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Design and construction of supramolecular polysulfurated metallodendrimers with various shapes and sizes via coordination-driven self-assembly

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ABSTRACT

A new family of 120° polysulfurated dipyridine donors have been successfully designed and synthesized, from which a series of novel rhomboidal and hexagonal supramolecular polysulfurated metallodendrimers were prepared via coordination-driven self-assembly. The structures of the newly designed polysulfurated metallodendrimers were characterized by multinuclear NMR (^{1}H and ^{31}P), mass spectrometry (CSI-TOF-MS), and elemental analysis. Moreover, the shape and size of these novel metallodendrimers were investigated with PM6 semi-empirical molecular orbital methods.

1. Introduction

Coordination-driven self-assembly[1] has proven to be a particularly powerful tool for the construction of delicate supramolecular two-dimensional (2-D) and three-dimensional (3-D) metal-containing architectures with well-defined shape and size. Metal–ligand directional bonds between two or more predesigned molecular building blocks often feature significant synthetic advantages such as few steps, fast and facile construction of the final products, and inherently self-correcting, defect-free assembly. Thus by employing coordination-driven self-assembly, a great number of well-defined 2-D and 3-D metal-containing structures have been successfully designed and constructed during the past few decades.[2] However, the most 2-D metal-containing polygons were built from simple, fairly inert building blocks that are often aliphatic or aromatic in nature. Therefore many self-assembled metallocycles are, for the most part, unfunctionalized. Recently, substantial efforts have focused on incorporating suitable functional moieties onto the resulted supramolecular complexes with the aim to the fabrication of functional artificial molecular devices.[3] For instance, an *exo-functionalization* approach has been widely utilized to prepare discrete supramolecular metal-containing assemblies functionalized with crown ether, ferrocene, and hydrophobic and hydrophilic units that have been distributed within building blocks.[4]

Dendrimers have a highly branched, three-dimensional architecture, composed of several dendritic wedges that extend outward from an internal core.[5] In the past few decades, the design and synthesis of diverse dendrimers have 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, encapsulation and delivery, and materials science.[6] It should be noted that, since the pioneering work by Newkome and co-workers[7] and Balzani and co-workers[8] in the early 1990s, metallodendrimers[9] have received considerable attention because of their potential application in catalysis,[10] biological mimetics,[9l,11] and photo- and electrochemistry.[12] For example, we have previously reported the self-assembly of a variety of metallodendrimers with cavities of various shapes and sizes such as rhomboids, triangle, and hexagons.[4f,13] Moreover, Schalley and co-workers have synthesized a family of new metallodendritic squares from 4,4′-bipyridines functionalized with Fréchet dendrons and (dppp)-Pt(II) or Pd(II) triflate.[14] 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.[15]

During the past few decades, a new family of polysulfurated aromatic dendrimers have received considerable attention because of their unique structures and potential application in photo- and electrochemistry.[16] The investigation of these dendrons containing thiol groups opened a door to some novel and rare sulfur-containing arenes. For example, the synthesis and

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characterization of a novel class of dendrimers consisting of a polysulfurated pyrene core were presented by Gingras' group.[16a] It was found that their photophysical behavior and redox properties could be fine-tuned by the length of their branches. Moreover, a great deal of polysulfurated dendrimers with various molecular shapes such as asterisks, chains, wheels, and windmills were reported.[16b] Stimulated by our previous successful examples of supramolecular metallodendrimers,[4f,13] we envisioned that the construction of a new family of polysulfurated dendrimers with well-designed and controlled metal-containing rings would be realized by the proper choice of subunits with predefined angles and symmetry. This study could likely give rise to the design and synthesis of novel polysulfurated metallodendrimers possessing rings of various size and shape at the core from newly designed [G-0]–[G-2] 120° polysulfurated dendritic donors **3a**–**c** (Fig. 1).

2. Results and discussion

2.1. Synthesis of [G-0]–[G-2] 120° Polysulfurated Dendritic Donors 3a–c

The new 120° polysulfurated dendritic donors can be easily synthesized in two steps as shown in Scheme 1. The polysulfurated dendrimers were introduced by a nucleophilic substituting reaction of 1,3,5-tribromobenzene with the corresponding thiolate of the dendrimers.[17] The selectivity for substituting monobromide of 1,3,5-tribrotnobenzene was achieved through using a controlled amount of thiolate. From dendritic 3,5-dibromobenzene derivatives **2a**–**c**, the desired 120° dendritic donor building blocks **3a**–**c** were obtained by the coupling reaction with 4-ethynylpyridine in satisfactory yields in the presence of $Pd(PPh_3)_4$ and CuI as catalysts. The molecular structures of polysulfurated dendritic precursors **3a**–**c** were well characterized by using multiple nuclear NMR (^1H and ^{13}C) and mass spectrometry.

