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Design and Synthesis of 60° Dendritic Donor Ligands and Their Coordination-Driven Self-Assembly into Supramolecular Rhomboidal Metallodendrimers

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Supporting Information

ABSTRACT: The design and self-assembly of novel rhomboidal metallodendrimers via coordination-driven self-assembly is described. By employing newly designed 60° ditopic donor linkers substituted with Fréchet-type dendrons and appropriate 120° rigid di-Pt(II) acceptor subunits, a variety of [G-1]−[G-3] rhomboidal metallodendrimers with well-defined shape and size were prepared under mild conditions in high yields. The supramolecular metallodendrimers were characterized with multinuclear NMR (^{1}H and ^{31}P), mass spectrometry (CSI-TOF-MS), and elemental analysis. Isotopically resolved mass spectrometry data support the existence of the metallodendrimers with rhomboidal cavities, and NMR data were consistent with the formation of all ensembles. The shape and size of all rhomboidal metallodendrimers were investigated with the PM6 semiempirical molecular orbital method.

INTRODUCTION

The self-assembly of delicate supramolecular architectures via noncovalent interactions has evolved to be one of the most attractive subjects within modern chemistry.[1] Generally, noncovalent interactions, such as hydrogen bonding, charge−charge, donor−acceptor, π−π, van der Waals, etc., play essential roles during the process of supramolecular self-assembly. The highly efficient formation of noncovalent bonds often offers considerable synthetic advantages like few steps as well as fast and facile construction of the final products. Over the past few decades, synthetic chemists have developed various means of achieving abiological self-assembly that have both furthered our understanding of the self-assembly process itself and also opened the door to a variety of complicated supramolecular structures.[2]

A particularly powerful method for self-assembling large, rigid metal−organic frameworks with well-defined shapes, sizes, and geometries is the directional-bonding approach provided by coordination-driven self-assembly.[3] By using a directional-bonding coordination-driven approach, a wide variety of discrete two-dimensional (2D) and three-dimensional (3D) supramolecular polygons and polyhedra have been constructed.[4] Included among the 2D species is an array of squares, rectangles, rhomboids, triangles, and hexagons as well as polygons of higher symmetry.[5] However, many of the ensembles prepared to date were built from simple, fairly inert building blocks that are often aliphatic or aromatic in nature. Therefore, many examples of self-assembled metallacycles are, for the most part, unfunctionalized. Stimulated by the possibility of constructing functional nanoscale devices with predesigned shapes and sizes, recent efforts have focused on incorporating functionality into the final discrete assemblies. Recently, an *exo-functionlization* approach has been developed to prepare functionalized supramolecular assemblies with well-defined shape, size, and symmetry through coordination-driven self-assembly.[6] This strategy allows for precise control over the shape and size of the final construction as well as the distribution and total number of incorporated functional moieties. Up to date, this approach has been utilized to prepare, for example, discrete supramolecular metal−organic assemblies functionalized with crown ether,[7] ferrocene,[8] and hydrophobic and hydrophilic units[9] that have been distributed within building blocks.

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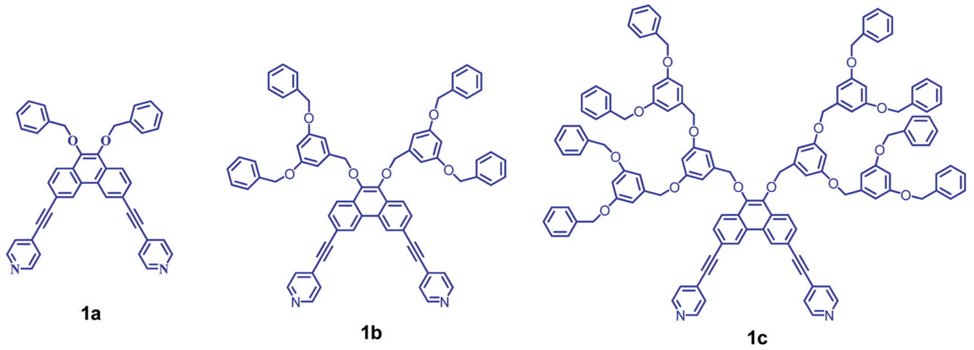


Figure 1. Molecular structures of 60° dendritic donor subunits **1a**−**c**.

Dendrimers are highly branched macromolecules composed of several dendritic wedges that extend outward from an internal core.[10] In the past few decades, the design and synthesis of diverse dendrimers has evolved to be one of the most important subjects within modern chemistry not only because of their aesthetically pleasing structures but also as a result of their various applications in catalysis, light-harvesting, and sensing.[11] Since the pioneering work by Newkome et al.[12] and Balzani et al.[13] in the early 1990s, metallodendrimers[14] have received considerable attention because of their potential application in catalysis,[15] biological mimetics,[16] and photo- and electrochemistry.[17] Particularly, dendritic metallacycles[18] are of interest because of their potential application[19] in the recognition and delivery of guests incorporated within their cavities. For instance, 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.[18a] Moreover, by combining predesigned 120° angular dendritic organic donors with 180° di-Pt(II) acceptors, "snowflake-shaped" [6 + 6] metallodendrimers were prepared via coordination-driven self-assembly.[18e] Very recently, a family of new metallodendritic squares has been synthesized from 4,4′-bipyridines functionalized with Fréchet dendrons and (dppp)Pt(II) or Pd(II) triflate by Schalley's group.[18g] However, the precise control of the size and the shape of the metallodendrimers remains a challenge.

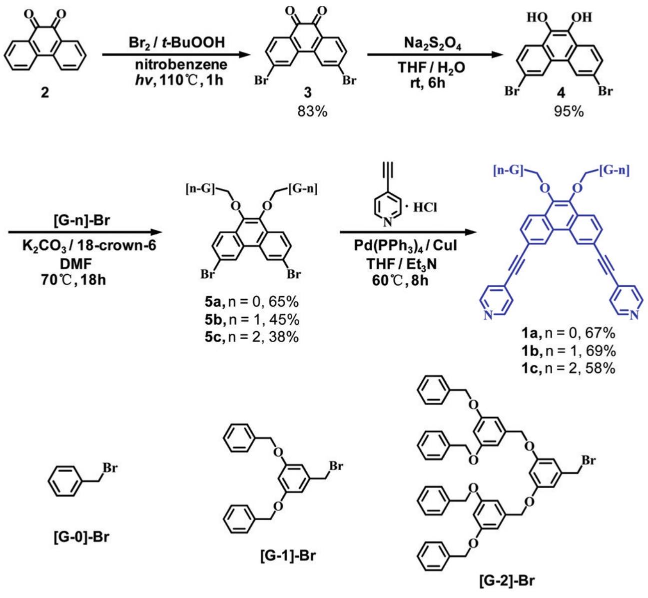
In the previous research, we have synthesized a series of 120° di-Pt(II) acceptors and 120° dipyridine donors, both substituted with Fréchet-type dendrons, from which a wide range of hexagonal dendritic metallacycles have been prepared.[18c−f] However, compared to many reports on the construction of hexagonal metallodendrimers via *exo-function-unctionalized* strategy, the synthesis of dendritic metallacycles with rhomboidal cavities is relatively few.[18c] Encouraged by the power and versatility of *exo*-functionalized strategy, we envisioned that the construction of rhomboidal 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 distribution and total number of incorporated dendron moieties 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 inspired functionality arising from their unique interior cavities and dendritic exteriors.

