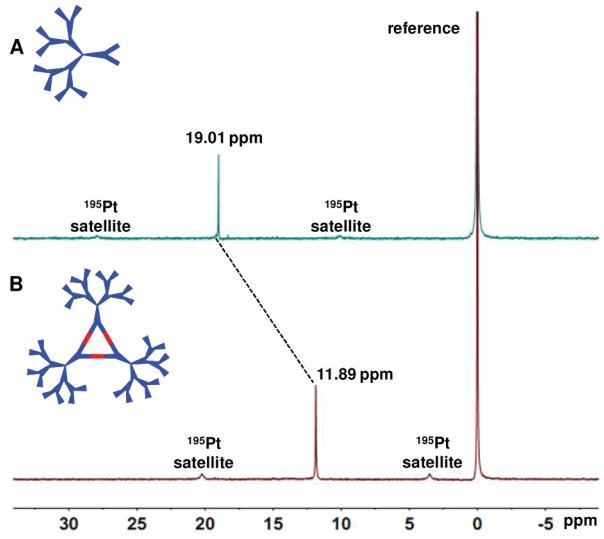

Figure 2. Partial $^{31}P\{^{1}H\}$ NMR spectra (400 MHz, $CDCl_3$, 298K) of [G-3] 60° di-Pt(II) acceptor **1c** (A) and [G-3] triangular metallodendrimer **6c** (B).

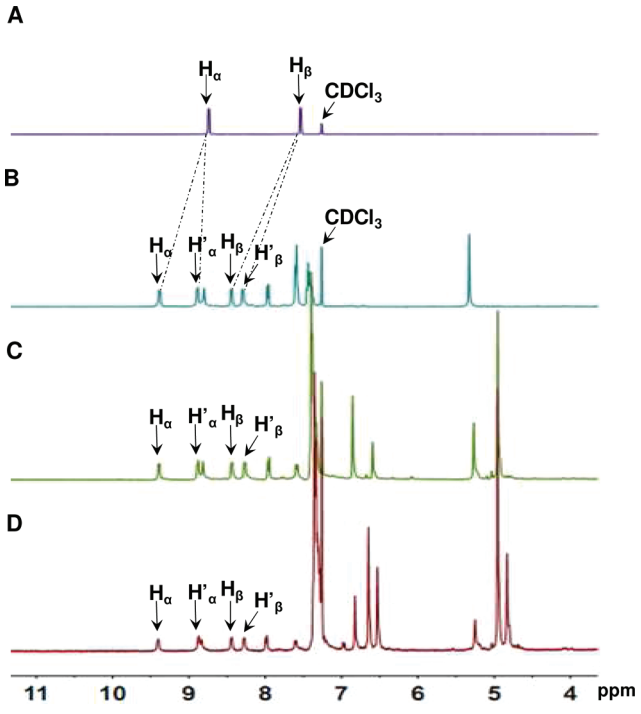

Figure 3. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298K) of 4,4′-dipyridine (A) and [G-1]−[G-3] triangular metallodendrimers **6a** (B), **6b** (C), and **6c** (D).

N atom with the Pt(II) metal center. It is noteworthy that the existence of two sets of doublets for both the α- and β-pyridine protons is an important characteristic feature of the ^{1}H NMR of these triangles.[7a,14a] Given that the pyridine rings of the side unit and the phenanthrene system of the corner lie in the same plane, the formation of the macrocyclic structure creates a different environment for the inner and outer pyridine protons, hence the different chemical shifts. The similar results have been reported in the previous literature.[7a,14a] The sharp NMR signals in both the $^{31}P\{^{1}H\}$ 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 triangular metallodendrimers **6a−c** were performed by the cold-spray ionization (CSI)-TOF-MS technique, 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.[18] 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 byproduct assembly. All results of mass studies of assemblies **6a−c** have provided strong support for the formation of triangular metallodendrimers. In the CSI-TOF-MS spectrum of [G-1] assembly **6a**, for example, peaks at m/z = 2401.5 and m/z = 1552.8, corresponding to the charge states $[M - 2\ PF_6]^{2+}$ and $[M - 3\ PF_6]^{3+}$, respectively, were observed and their isotopic resolutions are in excellent agreement with the theoretical distributions (Figure 4A). Similarly, the CSI-TOF-MS spectrum of [G-2] triangular metallodendrimer **6b** (Figure 4B) exhibited two charged states at m/z = 1977.1 and m/z = 1466.8, related to $[M - 3\ PF_6]^{3+}$ and $[M - 4\ PF_6]^{4+}$, respectively. These peaks were isotopically resolved, and they agree very well with their theoretical distribution. Given the significantly larger molecular weight (8,906.8 Da) of the [G-3] triangular metallodendrimer **6c** it is more difficult to get strong mass signals even under the CSI-TOF-MS conditions. With considerable effort, the peak at m/z = 2083.19 was observed in the CSI-TOF-MS spectrum of [G-3]-assembly **6c**, which corresponds to the $[M - 4\ PF_6]^{4+}$charge state. This peak was isotopically resolved and agrees with the theoretical distribution, although overlap with the signals of minor unknown fragments was also observed (Figure 3C).