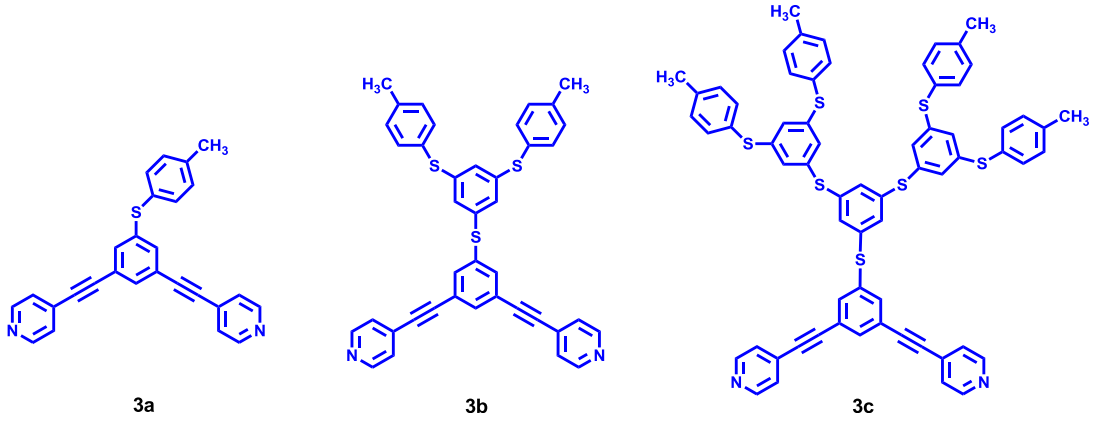
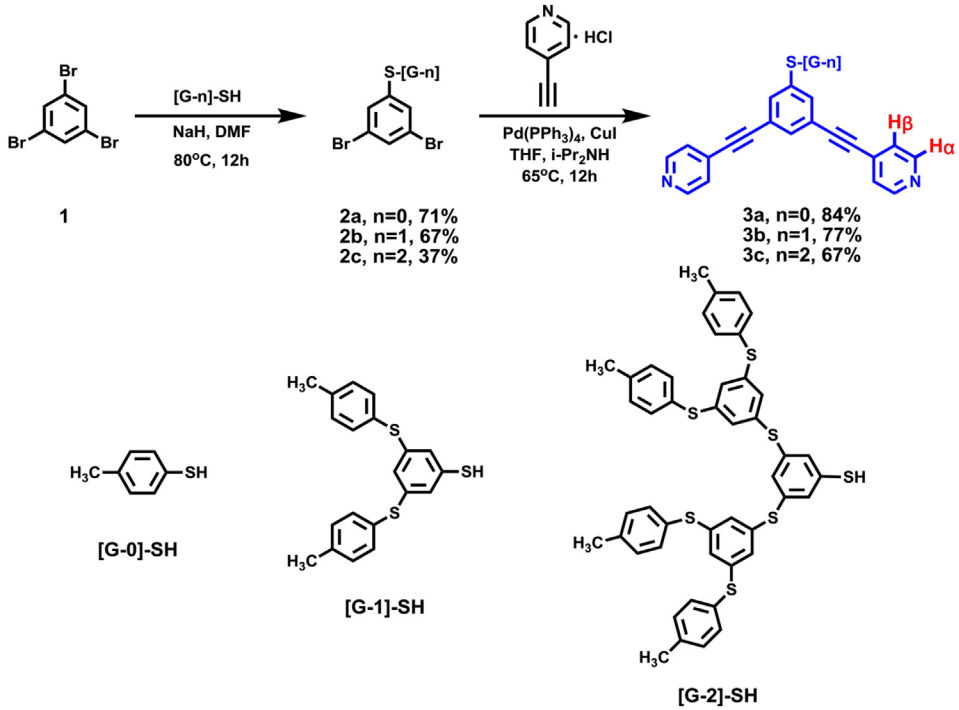


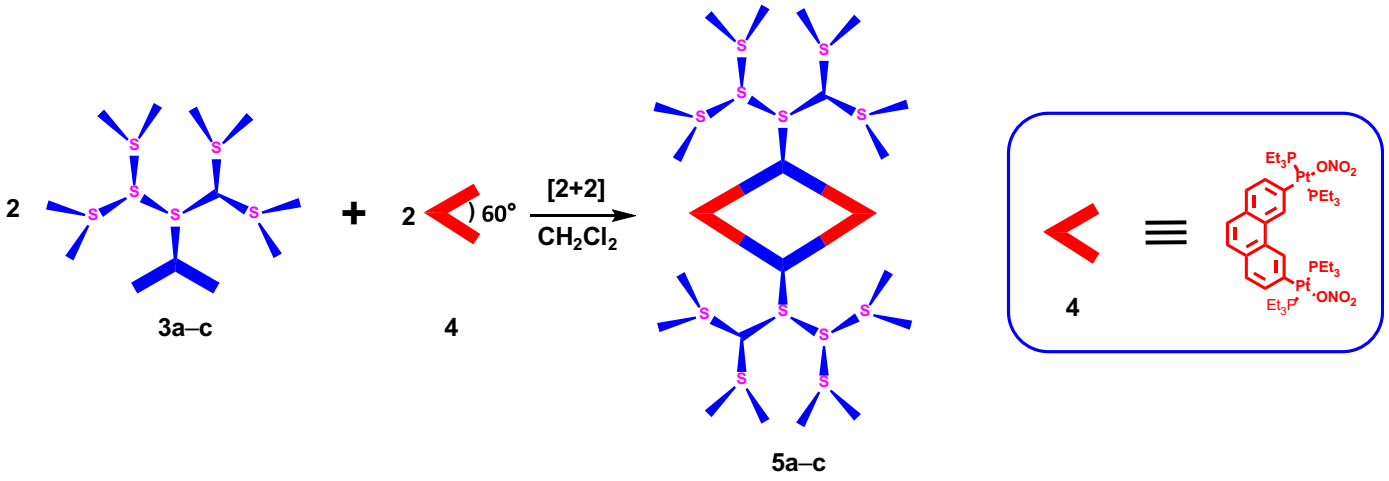
Fig. 1. Molecular structures of [G-0]–[G-2] 120° polysulfurated dendritic donors **3a**–**c**.



Scheme 1. Synthesis of [G-0]–[G-2] 120° polysulfurated dendritic donors **3a**–**c**.

2.2. Self-assembly of [G-0]–[G-2] polysulfurated dendritic rhomboids 5a–c

In general, the shape of an individual two-dimensional polygon is determined by the value of the turning angle within its angular components.[1a–c] For example, the combination of 60° units with complementary 120° linking components will yield a molecular rhomboid.[13c] With the newly designed 120° polysulfurated dendritic precursors in hand, the self-assembly of polysulfurated metallodendrimers with rhomboidal cavities was investigated. Stirring the [G-0]–[G-2] 120° angular donors **3a–c** with an equimolar amount of the known 60° angular acceptor, 2,9-(*trans*-$Pt(PEt_3)_2NO_3)_2$-phenanthrene (**4**),[2h] in CD_2Cl_2 for 1 h resulted in the formation of [2+2] rhomboidal metallodendrimers **5a–c**, respectively (Scheme 2).



Scheme 2. Cartoon representations of the formation of rhomboidal polysulfurated metallodendrimers **5a–c** from 120° polysulfurated dendritic donors **3a–c** and 60° di-platinum acceptor **4**.