With the aim of developing new self-assembly of rhomboidal metallodendrimers, a family of new 60° dendritic donor ligands (Figure 1) were synthesized and used to build three different series of metallodendrimers with rhomboidal cavities. For example, the combination of newly designed 60° dendritic donors with the complementary 120° di-Pt(II) acceptor could yield "two-component" metallodendrimers. Similarly, when 120° dendritic di-Pt(II) acceptor was employed, four-component rhomboidal metallodendrimers were formed. It is noted that a new family of dendritic bisferrocenyl rhomboids were prepared through this strategy when 120° ferrocenyl di-Pt(II) acceptor was used as a complementary building block. All newly designed dendritic rhomboids were characterized with multinuclear NMR (^{1}H and ^{31}P), mass spectrometry (CSI-TOF-MS), and elemental analysis.

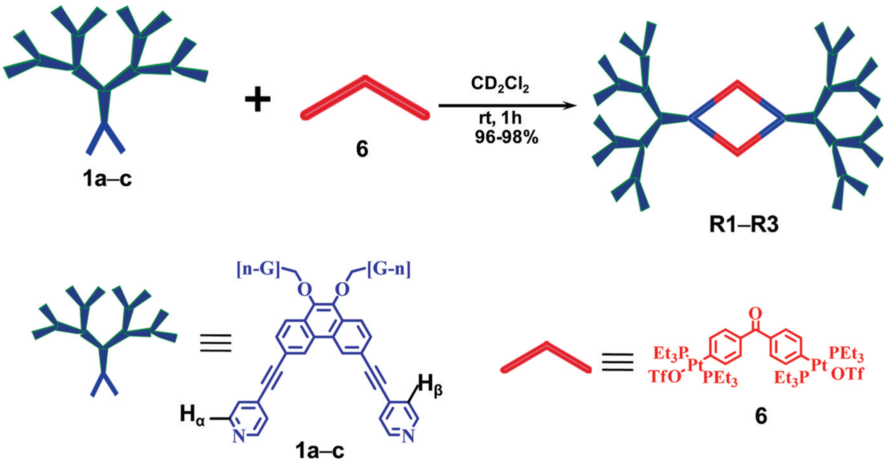
RESULTS AND DISCUSSION

Synthesis of the 60° Dendritic Donor Ligands. Substituted and heterocyclic aromatic compounds have proven useful as rigid building blocks in self-assembly.[20] For example, we selected 2,9-dibromophenanthrene as the scaffold for the synthesis of 60° di-Pt(II) acceptors, which has been successfully employed in the self-assembly M_3L_2 trigonal-bipyramidal (TBP) cages.[21] Herein, we chose phenanthrene-9,10-dione (**2**) as starting material to prepare the desired 60° dendritic donor tectons as shown in Scheme 1. 3,6-Dibromophenan-

Scheme 1. Synthesis of 60° Dendritic Donor Subunits 1a−c



Scheme 2. Schematic and Molecular Structures of 60° Dendritic Donor (1a−c) and Acceptor (6) Building Blocks and Their Self-Assembly into [2 + 2] Rhomboidal Metallodendrimers R1−R3



threne-9,10-diol (4) was synthesized in two steps according to the similar procedures reported previously in the literature.[22] Then Fréchet-type dendrons were introduced by an etherification reaction of **4** with corresponding dendritic bromides. From dendritic 3,6-dibromophenanthrene derivatives **5a−c**, the desired 60° dendritic donor building blocks **1a−c** were obtained by the coupling reaction with 4-ethynlpyridine in satisfactory yields in the presence of $Pd(PPh_3)_4$ and CuI as catalysts.

Self-Assembly of "Two-Component" Rhomboidal Metallodendrimers. According to the "directional bonding" model and the "symmetry interaction" model, the shape of an individual 2D polygon is usually determined by the value of the turning angle within its angular components.[3a,c] For example, the combination of 60° units with complementary 120° linking components will yield a molecular rhomboid.[23] With the newly designed 60° dendritic pyridyl precursors **1a−c** in hand, the self-assembly of two-component rhomboidal metallodendrimers was investigated. Upon mixing [G-1]−[G-3] 60° donors **1a−c** and the 120° di-Pt(II) acceptors **6** in dichloromethane, two-component metallodendritic rhomboids **R1−R3** were obtained, respectively (Scheme 2).

The self-assembly of two-component dendritic rhomboids **R1−R3** was monitored by multinuclear NMR spectroscopy. Analysis of the ^{31}P NMR spectrum (Figure 2 and Supporting Information) of each reaction solution is consistent with the formation of highly symmetric species by the appearance of a sharp singlet at ca. 13.5 ppm, shifted by ca. 6.1 ppm upfield relative to the position of the phosphorus signal of starting acceptor unit **6**. This change, as well as the decrease in coupling of the flanking ^{195}Pt satellites (ca. $\Delta {}^1J_{PPt} = -130$ Hz), is consistent with electron back-donation from the platinum atoms. Examination of the ^1H NMR spectra (Figure 3 and Supporting Information) also indicates the existence of highly symmetric structures. The ^1H NMR spectra display significant downfield shifts of the pyridyl proton signals (for α proton, ca. $\Delta\delta = 0.06$ ppm; for β proton, ca. $\Delta\delta = 0.44$ ppm) associated with the loss of electron density on coordination by the nitrogen lone pair to platinum metal centers. Notably, two doublets are usually observed for α-hydrogen nuclei on pyridine rings in the ^1H NMR spectrum of supramolecular rhomboids, and this might be attributed to the hindered rotation about the Pt−N(pyridyl) bond that has been reported previously.[18e] On the contrary, the ^1H NMR spectra of **R1−R3** showed only one doublet for the α-H protons that may be due to free rotation of the Pt−N(pyridyl) bond in these rhomboidal dendrimers, which have a larger sized metallacycle. The sharp NMR signals in both the ^{31}P and ^1H NMR spectra along with the solubility of these species ruled out the formation of oligomers.

Mass spectrometric studies of all three rhomboids were performed using the cold-spray ionization (CSI)-TOF-MS technique, which allows the assemblies to remain intact during the ionization process while obtaining the high resolution required for isotopic distribution. In the CSI-TOF-MS spectrum of [G-0] rhomboid **R1** (Figure 4), for example, peaks attributable to the loss of nitrate counterions, $[M - 2OTf]^{2+}$ ($m/z = 1784.8$), $[M - 3OTf]^{3+}$ ($m/z = 1140.5$), and $[M - 4OTf]^{4+}$ ($m/z = 817.9$), where M represents the intact assembly, were observed, and their isotopic resolution is in excellent agreement with the theoretical distribution. Similarly, the CSI-TOF-MS spectra of [G-2] and [G-3] rhomboidal metallodendrimers **R2** and **R3** (Figure 4B,C) exhibited two charged states at $m/z = 1423.1$ and $m/z = 1030.0$ for **R2**, corresponding to $[M - 3OTf]^{3+}$ and $[M - 4OTf]^{4+}$, and $m/z = 1989.3$ and $m/z = 1454.7$ for **R3**, related to $[M - 3OTf]^{3+}$ and $[M - 4NO_3]^{4+}$, respectively. These peaks were isotopically resolved, and they agree very well with their theoretical distribution.

