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Incorporation of 2,6-Di(4,4′-dipyridyl)-9-thiabicyclo[3.3.1]nonane into Discrete 2D Supramolecules via Coordination-Driven Self-Assembly

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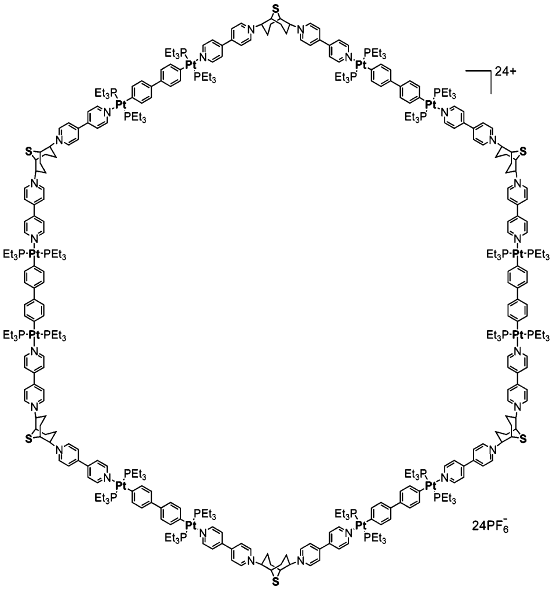

The synthesis and characterization of three new supramolecular complexes **6**−**8** (a rhomboid and two hexagons) via coordination-driven self-assembly are reported in excellent yields (>90%). These assemblies have 2,6-di(4,4′-dipyridyl)-9-thiabicyclo[3.3.1]nonane **2** as the bridging tecton. All assemblies were characterized by multinuclear NMR (^{1}H and ^{31}P), mass spectrometry (ESI-MS and ESI-FT-ICR), and elemental analysis. The X-ray structure of the 120° tecton **2** is also discussed.

The design and synthesis of transition-metal-containing discrete nanoscopic structures via coordination-driven self-assembly is a very popular methodology often utilized in supramolecular chemistry.[1−11] Several two-dimensional and three-dimensional supramolecular structures with well-defined shapes have been synthesized with potential applications in host−guest chemistry,[12−15] catalysis,[16−18] and chemical sensing.[19−21] As far as two-dimensional macrocyclic structures are concerned, there are numerous examples of smaller polygons, such as triangles,[22−27] rectangles,[28−30] and squares.[22,31−34] In

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comparison,there are fewer examples of larger polygons such as pentagons and hexagons.[35−39] Hexagonal structures are especially interesting because they are one of the most common patterns found in nature. In this context, one instantly remembers the crystal structure of graphite where the flat sheets of carbon atoms are bonded into hexagonal structures. In nature, the hexagonal pattern is also observed in the cells of a beehive honeycomb, and it is believed that this is the most efficient shape as far as space and building material are concerned. A hexagonal pattern is also observed in the skeletal arrangement of red corals. Planar hexagonal two-dimensional structures can be self-assembled in two different ways. One method is the combination of three 120° donor building blocks and three 120° acceptor angular linkers.[36] The other method is the combination of six linear ditopic subunits (180°) with six angular subunits possessing a 120° angle between their binding sites.[35]

The addition products of sulfur dichloride to cyclic dienes to form divalent "mustard" electrophiles were discovered nearly 40 years ago.[40−44] Because of their special reactivity,[45−48] these structures can serve as highly reliable scaffolds and connectors. We have identified one such molecule, 2,6-dichloro-9-thiabicyclo-[3.3.1]nonane (**1**, the product of SCl_2 + 1,4-cyclooctadiene), as a particularly attractive member of this class.[49] 2,6-Di(4,4′-dipyridyl)-9-thiabicyclo[3.3.1]nonane (**2**) is easily obtained by reaction of **1** with an excess of 4,4′-bipyridine, followed by anion exchange.[49a] Suitable single crystals of linker **2** were obtained at ambient temperature by vapor diffusion of *n*-pentane into a concentrated acetone solution. X-ray diffraction of the single crystal of **2** revealed that it possessed C_2 symmetry. The angle between the two dipyridyl rings is ca. 120°, which renders it a suitable 120° donor linker required for the formation of molecular hexagons and rhomboids. Figure 1 shows the ORTEP representation of **2**. Relevant crystallographic data for **2** are available in the Supporting Information.