Large supramolecular coordination compounds and flexible, high-generation dendrimers often prove difficult to crystallize. All attempts to grow X-ray quality single crystals of triangular metallodendrimers **6a−c** have proven to be unsuccessful to date. Therefore, the geometry structures of the supramolecular metallodendritic triangles **6a−c** were optimized by PM6 semiempirical molecular orbital methods, respectively. In the optimized structure (Figure 5), it was found that **6a−c** have a roughly planar triangular ring at its core surrounded by three-component dendron subunits. The sides of the triangles **6a−c** are 4.0, 4.7, and 5.9 nm in length, respectively, and the internal cavity is approximately 1.7 nm. Moreover, simulations reveal that the underlying triangular structures, "scaffolds", all retain their planar and rigid structures even when derivatized with dendrons units. In all cases, the flexible nature of the pendent dendron moieties and the rigid nature of the triangular cavity can be observed from modeling studies. In order to obtain further structural information, the diffusion coefficient (D) of newly designed dendritic triangles was determined by two-dimensional diffusion-ordered NMR (DOSY) experiments. The ^{1}H DOSY NMR measurements for assemblies **6a−c** in $CDCl_3$ were carried out under similar conditions (3.06×10^{-3} mol/L, 293 K), respectively. It was found that the D values decrease gradually with an increase of the molecular weight (see the Supporting Information), which is in good agreement with the modeling results.

■ CONCLUSION

In summary, we have designed and synthesized a new class of 60° dendritic di-Pt(II) acceptor subunits, from which novel

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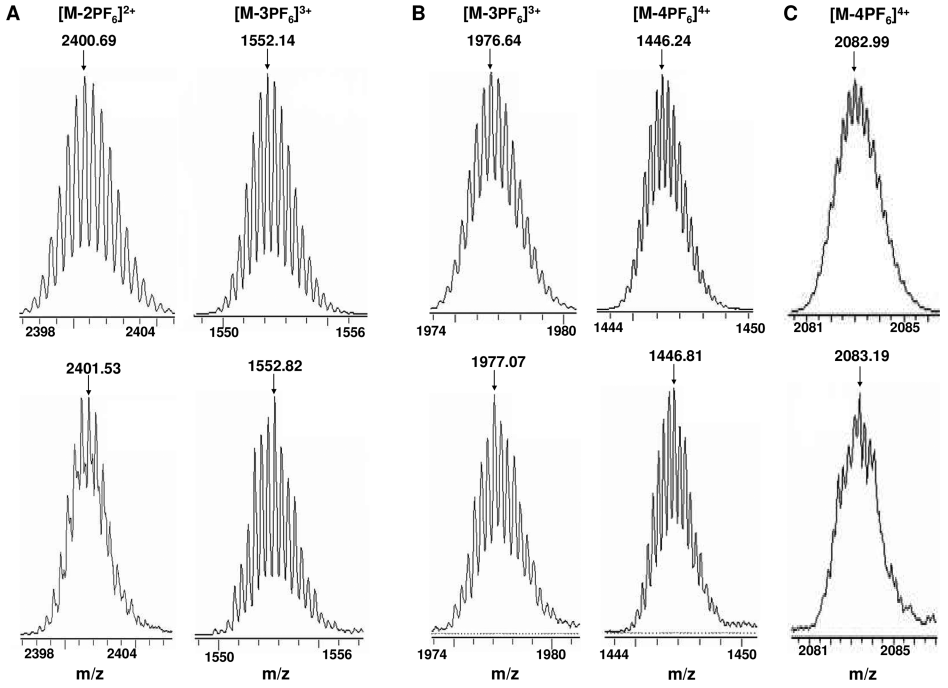