Multinuclear NMR (^1H and ^{31}P) analysis of [G-0]–[G-2] assemblies **5a–c** exhibited very similar characteristics, which all suggested the formation of discrete, highly symmetric polysulfurated metallodendrimers with rhomboidal cavities. The $^{31}P\{^1H\}$ NMR spectra of the [G-0]–[G-2] assemblies **5a–c** displayed a sharp singlet (ca. 12.5 ppm) shifted upfield from the signal of the starting platinum acceptor **4** by approximately 6.2 ppm (Fig. 2). This change, as well as the decrease in coupling of the flanking ^{195}Pt satellites (ca. $\Delta^1J_{PPt}=-134$ Hz), is consistent with electron back-donation from the platinum atoms. Examination of the ^1H NMR spectra (Fig. 3 and Supplementary data) also indicated the existence of highly symmetric structures. In the ^1H NMR spectrum of each assembly, the α-hydrogen nuclei of the pyridine rings exhibited 0.1–0.7 ppm downfield shifts, and the β-hydrogen nuclei showed about 0.3–0.6 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. Notably, two doublets were found for α-hydrogen nuclei and β-hydrogen nuclei on pyridine rings in the ^1H NMR spectrum of rhomboidal polysulfurated metallodendrimers. This observation might be attributed to the hindered rotation about the Pt–N(pyridyl) bond that has been reported previously.[13d]

The structures of the rhomboidal metallodendrimers **5a–c** have also been confirmed by cold-spray ionization mass (CSI-TOF-MS), 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 spectra of the [G-0]–[G-2] assemblies **5a–c**, peaks attributable to the loss of nitrate counterions, $[M-2NO_3]^{2+}$ (m/z=1503.49 for **5a**, m/z=1733.51 for **5b**, and m/z=2194.56 for **5c**) and $[M-3NO_3]^{3+}$ (m/z=981.66 for **5a**, m/z=1135.01 for **5b**, and m/z=1442.39 for **5c**), where M represents the intact [2+2] assemblies, were observed. These peaks were isotopically resolved, and they agree very well with their respective theoretical distribution (Fig. 4).

2.3. Self-assembly of hexagonal polysulfurated metallodendrimers 7a–c

According to the 'directional bonding' model and the 'symmetry interaction' model,[1a,b] discrete molecular hexagons can be prepared via the combination of two complementary ditopic building blocks A^2 and X^2, each incorporating 120° angles between their coordination sites, leading to the formation of hexagonal structures of type $A_3^2X_3^2$.[18a] Recently, we have reported the construction of dendritic multiferrocenyl hexagons by using this strategy.[13a] In order to extend the

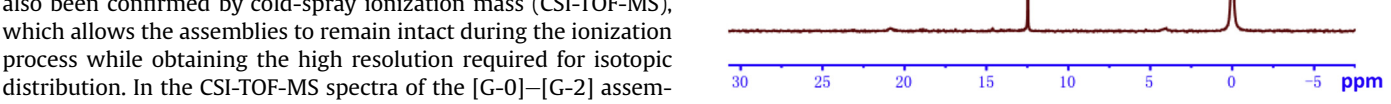


Fig. 2. Partial $^{31}P\{^1H\}$ NMR spectra (400 MHz, CD_2Cl_2, 298 K) of 60° di-Pt(II) acceptor **4** (A) and polysulfurated dendritic rhomboids (for [G-0] **5a**, B; for [G-1] **5b**, C; for [G-2] **5c**, D).

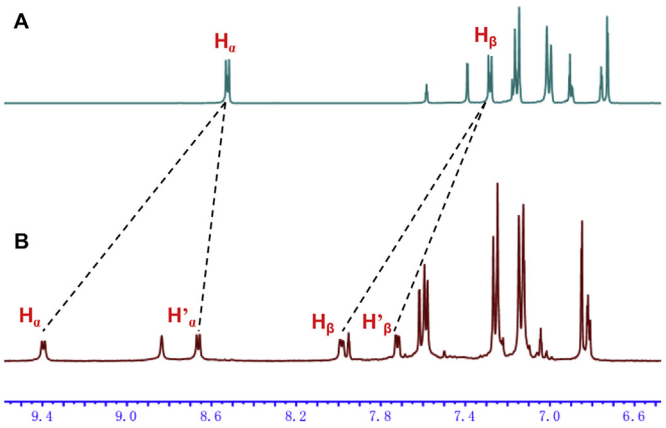


Fig. 3. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of [G-2] polysulfurated dendritic donor **3c** (A) and [G-2] polysulfurated dendritic rhomboid **5c** (B).

scope of this approach to the construction of hexagonal polysulfurated metallodendrimers, we have investigated the self-assembly of 120° polysulfurated dendritic donors **3a**–**c** with 120° di-platinum acceptor **6**. When the [G-0]–[G-2] 120° angular donor subunits **3a**–**c** were reacted with the 120° ketone di-Pt(II) acceptor **6**[18b] in CD_2Cl_2 at room temperature, the [3+3] hexagonal polysulfurated metallodendrimers **7a**–**c** was formed, respectively (Scheme 3).

$^{31}P\{^1H\}$ NMR analysis of the reaction mixtures **7a**–**c** is consistent with the formation of a single, highly symmetric species, as indicated by the appearance of a sharp singlet (ca. 13.3 ppm) with concomitant ^{195}Pt satellites, shifted upfield by ca. 6.0 ppm as compared to **6** (Fig. 5). As expected, a decrease in coupling of the flanking ^{195}Pt satellites was also observed (ca. $\Delta^1J_{PPt}=-148$ Hz), lending the further support to the formation of the hexagonal polysulfurated metallodendrimers **7a**–**c**. In the ^{1}H NMR spectra of metallodendrimers **7a**–**c**, the α-H and β-H of the pyridine rings exhibited ca. 0.2–0.3 ppm and ca. 0.4–0.5 ppm downfield shifts, respectively, relative to free ligands **3a**–**c** (Fig. 6). In contrast to the results for rhomboidal polysulfurated metallodendrimers **5a**–**c**, the ^{1}H NMR spectra of **7a**–**c** showed only one doublet for the α-H and β-H protons of the pyridine ring linked to the Pt(II) center.