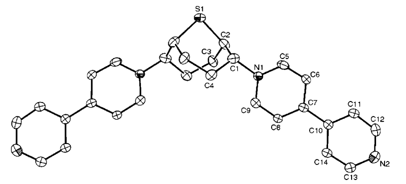

FIGURE 1. ORTEP diagram of **2**. The anion PF_6 has been omitted for clarity. Thermal ellipsoids are drawn to 30% probability.

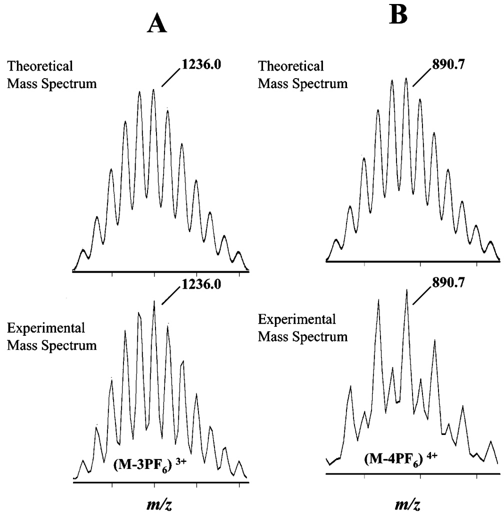

FIGURE 2. Electrospray ionization mass spectrum of rhomboid **6** (A) $[M - 3PF_6]^{3+}$, (B) $[M - 4PF_6]^{4+}$.

We describe here the first use of this type of readily available and structurally rigid connector in the coordination-driven self-assembly of metal-based supramolecular ensembles. In particular, **2** combines with linear and bent bifunctional Pt coordination modules to produce rhomboid and hexagonal structures in high yields (Scheme 1). All assemblies have been characterized by ^1H and ^{31}P NMR, ESI and FT-ICR mass spectrometry, and elemental analysis.

The reaction of **2** with an equimolar amount of the 60° diplatinum acceptor **3** in a 5:1 (v:v) acetone-d_6/D_2O mixture gave the [2+2] rhomboidal assembly **6**. Anion exchange with KPF_6 facilitated straightforward isolation of the assembly **6** as a hexafluorophosphate salt in excellent yield (95%). The ^{31}P $\{^1H\}$ NMR spectrum of **6** showed a single sharp peak at 18.77 ppm shifted approximately 5 ppm upfield relative to that of **3**. This change, as well as the decrease in coupling of the flanking ^{195}Pt satellites ($\Delta J = -203$ Hz), is consistent with back-donation from the platinum atoms. In the ^1H NMR spectrum of **6**, the α_1-hydrogen atoms of the pyridine rings connected to the Pt−center of **2** experienced 0.5 ppm downfield shifts due to the loss of electron density upon coordination of the pyridine−N atom with the Pt(II) metal center. Two doublets have been observed for these $H\alpha_1$ of the pyridine ring, and this might be attributed to hindered rotation about the Pt−N(bipyridyl) bond.[50] In the ESI mass spectrum of rhomboid **6**, two charged states were observed at $m/z = 890.3$ and 1235.0, corresponding to the $[M - 4PF_6]^{4+}$ and $[M - 3PF_6]^{3+}$ species, respectively (see Supporting Information for full mass spectrum). These peaks were isotopically resolved (Figure 2), and they agreed very well with the theoretical distribution. However, the rhomboid does not appear to be very stable under the ESI-MS conditions. In Figure 2B, the isotopically resolved $[M - 4PF_6]^{4+}$ peak ($m/z = 890.3$) of the assembly overlaps with a peak corre-