Self-Assembly of "Four-Component" Rhomboidal Metallodendrimers. Stirring the 60° [G-1] dendritic donor building block **1a** with an equimolar amount of [G-1] dendritic di-Pt(II) acceptors **7a** in a mixed solvents of CD_2Cl_2 and acetone-d_6 (v/v 2/1) for 12 h resulted in the formation of [G-1] "four-component" rhomboidal metallodendrimers **R4**. A similar procedure was carried out for the self-assembly of [G-2] and [G-3] rhomboidal metallodendrimers **R5** (**1b** + **7b**) and **R6** (**1c** + **7c**), respectively (Scheme 3). Multinuclear NMR (^1H and ^{31}P) analysis of [G-1]−[G-3] assemblies **R4−R6** exhibited very similar characteristics, which all suggested the formation of discrete, highly symmetric metallodendrimers with rhomboidal cavities. The ^{31}P {^1H} NMR spectra of the [G-1]−[G-3] assemblies **R4−R6** displayed a sharp singlet (ca. 16.3 ppm) shifted upfield from the starting platinum acceptors **7a−c** by ~4.3 ppm (Figure 2 and Supporting Information). In addition, the decrease in coupling of the flanking ^{195}Pt satellites (ca. $\Delta {}^1J_{PPt} = -158$ Hz) was found, which is consistent with back-donation from the platinum atoms. In the ^1H NMR spectrum of each assembly (Figure 3 and Supporting Information), the α-

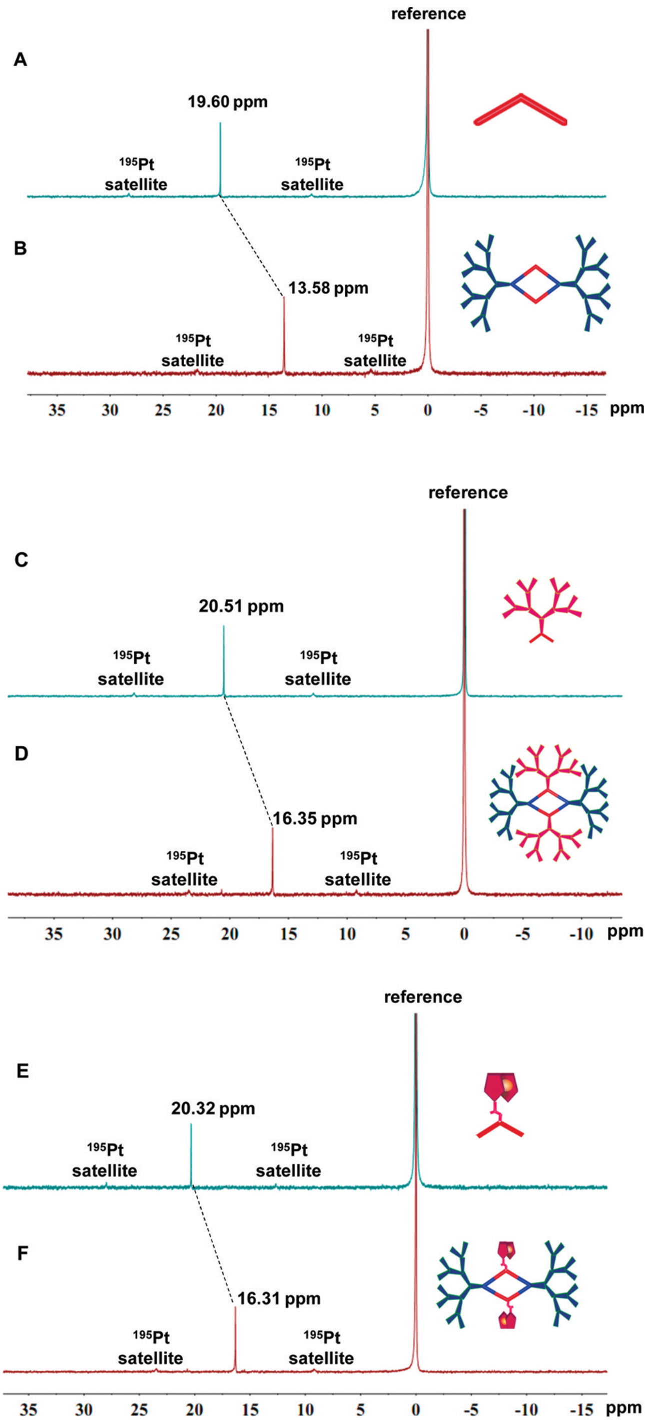


Figure 2. Partial $^{31}P\{^{1}H\}$ NMR (400 MHz, CD_2Cl_2, 298 K) spectra of 120° di-Pt(II) acceptors **6** (A), **7** (C), and **8** (D) and [G-3] self-assembled rhomboidal metallodendrimers **R3** (B), **R6** (D), and **R9** (F).

hydrogen nuclei of the pyridine rings exhibited about 0.02 ppm downfield shifts and the β-hydrogen nuclei showed about 0.45 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. Similar to the observation in the ^{1}H NMR spectra of **R1**−**R3**, one doublet for the α-H protons was found in the ^{1}H NMR spectra of **R4**−**R6**.

Compared to the previous "two-component" rhomboidal metallodendrimers **R1**−**R3**, it has proven more difficult to get strong mass signals for "four-component" rhomboidal metallodendrimers **R4**−**R6**, on account of their larger molecular weight, even under the CSI-TOF-MS conditions. [G-3] four-component metallodendrimer **R6**, as a representative example, has a molecular weight of 9159 Da ($C_{530}H_{504}N_8O_{72}P_8Pt_4$). With considerable effort, the peaks attributable to $[M - 3NO_3]^{3+}$ (m/z = 1295.2) and $[M - 4NO_3]^{4+}$ (m/z = 955.9) were observed for [G-1] metallodendrimer **R4** in the CSI-TOF-MS spectrum along with isotopically resolved peaks (i.e., direct charge state determination), allowing for the molecularity of the four-component rhomboidal metallodendrimer to be unambiguously established (Figure 5A). Moreover, the CSI-TOF-MS spectrum of [G-2] rhomboidal metallodendrimer **R5** exhibited one charged state at m/z = 1380.3 corresponding to $[M - 4NO_3]^{4+}$. This peak was isotopically resolved, and it agrees well with its theoretical distribution (Figure 5B). For [G-3] assembly **R6**, a peak at m/z = 2229.6 corresponding to $[M - 4NO_3]^{4+}$ was observed in the CSI-TOF-MS spectrum; however, the peak could not be isotopically resolved because of the high molecular weight of assembly **R6** (see Supporting Information).

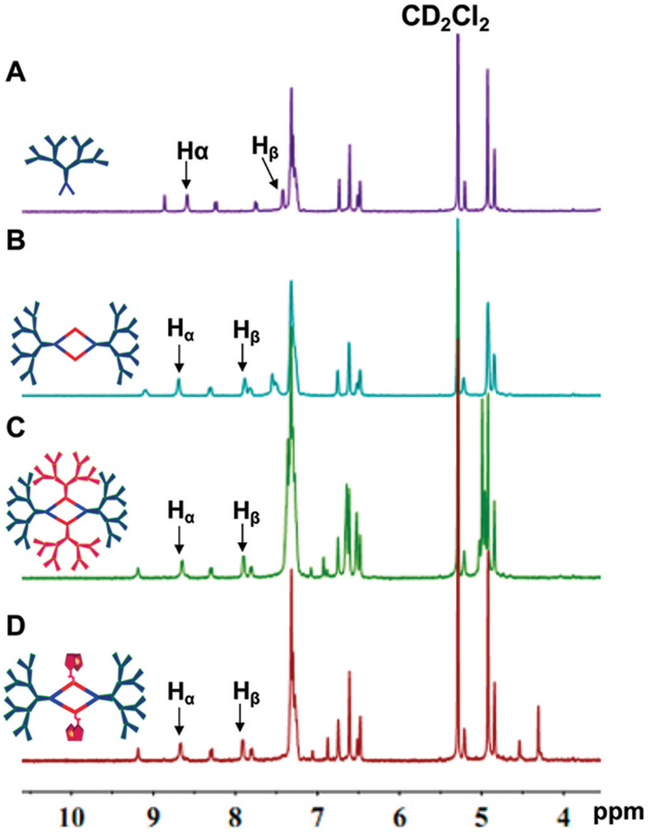


Figure 3. Partial ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectra of [G-3] 60° dendritic donor building block **1c** (A), [G-3] "two-component" metallodendrimer **R3** (B), [G-3] "four-component" rhomboidal metallodendrimer **R6** (C), and [G-3] rhomboidal bisferrocenyl metallodendrimer **R9** (D).