Figure 4. Theoretical (top) and experimental (bottom) CSI-TOF-MS spectra of [G-1]−[G-3] triangular metallodendrimers **6a** (A), **6b** (B), and **6c** (C).

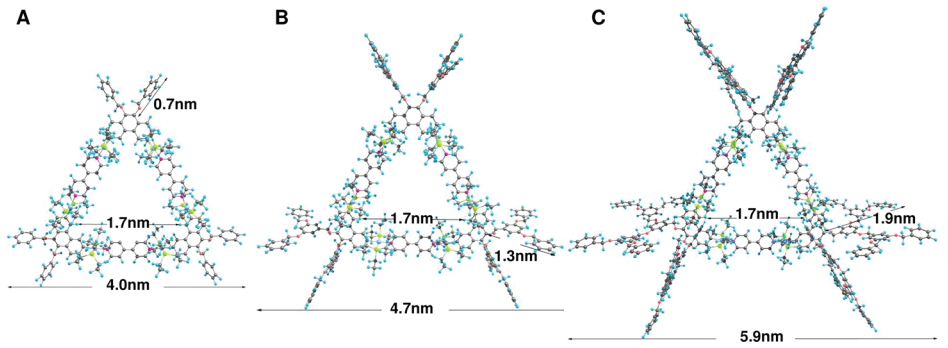

Figure 5. Simulated molecular model of triangular metallodendrimers **6a** (A), **6b** (B), and **6c** (C).

three-component triangular metallodendrimers can be easily formed via [3 + 3] coordination-driven self-assembly, thus enriching the library of dendritic metallacycles. More importantly, compared to some previous reports of the construction of supramolecular triangles, this study provides highly efficient approach to the construction of such species without any assistance of templates. All triangular metallodendrimers were characterized with multinuclear NMR, CSI-TOF-MS, and elemental analysis. Their structural properties have been studied by using PM6 semiempirical molecular orbital methods, which indicate that all metallodendrimers have triangular rings with internal radii of approximately 1.7 nm. This research has once again proven the versatility and modularity of the directional bonding approach to self-assembly, which surely will be employed for the synthesis of other functional dendritic metallacycles in the future.

■ EXPERIMENTAL SECTION

General Information. All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Toluene was distilled from sodium/benzophenone. Dimethylformamide (DMF) was distilled before use. All solvents were degassed under N_2 for 30 min before use. Deuterated solvents and all other reagents were purchased and used without further purification. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on a 300 MHz spectrometer (^{1}H: 300 MHz; ^{13}C: 75 MHz; ^{31}P: 121.4 MHz) at 298 K or a 400 MHz spectrometer (^{1}H: 400 MHz; ^{13}C: 100 MHz; ^{31}P: 161.9 MHz) at 298 K. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P NMR resonances are referenced to an internal standard sample of 85% H_3PO_4 (δ 0.0). Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, t = triplet.

Synthetic Procedures. *Synthesis of* ***3a−c.*** Under an atmosphere of nitrogen, **2** (772 mg, 2.10 mmol), [G-n]-Br (for G-0, 0.59 mL, 4.83 mmol; for G-1, 1.85 g, 4.83 mmol; for G-2, 3.9 g, 4.83 mmol), and K_2CO_3 (2.9 g, 21.0 mmol) were dissolved in DMF (25 mL). The mixture was heated at reflux for 18 h and then cooled to room temperature. Solvent was then distilled, and the resulting mixture was poured into water and extracted with methylene chloride (15 mL × 3). The methylene chloride solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. The crude products were purified by column chromatography on silica gel (dichloromethane/petroleum ether ∼1/1) to give compounds **3a−c**.