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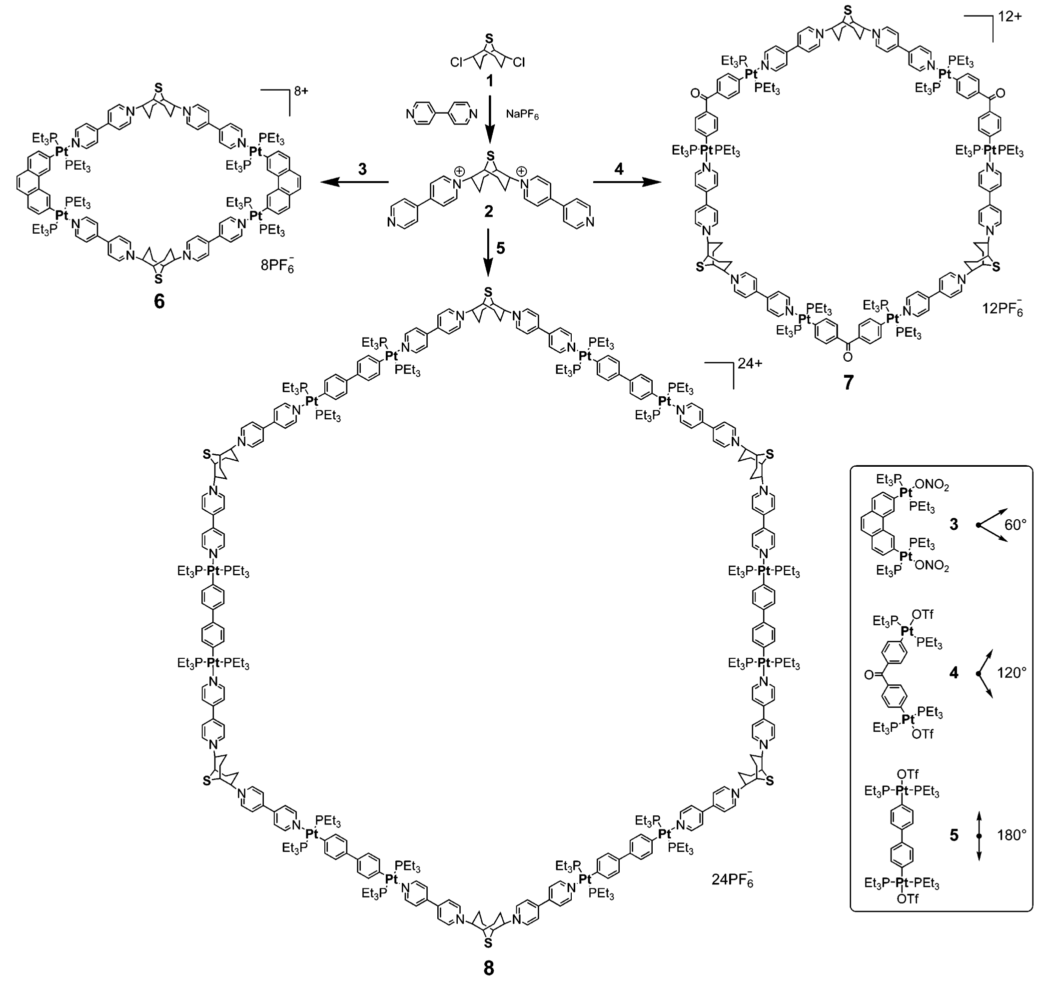
SCHEME 1. Self-Assembly of 2 with Platinum Acceptors 3−5



sponding to a +2 species. The latter is most likely due to a 1+1 dissociation fragmentation of **6**.

When **2** was reacted with the 120° platinum acceptor **4** in acetone-d_6 at room temperature, after the anion exchange with PF_6, the [3+3] assembly **7** was formed in high yield (96%). $^{31}P\ \{^1H\}$ NMR analysis of the reaction mixture is consistent with the formation of a single, highly symmetrical species by the appearance of a sharp singlet at 9.25 ppm with concomitant ^{195}Pt satellites, shifted 14.5 ppm upfield ($\Delta\delta$) relative to **4** ($\Delta^1J_{PPt} = -96$ Hz). As expected, in the ^1H NMR spectrum of **7**, the α_1-hydrogen nuclei of the pyridine rings exhibited ~0.6 ppm downfield shifts. Two charged states at $m/z = 1099.5$ and 1410.8 were observed in the ESI mass spectrum of hexagon **7**, corresponding to the $[M - 5PF_6]^{5+}$ and $[M - 4PF_6]^{4+}$ species, respectively (see Supporting Information for full mass spectrum). The isotopic resolution of these peaks ($m/z = 1410.8$ and 1099.5) was not good due to overlap with some unidentifiable fragments (see Supporting Information Figure S5). The peak at $m/z = 1410.8$ ($[M - 4PF_6]^{3+}$) was also observed in the ESI-FT-ICR mass spectrum of **7**, and its isotopic resolution is in excellent agreement with the theoretical distribution (Figure 3A).