The structures of the hexagonal metallodendrimers have been further confirmed by CSI-TOF-MS spectrometry and elemental analysis as well. However, compared to the previous rhomboidal polysulfurated metallodendrimers **5a**–**c**, it has proven more difficult to get strong mass signals for the charged hexagons **7a**–**c** on account of their larger molecular weight even under the CSI-TOF-MS conditions. With considerable effort, the peaks attributable to $[M-5OTf]^{5+}$ (m/z=897.08 for **7a**, m/z=1035.52 for **7b**, m/z=1311.55 for **7c**) were observed, where M represents the intact [3+3] assemblies. These peaks were isotopically resolved, and they agree with their respective theoretical distribution, although the resolution is not as good as that in the case of rhomboidal polysulfurated metallodendrimers **5a**–**c** (see Supplementary data).

As mentioned previously, the [3+3] discrete hexagonal structures can be self-assembled by combining three 120° pyridyl donor

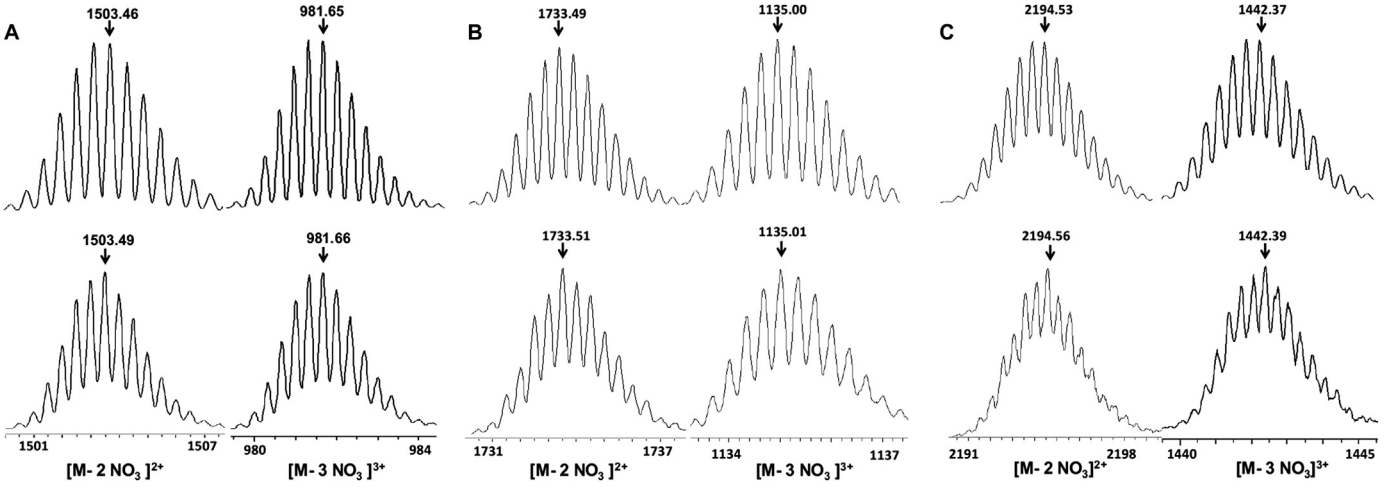
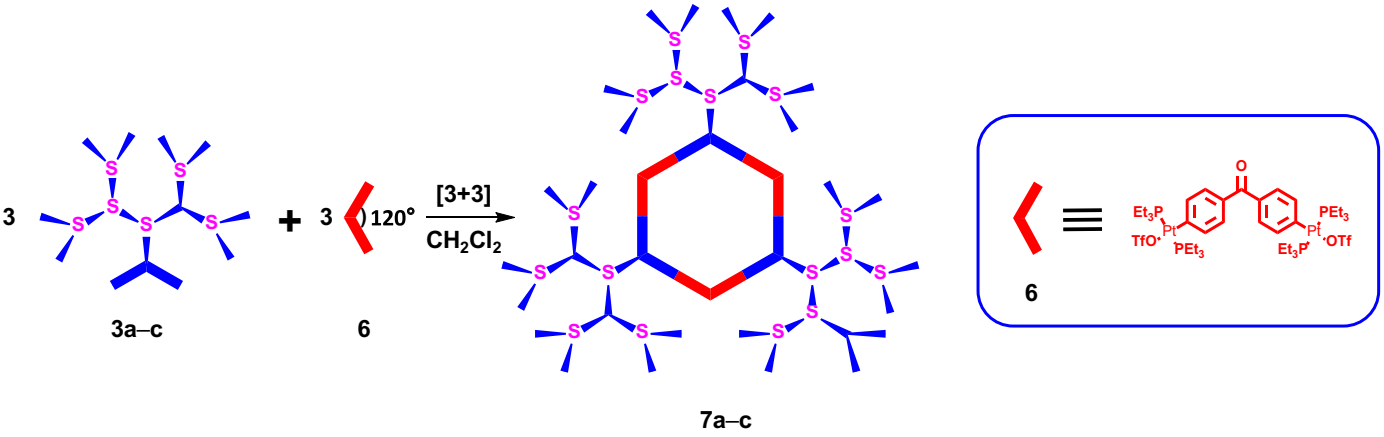


Fig. 4. Theoretical (top) and experimental (bottom) CSI-TOF-MS spectra of polysulfurated dendritic rhomboids (for [G-0] **5a**, A; for [G-1] **5b**, B; for [G-2] **5c**, C).



Scheme 3. Cartoon representations of formation of hexagonal polysulfurated metallodendrimers **7a**–**c** from 120° polysulfurated dendritic donors **3a**–**c** and 120° di-platinum acceptor **6**.