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3a. Yield: 0.58 g (white solid), 65%. R_f = 0.74 (dichloromethane/*n*-hexane 1/1). Mp: 190−193 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.66 (s, 2H), 8.10 (d, J = 8.7 Hz, 2H), 7.69 (d, J = 6.3 Hz, 2H), 7.52−7.49 (m, 4H), 7.43−7.36 (m, 6H), 5.27 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.2, 136.9, 130.6, 129.0, 128.6, 128.4, 125.4, 124.3, 120.6, 75.5. MALDI-MS for $C_{28}H_{20}Br_2O_2Na$ [(M + Na) $^+$]: 569.00. IR (neat) ν/cm^{-1}: 2925, 1589, 1564, 1455, 1344, 1310, 1048, 813, 753, 734, 696.

3b. Yield: 0.92 g (white glassy solid), 45%. R_f = 0.50 (dichloromethane/*n*-hexane 3/1). Mp: 150−152 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.67 (d, J = 1.5 Hz, 2H), 8.08 (d, J = 8.7 Hz, 2H), 7.69 (d, J = 9.0 Hz, 2H), 7.37−7.29 (m, 20H), 6.74 (d, J = 2.1 Hz, 4H), 6.57 (t, J = 2.1 Hz, 2H), 5.18 (s, 4H), 4.93 (s, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.1, 143.1, 139.3, 136.7, 130.7, 129.1, 128.6, 128.3, 128.0, 127.5, 125.5, 124.3, 120.7, 106.9, 101.9, 75.3, 70.1. MALDI-MS for $C_{56}H_{44}Br_2O_6Na$ [(M + Na)$^+$]: 993.20. IR (neat) ν/cm^{-1}: 2893, 1595, 1451, 1376, 1290, 1165, 1013, 819, 752, 730, 694. Anal. Calcd for $C_{56}H_{44}Br_2O_6$: C, 69.14; H, 4.56. found: C, 69.10; H, 4.33.

3c. Yield: 1.45 g (white glassy solid), 38%. R_f = 0.36 (dichloromethane/*n*-hexane 4/1). Mp: 45− 47 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (s, 2H), 8.09 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 6.3 Hz, 2H), 7.34−7.28 (m, 40H), 6.72 (s, 4H), 6.62 (s, 8H), 6.51 (s, 6H), 5.15 (s, 4H), 4.93 (s, 16H), 4.82 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.1, 160.0, 143.2, 139.4, 139.2, 136.7, 130.7, 129.1, 128.5, 128.3, 127.9, 127.5, 124.3, 120.8, 106.8, 106.4, 102.0, 101.6, 70.0, 69.9. MALDI-MS for $C_{112}H_{92}Br_2O_{14}Na$ [(M + Na)$^+$] 1841.60. IR (neat) ν/cm^{-1}: 2971, 2901, 2361, 1595, 1451, 1407, 1393, 1253, 1066, 892, 735, 697. Anal. Calcd for $C_{112}H_{92}Br_2O_{14}$: C, 73.84; H, 5.09. Found: C, 74.00; H, 5.30.

Synthesis of ***4a−c.*** A 50-mL Schlenk flask was charged under nitrogen with **3a−c** (for **3a**, 72 mg, 0.13 mmol; for **3b**, 126 mg, 0.13 mmol; for **3c**, 237 mg, 0.13 mmol) and $Pt(PEt_3)_4$ (334 mg, 0.5 mmol). Freshly distilled toluene (8.0 mL) was added to the flask under nitrogen by syringe, and the resulted bright yellow solution was stirred for 72 h at 99 °C. The solvent was then removed in vacuo. The residue was washed with methanol (4 × 2.0 mL) and purified by column chromatography on silica gel (dichloromethane/methyl alcohol ∼500/1) to give compounds **4a−c**.