Self-Assembly of Dendritic Bisferrocenyl Rhomboids. Ferrocene has been widely utilized in multifunctional systems because of a variety of materials and synthetic applications.[24] Recently, multiferrocenyl structures have received considerable attention due to their potential applications in photochemical sensors and information storage.[25] For example, we have reported the self-assembly of

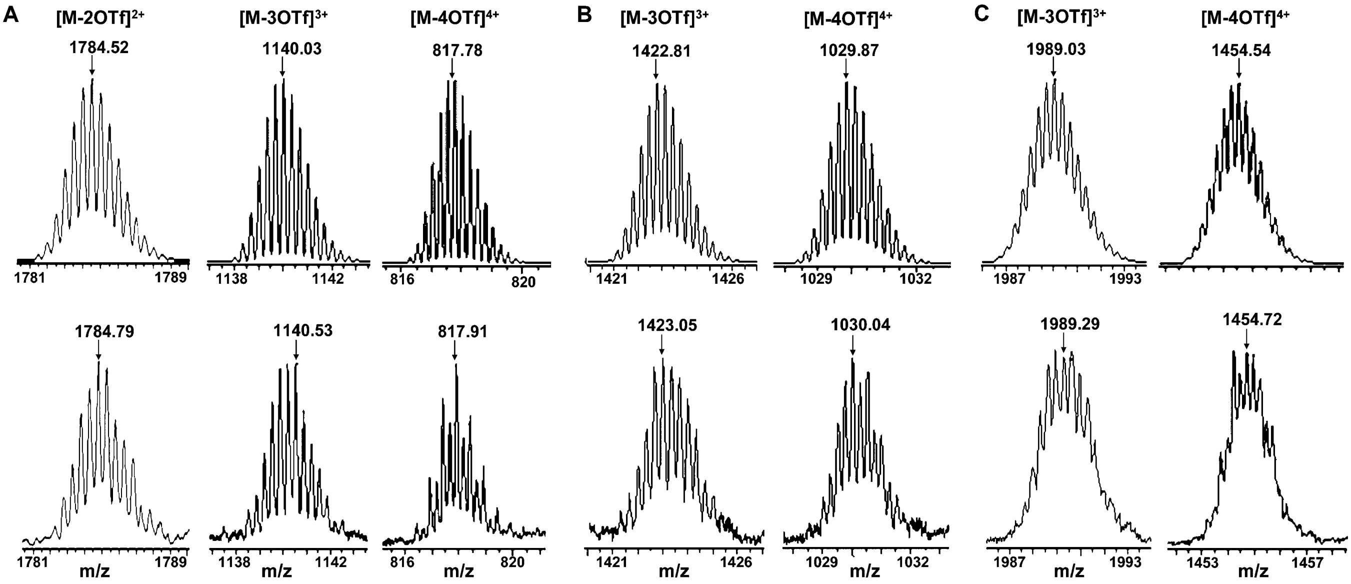
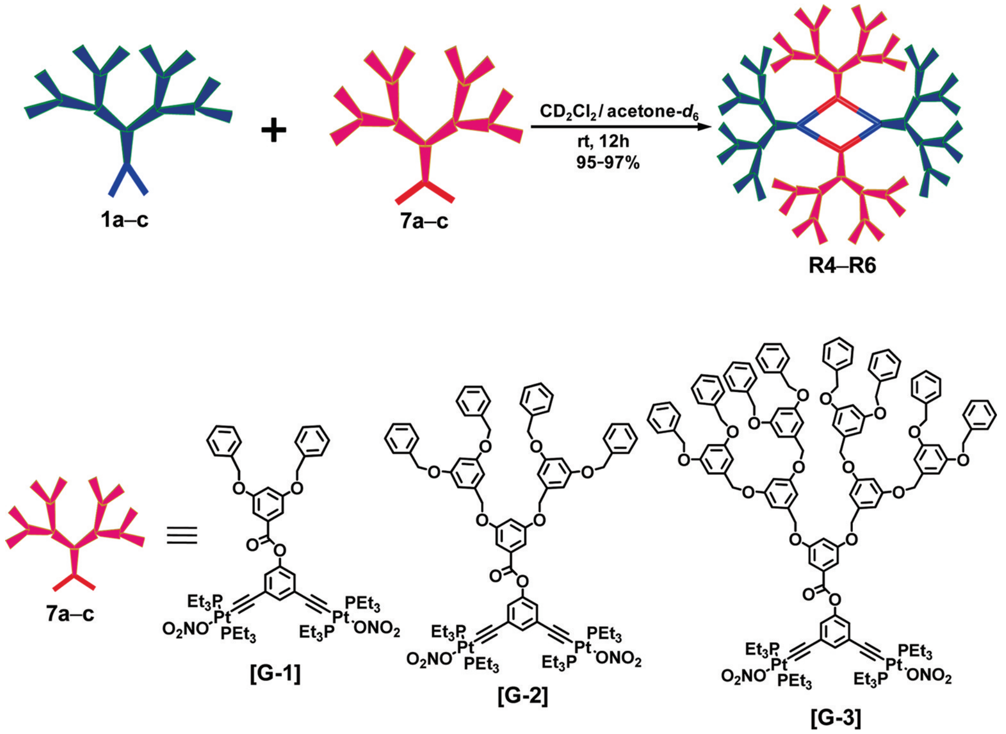


Figure 4. Theoretical (top) and experimental (bottom) CSI-TOF-MS spectra of [G-1]−[G-3] "two-component" metallodendrimers **R1** (A), **R2** (B), and **R3** (C).

Scheme 3. Self-Assembly of [G-1]−[G-3] "Four-Component" Rhomboidal Metallodendrimers R4−R6



a class of new dendritic multiferrocenyl hexagons via [3 + 3] coordination-driven self-assembly.[8b] Herein we extended the investigations to the construction of dendritic bisferrocenyl rhomboids. The self-assembly of 60° dendritic pyridine donors **1a−c** with 120° ferrocenyl acceptor **8** (Scheme 4) was investigated in dichloromethane, leading to the formation of [G-1]−[G-3] rhomboidal bisferrocenyl metallodendrimers **R7−R9**, respectively. After 12 h of continuous stirring at room temperature, initial visual evidence of the completion of self-assembly processes was indicated by the complete dissolution of starting materials and formation of a homogeneous yellow solution. More quantitative evidence of successful self-assembly is then obtained from characteristic changes observed in each NMR spectrum of assembly. In all three cases, the analysis of ^{31}P NMR spectra of the reaction solution is consistent with the formation of highly symmetric species as indicated by the appearance of one sharp singlet (ca. 16.2 ppm) with concomitant ^{195}Pt satellites shifted upfield (ca. $\Delta\delta = -4.0$ ppm) from the starting platinum acceptor **8** (Figure 2 and Supporting Information). As expected, a decrease in coupling of the flanking ^{195}Pt signals (ca. $\Delta\,^1J_{\mathrm{PPt}} = -178$ Hz) was also observed. Examination of the ^{1}H NMR spectrum (Figure 3 and Supporting Information) of each assembly is also indicative of highly symmetric structures. Only one set of peaks in the final