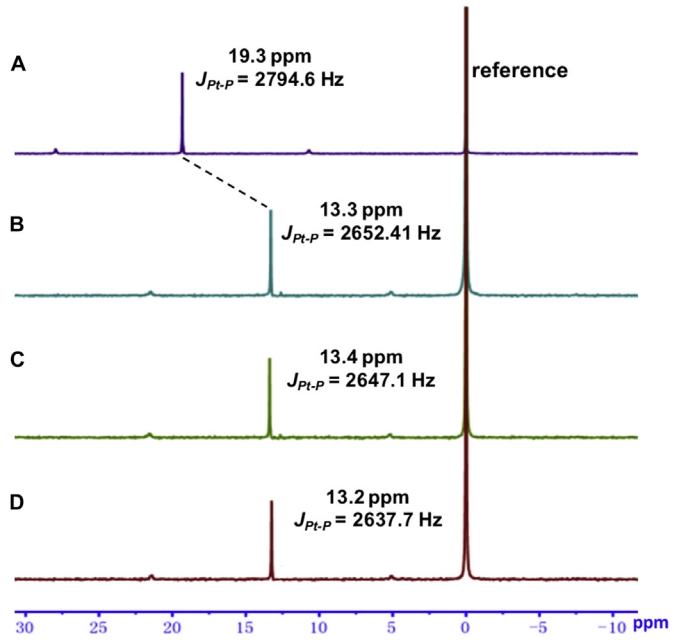


Fig. 5. Partial $^{31}P\{^{1}H\}$ NMR spectra (400 MHz, CD_2Cl_2, 298 K) of 120° di-Pt(II) acceptor **6** (A) and [3+3] hexagons [G-0] **7a** (B), [G-1] **7b** (C), [G-2] **7c** (D).

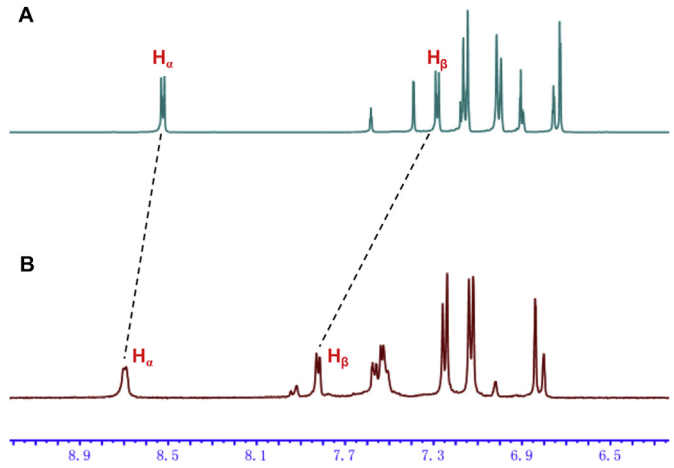


Fig. 6. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of [G2]-donor **3c** (A) and [G-2] polysulfurated dendritic hexagon **7c** (B).

building blocks and three 120° di-platinum acceptors.[18a] 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 supramolecular hexagons.[4b,13a] In this study, the sharp NMR signals in both the $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra along with the solubility of these species ruled out the formation of oligomers. Moreover, the CSI-TOF-MS results ensure that only [3+3] hexagonal polysulfurated metallodendrimers are formed in each self-assembly.

2.4. Molecular simulation

Large supramolecular coordination-compounds and flexible, high generation dendrimers often prove difficult to crystallize. All attempts to grow X-ray quality single crystals of the rhomboidal and hexagonal polysulfurated metallodendrimers **5a**–**c** and **7a**–**c** have proven to be unsuccessful to date. Thus PM6 semi-empirical molecular orbital method[19] was employed to optimize the geometry of all polysulfurated metallodendrimers. In the case of **5a**–**c**, the optimized structure of each assembly featured a very similar, roughly planar rhomboidal ring at the core surrounded by flexible polysulfurated dendrons. Moreover, it was found that the rhomboidal polysulfurated metallodendrimers **5a**–**c** possess a well-defined rhombus structure with a 2.4×1.3 nm cavity in average (Fig. 7A). With the increase of the dendron generation, the external dimensions of the rhomboidal structures increased (**5a**, 3.1×3.0 nm; **5b**, 4.1×3.0 nm; **5c**, 4.6×3.1 nm). The similar results were observed in the case of the hexagonal polysulfurated metallodendrimers **7a**–**c**. For example, in the case of [G-2] hexagonal polysulfurated metallodendrimers **7c** (Fig. 7B), the hexagonal ring-shaped metallodendrimer has an internal radius of approximately 1.4 nm and an average outer dendron radius of 3.2 nm. More simulated geometry information about the rhomboidal and hexagonal polysulfurated metallodendrimers **5a**–**c** and **7a**–**c** could be found in Supplementary data.

3. Conclusion

In summary, we have designed and synthesized a new family of 120° polysulfurated dendritic donor subunits, from which novel rhomboidal and hexagonal polysulfurated metallodendrimers **5a**–**c** and **7a**–**c** can be easily formed via coordination-driven self-assembly. All polysulfurated metallodendrimers were characterized with multinuclear NMR, CSI-TOF-MS, and elemental analysis. Their structural properties have been studied by using PM6 semi-empirical molecular orbital methods. Hence, we have demonstrated again that highly convergent synthetic protocols based on the simultaneous assembly of appropriate predetermined building block allow the rapid construction of novel polysulfurated metallodendrimers. In particular, this approach is capable of preparing a variety of metallodendrimers with different shape and size through the proper choice of subunits with predefined angles and symmetry, which enriches the library of polysulfurated arenes. Further studies on their applications of these supramolecular polysulfurated metallodendrimers are in progress.

4. Experimental section

4.1. General information

All solvents were dried according to standard procedures and all of them were degassed under N_2 for 30 min before use. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on Bruker 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 hertz (Hz) and chemical shifts (δ) in parts per million (ppm). Multiplicities are denoted as follows: s=singlet, d=doublet, m=multiplet, br=broad.

The CSI-TOF-MS spectra were acquired using an AccuTOFCS mass spectrometer (JMS-T100CS, JEOL, Tokyo, Japan). All the complexes were prepared and diluted to about 0.1 μg/μL in a solution of CH_2Cl_2, and the solution was delivered to the ion source by an infusion syringe pump at a flow rate of 20 μL/min. The needle voltage was set at 3000 V; the orifice 1 voltage was set at 40 V; the orifice 2 voltage was 20 V. The flow rate of spray gas was 2.5 L/min at room temperature. The resolution of the mass analyzer was optimized at 6000 (50% peak). Mass scan range was set at 100–3000 Da.