4a. Yield: 158 mg (yellow crystalline solid), 86%. R_f = 0.63 (dichloromethane/methyl alcohol 500/1). Mp: 155−157 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (s, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.59−7.57 (m, 6H), 7.43−7.34 (m, 6H), 5.28 (s, 4H), 1.69−1.68 (m, 24H), 1.12−1.04 (m, 36H). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 12.69 (s, $^1J_{Pt-P}$ = 2763.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.6, 138.1, 137.74, 127.65, 126.3, 129.3, 128.4, 128.2, 127.9, 124.7, 120.6, 75.0, 14.3, 14.1, 14.0, 7.78, 7.72. CSI-TOF-MS for $C_{52}H_{80}BrO_2P_4Pt_2$ [(M − Br)$^+$]: 1331.46. IR (neat) ν/cm^{-1}: 2962, 2874, 2361, 2343, 1661, 1572, 1454, 1085, 1306, 1034, 821, 765, 730, 696. Anal. Calcd for $C_{52}H_{80}Br_2O_2P_4Pt_2$: C, 44.26; H, 5.71. Found: C, 44.51; H, 5.94.

4b. Yield: 215 mg (yellow glassy solid), 90%. R_f = 0.56 (dichloromethane/methyl alcohol 500/1). Mp: 71−74 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52 (s, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.37−7.29 (m, 20H), 6.85 (s, 4H), 6.56 (s, 2H), 5.23 (s, 4H), 4.93 (s, 8H), 1.69−1.68 (m, 24H), 1.11−1.04 (m, 36H). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 12.68 (s, $^1J_{Pt-P}$ = 2762.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.1, 141.5, 130.5, 137.8, 136.9, 136.5, 129.4, 128.6, 128.0, 127.6, 124.5, 120.6, 106.8, 101.4, 74.8, 70.1, 14.3, 14.1, 14.0, 7.8. CSI-TOF-MS for $C_{80}H_{104}Br_2O_6P_4Pt_2Na$ [(M − Br)$^+$]: 1755.68. IR (neat) ν/cm^{-1}: 2962, 2931, 2907, 2872, 2353, 1672, 1594, 1452, 1374, 1151, 1033, 825, 764, 731, 697. Anal. Calcd for $C_{80}H_{104}Br_2O_6P_4Pt_2$: C, 52.35; H, 5.71. found: C, 52.69; H, 5.79.

4c. Yield: 265 mg (white glassy solid), 76%. R_f = 0.51 (dichloromethane/methyl alcohol 500/1). Mp: 46−51 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (s, 2H), 7.83 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.34−7.29 (m, 40H), 6.82 (s, 4H), 6.63 (s, 8H), 6.51 (s, 6H), 5.21 (s, 4H), 4.93 (s, 16H), 4.80 (s, 8H), 1.68 (br, 24H), 1.10−1.04 (m, 36H). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 12.48 (s, $^1J_{Pt-P}$ = 2729.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.1, 160.0, 141.5, 140.5, 139.3, 139.2, 136.7, 136.5, 129.3, 128.5, 128.3, 127.9, 127.7, 127.5, 124.5, 120.5, 106.7, 106.5, 106.4, 101.5, 101.4, 74.8, 70.0, 69.9, 14.3, 14.1, 13.9, 7.8, 7.7. CSI-TOF-MS for $C_{136}H_{152}BrO_{14}P_4Pt_2$ [(M − Br)$^+$]: 2603.86. IR (neat) ν/cm^{-1}: 2987, 2971, 2901, 2360, 1594, 1452, 1407, 1394, 1251, 1149, 1066, 1056, 892, 733, 697. Anal. Calcd for $C_{136}H_{152}Br_2O_{14}P_4Pt_2$: C, 60.85; H, 5.71. Found: C, 61.19; H, 5.93.

Synthesis of ***1a−c.*** A 50 mL round-bottom Schlenk flask was charged with 0.066 mmol of bromide complexes **4a−c** (for **4a**, 99 mg, 0.07 mmol; for **4b**, 128 mg, 0.07 mmol; for **4c**, 188 mg, 0.07 mmol) and 12 mL of dichloromethane. To the solution was added 56 mg (0.33 mmol) of $AgNO_3$ at once at room temperature, resulting in a yellowish precipitate of AgBr. After 24 h, the suspension was filtered through a glass fiber filter, and the filtrate was evaporated to dryness under reduced pressure. Through this experimental procedure, the yellow glassy solids were obtained as the desired products **1a−c**.