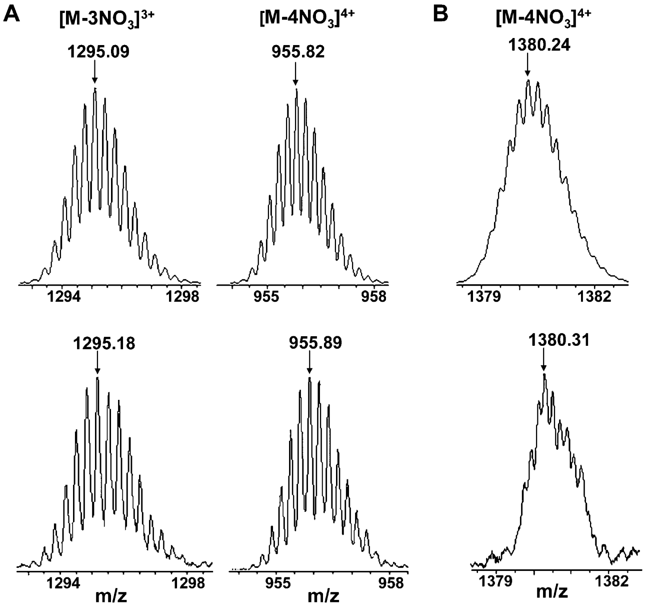
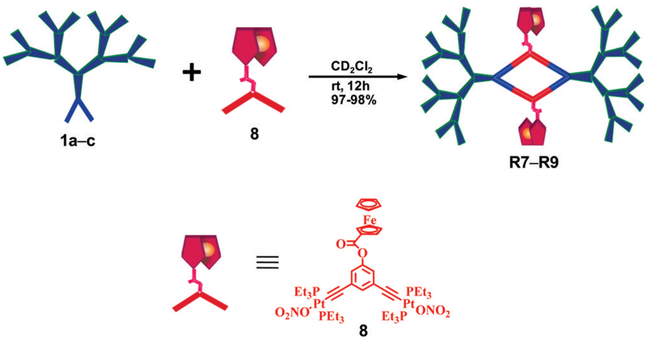


Figure 5. Theoretical (top) and experimental (bottom) CSI-TOF-MS spectra of [G-1] and [G-2] "four-component" rhomboidal metallodendrimers **R4** (A) and **R5** (B).

Scheme 4. Self-Assembly of [G-1]−[G-3] Bisferrocenyl Rhomboidal Metallodendrimers R7−R9



self-assembly arising from donor and acceptor units and significant downfield shifts of the pyridyl proton signals (for α proton, ca. $\Delta\delta = 0.03$ ppm; for β proton, ca. $\Delta\delta = 0.46$ ppm) associated with the loss of electron density on coordination by the nitrogen lone pair to the platinum metal center support the efficient self-assembly of dendritic bisferrocenyl rhomboids **R7−R9**.

The structures of the rhomboidal bisferrocenyl metallodendrimers **R7−R9** have also been confirmed by mass spectrometry (CSI-TOF-MS) (Figure 6). In the CSI-TOF-MS spectra of the [G-1] and [G-2] assemblies **R7** and **R8**, peaks attributable to the loss of nitrate counterions, $[M - 3NO_3]^{3+}$ (m/z = 1225.8 for **R7**; m/z = 1508.9 for **R8**) and $[M - 4NO_3]^{4+}$ (m/z = 904.1 for **R7**; m/z = 1116.2 for **R8**), where M represents the intact assemblies, were observed. These peaks were isotopically resolved, and they agree very well with their respective theoretical distribution (Figure 6A,B). The CSI-TOF-MS spectrum of the [G-3] rhomboidal metallodendrimer **R9** showed one charged state at m/z = 1540.6, corresponding to the $[M - 4NO_3]^{4+}$ species, and its isotopic resolution is in good agreement with the theoretical distribution (Figure 6C).

Cyclic voltammetry (CV) investigation of dendritic bisferrocenyl rhomboids **R7−R9** was performed in dichloromethane solution containing 0.2 M n-Bu_4NPF_6 as the supporting electrolyte at a ~7.0 mm^2 Pt disk electrode. The cyclic voltammograms corresponding to the one-electron oxidation of the ferrocene groups yielded anodic/cathodic peak current ratios of $i_a/i_c \approx 1$ (see Supporting Information). In addition, the nearly identical cathodic and anodic peak currents, as well as nearly scan-rate-independent peak potentials, indicate the oxidation of the ferrocene moieties in each assembly is chemically reversible. The difference between the anodic and cathodic peak potentials (ΔE_p) measured at different scan rates was found to be larger than the theoretical value of 59 mV expected for a reversible one-electron redox reaction, a consequence of the solution ohmic resistance. With the aim to obtaining the effects of dendron subunits in the electrochemical properties of ferrocenes, the further investigation of cyclic voltammetry of these complexes **R7−R9** was carried out. Different from our previous reports,[8b] the D values obtained via CV investigation did not change dramatically with the increase of the molecular weight and molecular size in this study. These results indicated that the dendron moieties are located far from the electrochemical active centers and do not influence the electrochemical activity of ferrocenyl groups. Moreover, two-dimensional diffusion-ordered NMR (DOSY) experiments were employed to characterize the structures of dendritic bisferrocenyl rhomboids **R7−R9** by determination of the diffusion coefficient (D). The ^{1}H DOSY NMR measurements for assemblies **R7−R9** in CD_2Cl_2 were carried out under the similar conditions (292.5 K, 3.38×10^{-3} mol/L) (see Supporting Information). It was found that the D values decrease gradually with the increase of the molecular weight, which is in good agreement with the previous report.[8b] This result is indicative of that the ^{1}H DOSY NMR might be a more suitable way to gain further insight into the structural characteristics in this system. The value of diffusion coefficient (D) for each complex was obtained as summarized in Table 1.

All attempts to grow X-ray quality single crystals of the rhomboidal metallodendrimers **R1−R9** have so far proven unsuccessful. Therefore, the PM6 semiempirical molecular orbital method was employed to gain further insight into the structural characteristics of these assemblies (Figure 7 and Supporting Information). At the molecular level, all structures feature a well-defined rhombus with different sized cavity. For example, 2.9 × 2.1 nm for **R3**, 2.7 × 1.7 nm for **R6**, and 2.8 × 1.6 nm for **R9** were found in the optimized structures. Moreover, simulations reveal that the underlying rhomboidal structures—"scaffolds"—all retain their planar and rigid structures even when derivatized with dendrons and/or ferrocene units. In all the cases the flexible nature of the pendent dendron moieties and the rigid nature of the rhomboidal cavity can be observed from modeling studies. Notably, in the case of **R7−R9**, simulation provides the unambiguous support for the fact that the dendritic moieties are far from ferrocenes and do not disturb the electrochemical activity of ferrocenyl groups.

■ CONCLUSION

A series of new 60° dendritic donor ligands from phenanthrene-9,10-dione were prepared in reasonable yields. By utilizing these novel dendritic substrates as ditopic donor subunits, a family of novel rhomboidal metallodendrimers was formed via coordination-driven self-assembly. The work presented here provides a very simple yet effective approach to the construction of various well-defined metallodendrimers