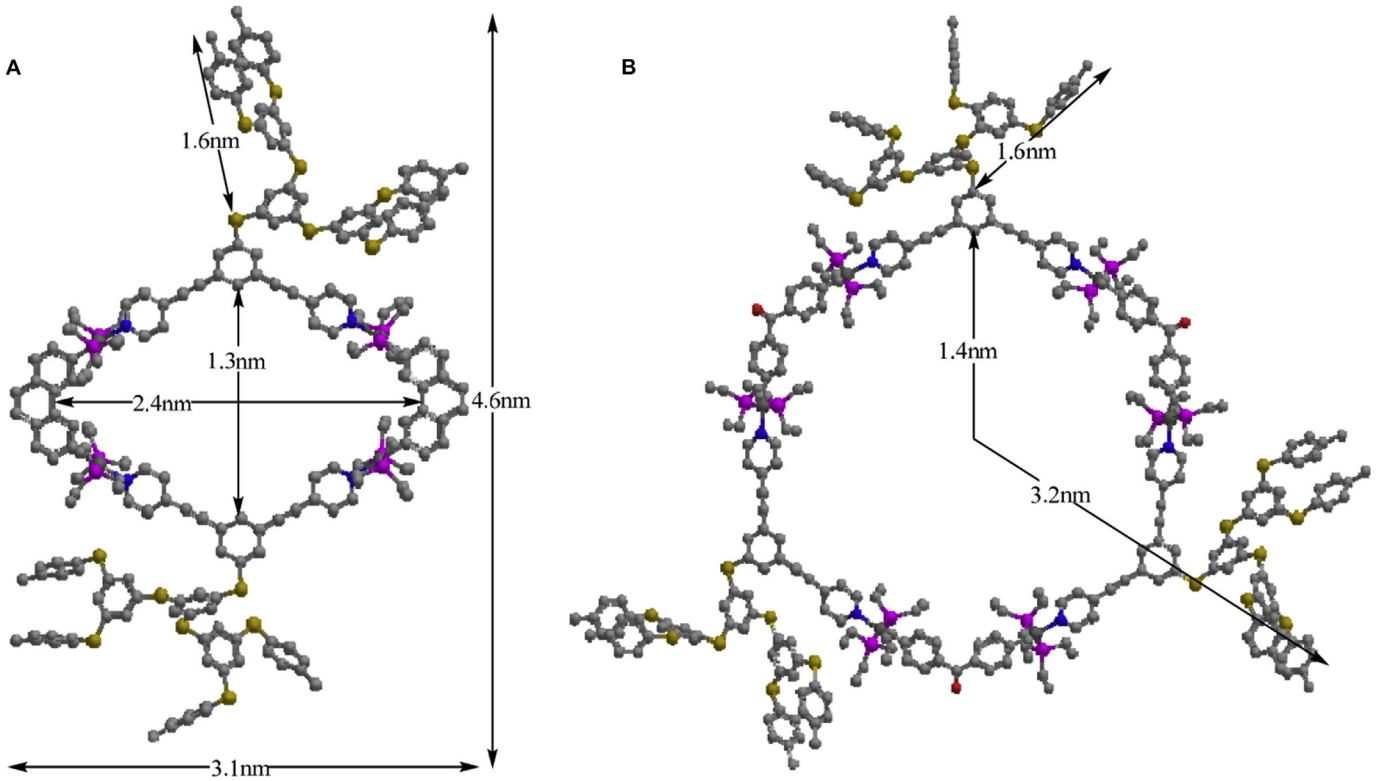


Fig. 7. Simulated molecular models of the [G-2] polysulfurated dendritic rhomboid **5c** (A) and [G-2] polysulfurated dendritic hexagon **7c** (B).

4.2. General procedure for the synthesis of 2a–c

Synthesis of compound ***2***. Under an atmosphere of nitrogen, [G-*n*]-SH[17] (for G-0, 394 mg, 3.18 mmol; for G-1, 443 mg, 1.25 mmol; for G-2, 145 mg, 0.178 mmol) and appropriate NaH were placed in a 50 mL Schlenk flask followed by 10–15 mL of anhydrous DMF. The mixture was stirred for 10 min at room temperature. The appropriate 1.0 equiv compound **1** was then added under nitrogen. The reaction was continued at 80 °C for another 12 h and then quenched by 10 mL of water, extracted with ethyl acetate, and dried with $MgSO_4$. The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2≈10:1) to give compounds **2a**–**c**.

4.2.1. Compound ***2a***. Yield: 71%. Colorless oil. R_f=0.80 (petroleum ether). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (t, J=1.2 Hz, 1H), 7.38 (d, J=8.4 Hz, 2H), 7.22–7.19 (m, 4H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.67, 139.15, 133.92, 131.00, 130.47, 128.86, 127.87, 123.09, 21.21. MS (EI): m/z (%)=356 (M^+, 52.55), 358 [$(M+2H)^+$, 100.00], 198 (66.78). HRMS (EI) calcd for $C_{13}H_{10}Br_2S$: 355.8870, found: 355.8871.

4.2.2. Compound ***2b***. Yield: 67%. Colorless oil. R_f=0.51 (petroleum ether/CH_2Cl_2 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (t, J=1.6 Hz, 1H), 7.29–7.26 (m, 6H), 7.15 (d, J=2.0 Hz, 4H), 6.90 (t, J=1.6 Hz, 1H), 6.78 (d, J=1.6 Hz, 2H), 2.37 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.93, 139.07, 138.72, 135.46, 133.72, 132.53, 131.80, 130.30, 128.39, 127.12, 126.07, 123.15, 21.24. MS (EI): m/z (%)=586 (M^+, 47.58), 587 [$(M+H)^+$, 14.90], 588 [$(M+2H)^+$, 100.00], 358 (36.90), 198 (88.90). HRMS (EI) calcd for $C_{26}H_{20}Br_2S_3$: 585.9094, found: 585.9097.