1a. Yield: 80 mg (yellow crystalline solid), 83%. Mp: 81−83 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.44 (s, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.60−7.55 (m, 6H), 7.43−7.34 (m, 6H), 5.26 (s, 4H), 1.3 (br, 24H), 1.20−1.12 (m, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.7, 137.8, 135.7, 128.5, 128.22, 128.17, 128.0, 125.1, 124.7, 124.6, 124.5, 120.8, 75.1, 12.9, 12.8, 12.6, 7.5. ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 12.27 (s, $^1J_{Pt-P}$ = 2888.3 Hz). CSI-TOF-MS for $C_{52}H_{80}NO_5P_4Pt_2$ [(M − NO_3)$^+$]: 1312.53. IR (neat) ν/cm^{-1}: 2924, 2855, 1608, 1575, 1454, 1378, 1276, 1152, 1085, 1034, 824, 765, 733, 700. Anal. Calcd for $C_{52}H_{80}N_2O_8P_4Pt_2$: C, 45.41; H, 5.86; N, 2.04. Found: C, 45.26; H, 5.96; N, 1.96.

1b. Yield: 101 mg (yellow glassy solid), 80%. Mp: 59−61 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.44 (s, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.37−7.33 (m, 20H), 6.82 (s, 4H), 6.56 (s, 2H), 5.20 (s, 4H), 4.92 (s, 8H), 1.54−1.52 (m, 24H), 1.17−1.13 (m, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.1, 141.5, 140.3, 136.7, 135.8, 128.6, 128.2, 128.0, 127.6, 124.9, 124.8, 120.7, 106.7, 101.3, 74.8, 70.0, 12.9, 12.8, 12.6, 7.8, 7.5. ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 19.29 (s, $^1J_{Pt-P}$ = 2870.5 Hz). CSI-TOF-MS for $C_{80}H_{104}NO_9P_4Pt_2$ [(M − NO_3)$^+$]: 1736.73. IR (neat) ν/cm^{-1}: 2960, 2925, 2871, 2736, 2353, 1670, 1595, 1453, 1378, 1262, 1152, 1084, 1035, 804, 765, 734, 698. Anal. Calcd for $C_{80}H_{104}N_2O_{12}P_4Pt_2$: C, 53.39; H, 5.82; N, 1.56. Found: C, 53.74; H, 6.05; N, 1.38.

1c. Yield: 265 mg (white glassy solid), 69%. Mp: 39−43 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.46 (s, 2H), 7.82 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.34−7.28 (m, 40H), 6.80 (s, 4H), 6.63 (s, 8H), 6.51 (s, 6H), 5.20 (s, 4H), 4.93 (d, J = 9.6 Hz, 16H), 4.80 (s, 8H), 1.52 (br, 24H), 1.15−1.13 (m, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.1, 160.0, 141.6, 140.2, 139.1, 136.7, 135.9, 128.5, 128.3, 128.2, 128.0, 127.5, 125.0, 120.7, 106.7, 106.5, 101.4, 74.8, 70.0, 69.9, 12.9, 12.8, 12.6, 7.8, 7.5. ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 19.00 (s, $^1J_{Pt-P}$ = 2888.3 Hz). CSI-TOF-MS for $C_{136}H_{152}NO_{17}P_4Pt_2$ [(M − $2NO_3$)$^{2+}$]: 1262.07. IR (neat) ν/cm^{-1}: 2964, 2928, 2875, 2736, 2352, 1669, 1596, 1452, 1378, 1277, 1154, 1084, 1036, 824, 765, 735, 699. Anal. Calcd for $C_{136}H_{152}N_2O_{20}P_4Pt_2{\cdot}H_2O$: C, 61.25; H, 5.82; N, 1.05. Found: C, 61.03; H, 5.97; N, 1.17.