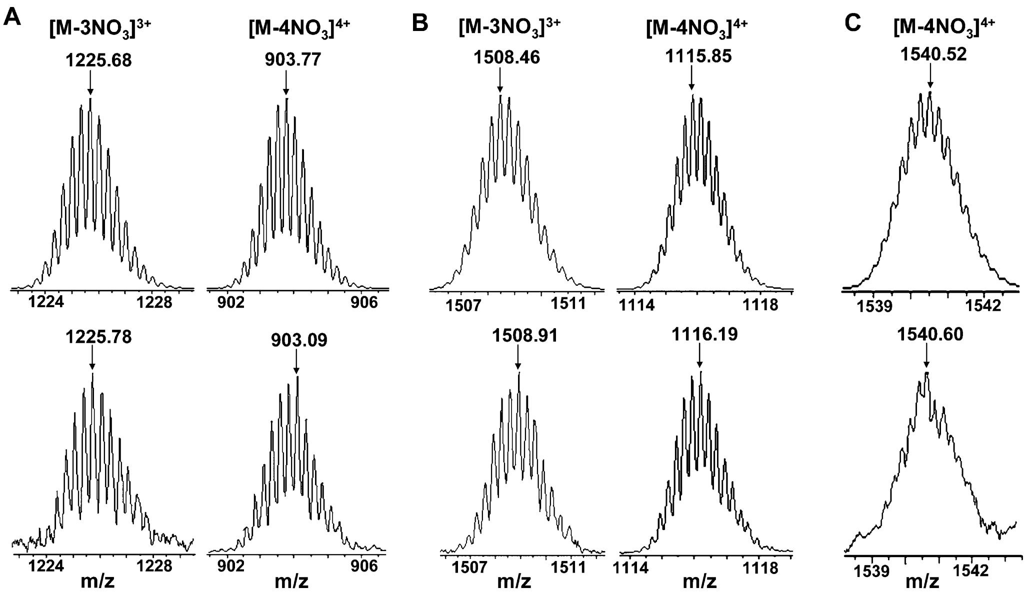


Figure 6. Theoretical (top) and experimental (bottom) CSI-TOF-MS spectra of [G-1]−[G-3] bisferrocenyl rhomboidal metallodendrimers **R7** (A), **R8** (B), and **R9** (C).

Table 1. Cyclic Voltammetry Data for complexes R7−R9 (CH_2Cl_2 with 0.2 M *n*-Bu_4NPF_6, 298 K) and Diffusion Coefficient (*D*) for Complexes R7−R9 Obtained from CV Investigation and ^{1}H DOSY NMR Spectroscopy (500 MHz, CD_2Cl_2, 292.5 K)

compd	$E_{1/2}$ (V vs SCE)	$10^{-5}D^a$ (cm^2 s^{-1})	$10^{-5}D^b$ (cm^2 s^{-1})
R7	0.757 ± 0.001	0.570 ± 0.02	0.3784
R8	0.739 ± 0.002	0.540 ± 0.01	0.3141
R9	0.760 ± 0.001	0.530 ± 0.01	0.2253

[a]Obtained from CV investigation. [b]Obtained from ^{1}H DOSY NMR spectroscopy.

possessing rhomboidal cavities. Multinuclear NMR (^{1}H and ^{31}P) analysis of all assemblies exhibited very similar characteristics that are suggestive of the formation of discrete, highly symmetric species. The sharp NMR signals in both the ^{31}P and ^{1}H NMR along with the solubility of these species ruled out the formation of oligomers. The structures of all metallodendrimers were further established by mass spectrometry (CSI-TOF-MS) and elemental analysis. Hence, we have demonstrated that highly convergent synthetic protocols based on the simultaneous assembly of appropriate predetermined building block allow the rapid construction of novel rhomboidal metallodendrimers. In particular, this approach is capable of preparing a variety of metallodendrimers with different functional substitutions through the proper choice of subunits with predefined angles and symmetry, which enriches the library of supramolecular metallodendrimers.

■ EXPERIMENTAL SECTION

All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Precursors **3**,[22] **4**,[22] **6**,[18f] **7**,[18d] and **8**[8b] were prepared according to the literature procedures. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Triethylamine (Et_3N) was dried from potassium hydroxide. Both of THF and Et_3N were degassed by nitrogen (N_2) for 30 min before use. 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

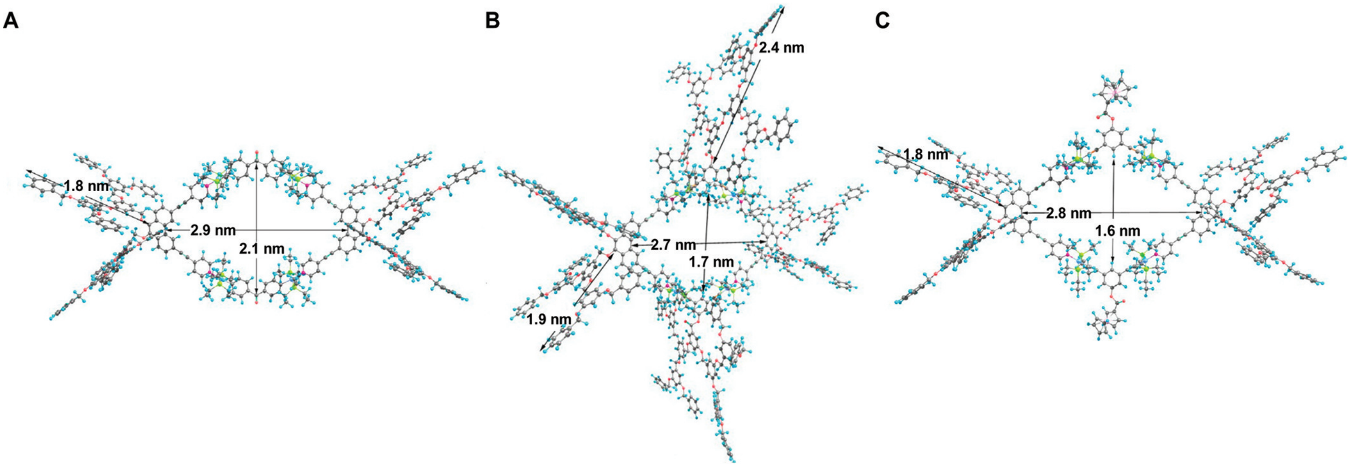


Figure 7. Simulated molecular model of rhomboidal metallodendrimers **R3** (A), **R6** (B), and **R9** (C).

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.

General Procedure for the Synthesis of 5a−c. Under an atmosphere of nitrogen, **4** (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 mixed in DMF (25 mL). The mixture was heated at reflux for 18 h and then cooled down to room temperature. Solvent was distilled, and the resulted mixture was poured into water and extracted with methylene chloride (15 mL × 3). The organic phase 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 **5a−c**.

5a. Yield 0.58 g (white solid), 65%. R_f = 0.74 (dichloromethane/petroleum ether 1/1); mp 192 °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. HR MALDI-MS for $C_{28}H_{20}Br_2O_2Na$ $[(M + Na)^{+}]$: 571.00.

5b. Yield 0.92 g (white glassy solid), 45%. R_f = 0.50 (dichloromethane/petroleum ether 3/1); mp 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. HR MALDI-MS for $C_{56}H_{44}Br_2O_6Na$ $[(M + Na)^{+}]$: 995.10.

5c. Yield 1.45 g (white glassy solid), 38%. R_f = 0.36 (dichloromethane/petroleum ether 4/1); mp 46 °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. HR MALDI-MS for $C_{112}H_{92}Br_2O_{14}Na$ $[(M + Na)^{+}]$: 1843.60.

General Procedure for the Synthesis of 1a−c. Under an atmosphere of nitrogen, 6.0 mL of THF and 3.0 mL of Et_3N were added to a mixture of 4-ethynylpyridine hydrochloride (105 mg, 0.75 mmol), compounds **4a−c** (**4a**, 110 mg, 0.25 mmol; **4b**, 216 mg, 0.25 mmol; **4c**, 429 mg, 0.25 mmol), CuI (4.8 mg, 0.025 mmol), and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol). The mixture was stirred at 60 °C for 8 h. Then the solvents were removed in vacuo, and the residue was purified by column chromatography on silica gel (dichloromethane/acetone: ∼3/1) to give **1a−c**.

1a. Yield 92 mg (pale yellow solid), 62%. R_f = 0.33 (dichloromethane/acetone 3:1); mp 175 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.87 (s, 2H), 8.66 (s, 4H), 8.26 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.54−7.53 (m, 4H), 7.47 (s, 4H), 7.42−7.40 (m, 6H), 5.32 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.8, 144.2, 137.0, 131.4, 130.0, 129.9, 128.6, 128.4, 128.0, 126.7, 125.6, 123.0, 119.9, 94.4, 87.6, 75.7. HR EI-MS calced for $C_{42}H_{28}N_2O_2$, 592.2151 $[M^{+}]$; found: 592.2154.