4.2.3. Compound ***2c***. Yield: 37%. Colorless oil. R_f=0.48 (petroleum ether/CH_2Cl_2 3:1). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.58 (t, J=1.6 Hz, 1H), 7.34 (d, J=2.0 Hz, 2H), 7.27 (d, J=8.0 Hz, 8H), 7.14 (d, J=8.0 Hz, 8H), 7.04 (d, J=1.6 Hz, 2H), 7.02 (t, J=1.6 Hz, 2H), 6.86–6.84 (m, 6H), 2.34 (s, 12H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 141.57, 139.67, 138.82, 136.85, 136.54, 134.34, 133.87, 132.61, 132.30, 132.21, 131.12, 129.52, 128.44, 127.30, 124.20, 21.80. MALDI-TOF-MS: m/z (%)=1046.0 (M^+, 40.58), 1047.9 [$(M+2H)^+$, 100.00]. MALDI-HRMS calcd for $C_{52}H_{40}Br_2S_7$: 1045.9542, found: 1045.9536.

4.3. General procedure for the preparation of [G-0]–[G-2] dendritic precursors 3a–c

Under an atmosphere of nitrogen, 10 mL THF and 10 mL *i*-Pr_2NH were added to a mixture of 4-ethynylpyridine hydrochloride (558 mg, 4.00 mmol), compounds **2a**–**c** (**2a**, 800 mg, 2.25 mmol; **2b**, 669 mg, 1.14 mmol; **2c**, 129 mg, 0.35 mmol), 0.05 equiv $Pd(PPh_3)_4$, and 0.05 equiv CuI in 100 mL Schlenk flask. The mixture was stirred at 65 °C for 12 h. Then insoluble materials were filtrated through filter paper and the solvent was removed by evaporation on a rotary evaporator. Column chromatography with CH_2Cl_2/methanol (50:1) as eluent afforded compounds **3a**–**c**.

4.3.1. Compound ***3a***. Yield: 84%. Gray solid. R_f=0.53 (CH_2Cl_2/methanol 50:1). Mp: 136 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.60 (d, J=6.0 Hz, 4H), 7.55 (t, J=1.6 Hz, 1H), 7.41–7.36 (m, 8H), 7.25 (d, J=8.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 150.13, 140.11, 139.36, 133.87, 132.73, 132.04, 130.81, 130.74, 129.10, 125.69, 123.69, 92.16, 88.24, 21.30. MS (EI): m/z (%)=402 (M^+, 100.00), 403 [$(M+1H)^+$, 32.00]. HRMS (EI) calcd for $C_{27}H_{18}N_2S$: 402.1191, found: 402.1192.

4.3.2. Compound ***3b***. Yield: 77%. Gray solid. R_f=0.48 (CH_2Cl_2/methanol 50:1). Mp: 164 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.62 (d, J=5.6 Hz, 4H), 7.62 (t, J=1.6 Hz, 1H), 7.46 (d, J=1.6 Hz, 2H), 7.42 (d, J=5.6 Hz, 4H), 7.28 (d, J=8.0 Hz, 4H), 7.14 (d, J=8.0 Hz, 4H), 6.83 (s, 1H), 6.82 (d, J=1.6 Hz, 2H), 2.39 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz):

δ 150.32, 141.25, 139.40, 136.93, 136.55, 135.17, 134.11, 134.07, 130.81, 130.69, 128.77, 127.06, 126.00, 125.82, 124.12, 91.77, 88.49, 21.35. MS (EI): *m/z* (%)=632 (M^+, 100.00), 633 [$(M+H)^+$, 50.26], 634 [$(M+2H)^+$, 22.90]. HRMS (EI) calcd for $C_{40}H_{28}N_2S_3$: 632.1415, found: 632.1414.

4.3.3. Compound ***3c***. Yield: 67%. Pale yellow solid. R_f=0.44 (CH_2Cl_2/methanol 50:1). Mp: 183 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.64 (d, *J*=6.0 Hz, 4H), 7.69 (t, *J*=1.2 Hz, 4H), 7.50 (t, *J*=1.2 Hz, 4H), 7.40 (d, *J*=6.0 Hz, 4H), 7.28 (d, *J*=8.0 Hz, 8H), 7.12 (d, *J*=8.0 Hz, 8H), 7.02–7.00 (m, 3H), 6.87 (t, *J*=1.6 Hz, 2H), 6.84 (d, *J*=1.6 Hz, 4H), 2.36 (s, 12H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 150.26, 141.14, 139.28, 138.19, 137.63, 136.31, 136.16, 135.26, 134.72, 133.90, 131.65, 131.32, 130.89, 130.72, 129.12, 127.90, 126.79, 125.95, 124.43, 91.84, 88.81, 21.39. LCMS (ESI): *m/z* (%)=1094 [$(M+2H)^+$, 10.00]. Anal. Calcd for $C_{66}H_{48}N_2S_7$: C, 72.49; H, 4.42; N, 2.56. Found: C, 72.86; H, 4.81; N, 2.84.

4.4. General procedure for the self-assembly of 5a–c

CD_2Cl_2 (1.0 mL) was added to a mixture of nitrate salts **4** (5.0 mg, 0.00430 mmol) and the appropriate [G-0]–[G-2] dendritic precursors **3a**–**c** (for **3a**, 1.73 mg, 0.00430 mmol; for **3b**, 2.71 mg, 0.00430 mmol; for **3c**, 4.70 mg, 0.00430 mmol). The reaction mixture was then stirred for 1 h at room temperature, upon which starting materials were completely dissolved and the reaction mixture attained a gray color. 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.

4.4.1. Compound ***5a***. Yield: 99%. Gray solid. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.30 (d, *J*=5.6 Hz, 4H), 8.79 (s, 4H), 8.70 (d, *J*=5.6 Hz, 4H), 7.96 (d, *J*=5.6 Hz, 4H), 7.83 (s, 2H), 7.73 (d, *J*=5.6 Hz, 4H), 7.60–7.53 (m, 12H), 7.46 (d, *J*=8.0 Hz, 4H), 7.30 (d, *J*=8.0 Hz, 4H), 2.42 (s, 6H), 1.36 (m, 48H), 1.18–1.10 (m, 72H). ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 12.65 (s, J_{Pt-P}=2705.67 Hz). CSI-TOF-MS $[M-2NO_3]^{2+}$, 1503.49; $[M-3NO_3]^{3+}$, 981.66. Anal. Calcd for $C_{130}H_{172}N_8O_{12}P_8Pt_4S_2\cdot CH_2Cl_2$: C, 48.92; H, 5.54; N, 3.58. Found: C, 48.86; H, 5.52; N, 3.57.