General Procedure for the Preparation of Supramolecular Triangular Metallodendrimers ***6a−c.*** 4.5 mL mixed solvents of acetone and H_2O (v/v 6/1) were added to a mixture of nitrate salts **1a−c** (for **1a**, 17.7 mg, 0.0129 mmol; for **1b**, 23.1 mg, 0.0129 mmol; for **1c**, 34.1 mg, 0.0129 mmol) and the appropriate donor building block 4,4′-bipyridyl (2.01 mg, 0.0129 mmol). The reaction mixture was then stirred for 14 h at 55−60 °C, upon which starting materials were completely dissolved and the reaction mixture attained a yellow color. The PF_6^- salt of **6a−c** was synthesized by dissolving the yellow NO_3^- salt **6a−c** in acetone/H_2O and adding a saturated aqueous solution of KPF_6 to precipitate the product, which was collected by vacuum filtration.

6a. Yield: 19.1 mg (yellow solid), 97%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.38 (d, J = 5.2 Hz, 6H), 8.89 (d, J = 4.8 Hz, 6H), 8.80 (s, 6H), 8.44 (d, J = 5.2 Hz, 6H), 8.29 (d, J = 5.6 Hz, 6H), 7.97 (d, J = 8.0 Hz, 6H), 7.61−7.59 (m, 18H), 7.46−7.39 (m, 18H), 5.33 (s, 12H), 1.38 (br, 72H), 1.18−1.13 (m, 108H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.0, 152.9, 144.6, 141.9, 137.8, 135.2, 129.3, 128.5, 128.3, 128.1, 126.0, 125.4, 124.4, 121.1, 75.2, 13.0, 12.8, 12.6, 7.6. ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 11.82 (s, $^1J_{Pt-P}$ = 2700.5 Hz). CSI-TOF-MS, $[M - 2PF_6]^{2+}$, 2401.53; $[M - 3PF_6]^{3+}$, 1552.82. Anal. Calcd for

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$C_{186}H_{264}F_{36}O_6N_6P_{18}Pt_6$: C, 43.87; H, 5.23; N, 1.65. found: C, 43.87; H, 5.38; N, 1.66.

6b. Yield: 23.9 mg (yellow solid), 95%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.42 (d, J = 5.4 Hz, 6H), 8.89 (d, J = 5.4 Hz, 6H), 8.84 (s, 6H), 8.45 (d, J = 5.7 Hz, 6H), 8.25 (d, J = 5.7 Hz, 6H), 7.96 (d, J = 8.1 Hz, 6H), 7.59 (d, J = 8.4 Hz, 6H), 7.40−7.33 (m, 60H), 6.85 (s, 12H), 6.60 (s, 6H), 5.27 (s, 12H), 4.96 (s, 24H), 1.37 (m, 72H), 1.18−1.08 (m, 108H). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 11.81 (s, $^1J_{Pt-P}$ = 2718.1 Hz). CSI-TOF-MS, $[M - 3PF_6]^{3+}$, 1977.07; $[M - 4PF_6]^{4+}$, 1446.81. Anal. Calcd for $C_{270}H_{336}F_{36}O_{18}N_6P_{18}Pt_6$: C, 50.94; H, 5.32; N, 1.32. Found: C, 50.92; H, 5.49; N, 1.12.

6c. Yield: 33.6 mg (yellow solid), 93%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.41 (br, 6H), 8.88−8.84 (m, 12H), 8.45 (d, J = 4.0 Hz, 6H), 8.28 (br, 6H), 8.00 (d, J = 7.6 Hz, 6H), 7.61 (d, J = 8.0 Hz, 6H), 7.36−7.30 (m, 120H), 6.83 (s, 12H), 6.66 (s, 24H), 6.54 (s, 18H), 5.26 (s, 12H), 4.96 (s, 48H), 4.84 (s, 24H), 1.38−1.36 (m, 72H). 1.15−1.11 (m, 108H). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 11.89 (s, $^1J_{Pt-P}$ = 2703.7 Hz). CSI-TOF-MS, $[M - 4PF_6]^{4+}$, 2083.19.

■ ASSOCIATED CONTENT

Supporting Information

Crystal data and structure of **4a**, characterization of the compounds **3a−c**, **4a−c**, and **1a−c**, ^{1}H and ^{31}P NMR spectra of **6a−c**, and ^{1}H DOSY NMR spectra of **6a−c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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