1b. Yield 142 mg (yellow glassy solid), 56%. R_f = 0.48 (dichloromethane/acetone 4:1); mp 58 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.87 (s, 2H), 8.65 (s, 4H), 8.24 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.48 (s, 4H), 7.37−7.23 (m, 20H), 6.78 (s, 4H), 6.58 (s, 2H), 5.23 (s, 4H), 4.93 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.2, 149.8, 144.1, 139.3, 136.7, 131.4, 130.0, 129.7, 128.6, 128.0, 127.5, 126.8, 125.6, 122.9, 119.9, 107.0, 101.9, 94.4, 87.6, 75.4, 70.1. HR ESI-MS calced for $C_{70}H_{53}N_2O_6$, $[M^{+}]$: 1017.3898; found: 1017.3845.

1c. Yield 215 mg (yellow glassy solid), 46%. R_f = 0.37 (dichloromethane/acetone 2:1); mp 56 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.86 (s, 2H), 8.64 (s, 4H), 8.25 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 9.2 Hz, 2H), 7.45 (s, 4H), 7.34−7.30 (m, 40H), 6.75 (s, 4H), 6.63 (s, 8H), 6.52 (s, 6H), 5.21 (s, 4H), 4.94 (s, 16H), 4.84 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.12, 160.05, 149.8, 144.2, 139.3, 139.1, 136.7, 131.3, 130.1, 129.7, 128.5, 128.0, 127.9, 127.7, 127.5, 126.8, 125.6, 122.9, 120.0, 106.9, 106.4, 102.0, 101.5, 94.4, 87.7, 75.4, 70.1. HR MALDI-MS for $C_{126}H_{100}N_2O_{14}Na$ $[(M + Na)^{+}]$: 1888.90.

General Procedure for the Self-Assembly of R1−R3. 1.0 mL of dichloromethane-d_2 was added to a mixture of triflate **6** (4.52 mg, 0.00337 mmol) and the appropriate [G-1]−[G-3] dendritic donor precursors **1a−c** (for **1a**, 2.0 mg, 0.003 37 mmol; for **1b**, 3.43 mg, 0.003 37 mmol; for **1c**, 6.29 mg, 0.003 37 mmol). The reaction mixture was then stirred for 1 h at room temperature. The self-assembly was monitored by ^{1}H and ^{31}P NMR spectroscopy and determined to be complete. The deuterated solvent was evaporated to dry, and the crude product was obtained. For further purification, the crude product was redissolved in a minimal amount of dichloromethane, and then *n*-pentane was carefully added to precipitate the final products.

R1. Yield 6.26 mg (yellow solid), 96%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.09 (br, 4H), 8.72 (br, 8H), 8.30 (d, *J* = 8.4 Hz, 4H), 7.92 (br, 8H), 7.82 (d, *J* = 7.2 Hz, 4H), 7.56−7.52 (m, 24H), 7.39 (br, 12H), 5.33 (s, 8H), 1.37 (br, 48H), 1.14 (br, 72H). ^{31}P NMR (CD_2Cl_2, 162 Hz): δ 13.49 (s, $^{1}J_{Pt-P}$ = 2657.3 Hz). CSI-TOF-MS, $[M - 2OTf]^{2+}$, 1784.79; $[M - 3OTf]^{3+}$, 1140.53; $[M - 4OTf]^{4+}$, 817.91. Anal. Calcd for $C_{162}H_{192}F_{12}N_4O_{18}P_8Pt_4S_4 \cdot H_2O$: C, 50.08; H, 5.03; N, 1.44. Found: C, 49.69; H, 5.23; N, 1.35.

R2. Yield 7.71 mg (yellow solid), 97%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.10 (d, *J* = 10.4 Hz, 4H), 8.71 (br, 8H), 8.28 (d, *J* = 8.4 Hz, 4H), 7.92 (br, 8H), 7.81 (d, *J* = 8.0 Hz, 4H), 7.56−7.50 (m, 16H), 7.35−7.31 (br, 40H), 6.77 (s, 8H), 6.55 (s, 4H), 5.25 (s, 8H), 4.94 (s, 16H), 1.37 (br, 48H), 1.15−1.14 (m, 72). ^{31}P NMR (CD_2Cl_2, 162 Hz): δ 13.31 (s, $^{1}J_{Pt-P}$ = 2666.5 Hz). CSI-TOF-MS, $[M - 3OTf]^{3+}$, 1423.05; $[M - 4OTf]^{4+}$, 1030.04. Anal. Calcd for $C_{218}H_{240}F_{12}N_4O_{26}P_8Pt_4S_4$: C, 55.51; H, 5.13; N, 1.19. Found: C, 55.20; H, 5.08; N, 1.12.

R3. Yield 10.6 mg (yellow solid), 98%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.10 (br, 4H), 8.69 (br, 8H), 8.31 (d, *J* = 8.4 Hz, 4H), 7.89 (br, 8H), 7.82 (br, 4H), 7.55−7.51 (m, 16H), 7.32 (br, 80H), 6.75 (s, 8H), 6.61 (s, 16H), 6.52−6.48 (m, 12H), 5.22 (s, 8H), 4.92 (s, 32H), 4.85 (s, 16H), 1.36 (br, 48H), 1.13 (br, 72). ^{31}P NMR (CD_2Cl_2, 162 Hz): δ 13.58 (s, $^{1}J_{Pt-P}$ = 2660.0 Hz). CSI-TOF-MS, $[M - 3OTf]^{3+}$, 1989.29; $[M - 4OTf]^{4+}$, 1454.72. Anal. Calcd for $C_{330}H_{336}F_{12}N_4O_{42}P_8Pt_4S_4 \cdot CH_2Cl_2$: C, 61.17; H, 5.15; N, 0.86. Found: C, 60.80; H, 5.03; N, 0.85.

General Procedure for the Self-Assembly of R4−R6. A mixed solvents of CD_2Cl_2 and acetone-d_6 (1.0 mL, v/v 2/1) was added to a mixture of [G-1] nitrate **7a** (4.86 mg, 0.00337 mmol) and [G-1] dendritic donor precursor **1a** (2.0 mg, 0.00337 mmol). The reaction mixture was stirred for 12 h at room temperature. The self-assembly was monitored by ^{1}H and ^{31}P NMR spectroscopy and determined to be complete. The deuterated solvent was evaporated to dry, and the crude product was obtained. For further purification, the crude product was redissolved in a minimal amount of dichloromethane, and then *n*-pentane was carefully added to precipitate the final product **R4**. A similar procedure was carried out for the preparation of **R5** ([G-2] nitrate **7b**, 5.47 mg, 0.002 93 mmol; [G-2] donor precursor **1b**, 2.98 mg, 0.002 93 mmol) and **R6** ([G-3] nitrate **7c**, 5.35 mg, 0.001 97 mmol; [G-3] donor precursor **1c**, 3.69 mg, 0.001 98 mmol).

R4. Yield 6.65 mg (yellow solid), 97%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.16 (s, 4H), 8.69 (br, 8H), 8.28 (d, *J* = 8.4 Hz, 4H), 7.93 (br, 8H), 7.80 (d, *J* = 8.4 Hz, 4H), 7.53−7.33 (m, 44H), 7.09 (s, 2H), 6.93 (s, 4H), 6.89 (s, 2H), 5.31 (s, 8H), 5.11 (s, 8H), 1.82−1.81 (m, 48H), 1.23−1.17 (m, 72H). ^{31}P NMR (CD_2Cl_2, 161.9 Hz): δ 16.29 (s, $^{1}J_{Pt-P}$ = 2313.6 Hz). CSI-TOF-MS, $[M - 3NO_3]^{3+}$, 1295.18; $[M - 4NO_3]^{4+}$, 955.89. Anal. Calcd for $C_{194}H_{216}N_8O_{24}P_8Pt_4 \cdot H_2O$: C, 56.97; H, 5.32; N, 2.74. Found: C, 56.75; H, 5.66; N, 2.64.