4.4.2. Compound ***5b***. Yield: 98%. Gray solid. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.39 (d, *J*=6.0 Hz, 4H), 8.83 (s, 4H), 8.72 (d, *J*=6.0 Hz, 4H), 8.01 (d, *J*=7.2 Hz, 4H), 7.91 (t, *J*=1.2 Hz, 2H), 7.76 (d, *J*=7.2 Hz, 4H), 7.61–7.58 (m, 12H), 7.31 (d, *J*=8.0 Hz, 8H), 7.18 (d, *J*=8.0 Hz, 8H), 6.90 (d, *J*=1.6 Hz, 4H), 6.84 (t, *J*=1.6 Hz, 2H), 2.37 (s, 12H), 1.37 (br, 48H), 1.19–1.11 (m, 72H). ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 12.51 (s, J_{Pt-P}=2713.77 Hz). CSI-TOF-MS $[M-2NO_3]^{2+}$, 1733.51; $[M-3NO_3]^{3+}$, 1135.01. Anal. Calcd for $C_{156}H_{192}N_8O_{12}P_8Pt_4S_6$: C, 52.17; H, 5.39; N, 3.12. Found: C, 52.03; H, 5.49; N, 3.10.

4.4.3. Compound ***5c***. Yield: 97%. Gray solid. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.39 (d, *J*=6.0 Hz, 4H), 8.83 (s, 4H), 8.72 (d, *J*=6.0 Hz, 4H), 8.01 (d, *J*=7.2 Hz, 4H), 7.91 (t, *J*=1.2 Hz, 2H), 7.76 (d, *J*=7.2 Hz, 4H), 7.61–7.58 (m, 12H), 7.31 (d, *J*=8.0 Hz, 8H), 7.18 (d, *J*=8.0 Hz, 8H), 6.90 (d, *J*=1.6 Hz, 4H), 6.84 (t, *J*=1.6 Hz, 2H), 2.37 (s, 12H), 1.37 (br, 48H), 1.19–1.11 (m, 72H). ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 12.46 (s, J_{Pt-P}=2716.68 Hz). CSI-TOF-MS $[M-2NO_3]^{2+}$, 2194.56; $[M-3NO_3]^{3+}$, 1442.39. Anal. Calcd for $C_{208}H_{232}N_8O_{12}P_8Pt_4S_{14}$: C, 55.35; H, 5.18; N, 2.48. Found: C, 55.30; H, 5.21; N, 2.29.

4.5. General procedure for the self-assembly of 7a–c

To a 0.5 mL CD_2Cl_2 solution of triflate **6** (6.02 mg, 0.00449 mmol) was added a 0.5 mL CD_2Cl_2 solution of the appropriate [G-0]–[G-2] dendritic donor precursor **3a**–**c** (for **3a**, 1.80 mg, 0.00449 mmol; for **3b**, 2.84 mg, 0.00449 mmol; for **3c**, 4.90 mg, 0.00449 mmol) drop by drop with continuous stirring (10 min). The reaction mixture was stirred 1 h at room temperature. The solution was evaporated to dryness, and the product was collected.

4.5.1. Compound ***7a***. Yield: 99%. Gray solid. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.70 (d, *J*=5.6 Hz, 4H), 7.81–7.77 (m, 5H), 7.56–7.43 (m, 12H), 7.29 (d, *J*=8.0 Hz, 2H), 2.41 (s, 3H), 1.36 (br, 24H), 1.18–1.10 (m, 36H). ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 13.30 (s, J_{Pt-P}=2652.41 Hz). CSI-TOF-MS $[M-5OTf]^{5+}$, 897.08. Anal. Calcd for $C_{198}H_{258}F_{18}N_6O_{21}P_{12}Pt_6S_9$: C, 45.46; H, 4.92; N, 1.61. Found: C, 45.58; H, 5.17; N, 1.59.

4.5.2. Compound ***7b***. Yield: 98%. Gray solid. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.72 (d, *J*=5.6 Hz, 4H), 7.88–7.84 (m, 5H), 7.56–7.53 (m, 9H), 7.30 (d, *J*=8.0 Hz, 4H), 7.17 (d, *J*=8.0 Hz, 4H), 6.91 (s, 2H), 6.82 (s, 1H), 2.36 (s, 6H), 1.36 (br, 24H), 1.19–1.11 (m, 36H). ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 13.38 (s, J_{Pt-P}=2647.06 Hz). CSI-TOF-MS $[M-5OTf]^{5+}$, 1035.52; Anal. Calcd for $C_{237}H_{228}F_{18}N_6O_{21}P_{12}Pt_6S_{15}$: C, 48.07; H, 4.90; N, 1.42. Found: C, 47.81; H, 4.95; N, 1.63.

4.5.3. Compound ***7c***. Yield: 98%. Gray solid. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.69 (d, *J*=5.6 Hz, 4H), 7.92–7.81 (m, 5H), 7.58–7.53 (m, 10H), 7.26 (d, *J*=8.0 Hz, 8H), 7.14 (d, *J*=8.0 Hz, 8H), 6.81 (s, 4H), 6.80 (s, 2H), 2.34 (s, 12H), 1.35 (br, 24H), 1.17–1.09 (m, 36H). ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 13.25 (s, J_{Pt-P}=2637.67 Hz). CSI-TOF-MS $[M-5OTf]^{5+}$, 1311.55. Anal. Calcd for $C_{315}H_{348}F_{18}N_6O_{21}P_{12}Pt_6S_{27}$: C, 51.80; H, 4.80; N, 1.15. Found: C, 51.90; H, 5.20; N, 1.29.

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Supplementary data

^{1}H NMR, ^{13}C NMR spectra of **2a**–**c**, **3a**–**c** and ^{1}H NMR, ^{31}P NMR spectra of **5a**–**c**, **7a**–**c**, and CSI-TOF-MS of **7a**–**c**. Supplementary data related to this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.04.058.

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