R5. Yield 8.03 mg (yellow solid), 95%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.19 (s, 4H), 8.88 (br, 8H), 8.68 (br, 4H), 8.29 (br, 8H), 8.25 (d, *J* = 11.6 Hz, 4H), 7.45−7.30 (m, 84H), 7.08 (s, 2H), 6.93 (s, 4H), 6.86 (s, 2H), 6.76 (s, 8H), 6.67 (s, 8H), 6.55 (br, 8H), 5.24 (s, 8H), 5.05−5.02 (m, 24H), 4.93 (s, 16H), 1.81 (br, 48H), 1.23−1.16 (m, 72H). ^{31}P NMR (CD_2Cl_2, 161.9 Hz): δ 16.37 (s, $^{1}J_{Pt-P}$ = 2303.8 Hz). CSI-TOF-MS, $[M - 4NO_3]^{4+}$, 1380.31. Anal. Calcd for

$C_{306}H_{312}N_8O_{40}P_8Pt_4\cdot H_2O$: C, 63.50; H, 5.47; N, 1.94. Found: C, 63.15; H, 5.66; N, 1.91.

R6. Yield 8.68 mg (yellow solid), 96%. ^1H NMR (CD_2Cl_2, 400 MHz): δ 9.19 (s, 4H), 8.65 (br, 8H), 8.30 (br, 4H), 7.90 (d, J = 4.0 Hz, 8H), 7.81 (d, J = 7.6 Hz, 4H), 7.36−7.28 (m, 84H), 7.08 (s, 2H), 6.93 (s, 4H), 6.75 (s, 8H), 6.65−6.61 (s, 30H), 6.52−6.48 (s, 24H), 6.55 (br, 8H), 5.24 (s, 8H), 5.05−5.02 (m, 24H), 4.93 (s, 16H), 1.81 (br, 48H), 1.23−1.16 (m, 72H). ^{31}P NMR (CD_2Cl_2, 161.9 Hz): δ 16.35 (s, $^1J_{Pt-P}$ = 2313.7 Hz). CSI-TOF-MS, $[M - 4NO_3]^{4+}$, 2229.55. Anal. Calcd for $C_{530}H_{504}N_8O_{72}P_8Pt_4$: C, 69.45; H, 5.54; N, 1.22. Found: C, 69.04; H, 5.24; N, 1.25.

General Procedure for the Self-Assembly of R7−R9. 0.8 mL of dichloromethane-d_2 was added to a mixture of nitrate **8** (3.96 mg, 0.002 96 mmol) and the appropriate [G-1]−[G-3] dendritic donor precursors **1a−c** (for **1a**, 1.75 mg, 0.002 96 mmol; for **1b**, 3.01 mg, 0.002 96 mmol; for **1c**, 5.52 mg, 0.002 96 mmol). The reaction mixture was stirred for 12 h at room temperature. The self-assembly was monitored by ^1H and ^{31}P NMR spectroscopy and determined to be complete. The deuterated solvent was evaporated to dry, and the crude product was obtained. For further purification, the crude product was redissolved in a minimal amount of dichloromethane, and then n-pentane was carefully added to precipitate the final product.

R7. Yield 5.60 mg (yellow solid), 98%. ^1H NMR (CD_2Cl_2, 400 MHz): δ 9.16 (s, 4H), 8.69 (d, J = 4.8 Hz, 8H), 8.28 (d, J = 8.4 Hz, 4H), 7.93 (d, J = 4.8 Hz, 8H), 7.79 (d, J = 8.4 Hz, 4H), 7.53−7.51 (m, 8H), 7.39−7.37 (m, 12H), 7.06 (s, 2H), 6.88 (s, 4H), 5.32 (s, 8H), 4.92 (s, 4H), 4.54 (s, 4H), 4.31 (s, 10H), 1.83−1.82 (br, 48H), 1.23−1.17 (m, 72H). ^{31}P NMR (CD_2Cl_2, 162 Hz): δ 16.06 (s, $^1J_{Pt-P}$ = 2319.8 Hz). CSI-TOF-MS, $[M - 3NO_3]^{3+}$, 1225.78; $[M - 4NO_3]^{4+}$, 904.09. Anal. Calcd for $C_{174}H_{200}Fe_2N_8O_{20}P_8Pt_4\cdot H_2O$: C, 53.84; H, 5.25; N, 2.89. Found: C, 53.46; H, 5.47; N, 2.93.

R8. Yield 6.83 mg (yellow solid), 98%. ^1H NMR (CD_2Cl_2, 400 MHz): δ 9.18 (s, 4H), 8.70 (d, J = 4.4 Hz, 8H), 8.28 (d, J = 8.0 Hz, 4H), 7.94 (d, J = 4.8 Hz, 8H), 7.80 (d, J = 8.4 Hz, 4H), 7.45−7.29 (m, 40H), 7.06 (s, 2H), 6.88 (s, 4H), 6.76 (s, 8H), 6.55 (s, 4H), 5.24 (s, 8H), 4.93 (s, 20H), 4.54 (s, 4H), 4.31 (s, 10H), 1.82 (br, 48H), 1.23−1.17 (m, 72H). ^{31}P NMR (CD_2Cl_2, 162 Hz): δ 16.27 (s, $^1J_{Pt-P}$ = 2305.3 Hz). CSI-TOF-MS, $[M - 3NO_3]^{3+}$, 1508.91; $[M - 4NO_3]^{4+}$, 1116.19. Anal. Calcd for $C_{230}H_{248}Fe_2N_8O_{28}P_8Pt_4$: C, 58.62; H, 5.30; N, 2.38. Found: C, 58.41; H, 5.16; N, 2.35.

R9. Yield 9.20 mg (yellow solid), 97%. ^1H NMR (CD_2Cl_2, 400 MHz): δ 9.18 (s, 4H), 8.67 (br, 8H), 8.30 (d, J = 9.6 Hz, 4H), 7.91 (br, 8H), 7.80 (d, J = 8.0 Hz, 4H), 7.43−7.25 (m, 80H), 7.06 (s, 2H), 6.88 (s, 4H), 6.75 (s, 8H), 6.61 (s, 16H), 6.52−6.48 (m, 12H), 5.21 (s, 8H), 4.92 (s, 36H), 4.84 (s, 16H), 4.54 (s, 4H), 4.31 (s, 10H), 1.81 (br, 48H), 1.23−1.17 (m, 72H). ^{31}P NMR (CD_2Cl_2, 161.9 Hz): δ 16.31 (s, $^1J_{Pt-P}$ = 2307.1 Hz). CSI-TOF-MS, $[M - 4NO_3]^{4+}$, 1540.60. Anal. Calcd for $C_{342}H_{344}Fe_2N_8O_{44}P_8Pt_4\cdot CH_2Cl_2$: C, 63.43; H, 5.37; N, 1.73. Found: C, 63.05; H, 5.22; N, 1.78.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR spectra of **5a−c** and **1a−c**, ^1H and ^{31}P NMR spectra of **R1−R9**, high resolution mass spectra of **5a−c** and **1a−c**, CSI-TOF-MS spectrum of **R6**, CV measurement of **R7−R9**, ^1H DOSY NMR spectra of **R7−R9**, and the model structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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