The [6+6] assembly **8** was synthesized by using similar conditions that were used to prepare **7**. In the $^{31}P\ \{^1H\}$ NMR spectrum of assembly **8**, a sharp singlet (19.0 ppm) suggests the formation of a discrete, highly symmetric assembly. The upfield shift ($\Delta\delta = 3.19$ ppm) relative to the platinum acceptor **5**, along with the change in coupling of the flanking ^{195}Pt satellites ($\Delta^1J_{PPt} = -152$ Hz), is indicative of coordination of platinum centers of **5** to pyridine moieties of **2**. Examination of the ^1H NMR spectrum of assembly **8** is also indicative of a highly symmetrical structure and displays a significant spectroscopic difference from its monomeric subunits. In the ^1H NMR spectrum of assembly **8**, the α_1-hydrogen nuclei of the pyridine rings exhibit about 0.5 ppm downfield shifts. In contrast to **6**, the ^1H NMR spectra of **7** and **8** show only one doublet for

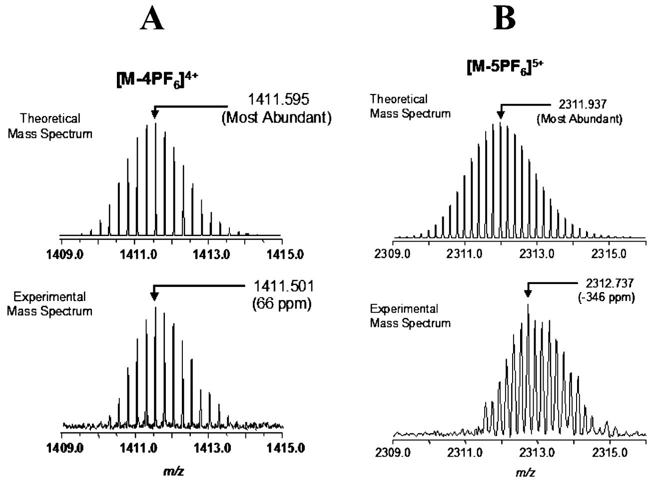


FIGURE 3. ESI-FT-ICR mass spectrum of hexagon **7** (A) and **8** (B).

the $H\alpha_1$ protons of the pyridine ring linked to the Pt(II) center. This may be due to free rotation of the Pt−N(bipyridyl) bond in these macrocycles (**7** and **8**) which are much larger than the rhomboidal ensemble **6**. The structure of assembly **8** was confirmed using ESI-FT-ICR due to the presence of the peak at $m/z = 2312.74$ which corresponds to a $[M - 5PF_6]^{5+}$ species derived from a [6+6] hexagonal macrocycle (Figure 3B). The theoretical (top spectrum) and externally calibrated experimental (bottom spectrum) isotopic distributions are exhibited in Figure 3B. No evidence for any other species such as a [5+5] pentagonal assembly was found.

The connector **2** is chiral and was used as a racemate. No conclusive evidence for the presence of diastereomers, resulting from the incorporation of different combinations of enantiomers of **2** in any of the supramolecular ensembles **6**−**8**, was observed by NMR. However, it is unlikely that such structures would be distinguishable by these means. In any event, we suspect that the cyclic structures are sufficiently large and flexible to be insensitive to the chirality of the 120° corner connectors.

The combination of a linear ditopic unit with a 120° angular unit in a 1:1 ratio can yield pentagons as well as hexagons because small distortions in the bond angles of the building blocks are energetically not very costly.[3] However, in the case of **2**+**5**, only hexagons are formed. This may be due to a particular conformational rigidity of the system (favoring the ideal geometry to a greater extent than usual) or to other factors (such as the highly charged nature of the assembled structures and the interplay between entropic and enthalpic contributions[38,51]) that are poorly understood.

Three new supramolecular polycationic complexes **6**−**8** (a rhomboid and two hexagons) containing a sulfur mustard-derived rigid donor ligand are obtained in excellent yields by a coordination-driven self-assembly process. The structures of all assemblies have been confirmed by multinuclear NMR, elemental analysis, and mass spectrometry with isotopic resolution. The two hexagons differ dramatically in size by virtue of the size of the Pt acceptor unit. The facile synthetic chemistry of the 120° scaffold precursor, **1**, suggests that other connectors of a different length or bearing additional functional groups can be readily made and incorporated into nanoscale architectures.

Experimental Section

Methods and Materials. Organoplatinum compounds **3**,[26] **4**,[36] and **5**[52] were prepared as reported.

Self-Assembly of Rhomboid 6. 2,9-(*trans*-$Pt(PEt_3)_2NO_3)_2$-phenanthrene **3** (3.85 mg, 0.0033 mmol) and the 120° donor linker **2** (2.45 mg, 0.0033 mmol) were placed in a 2-dram vial. A mixture solvent (acetone-d_6/D_2O 5:1, 1 mL) was added. The reaction mixture was stirred overnight at 55 °C, upon which **3** was completely dissolved and the reaction mixture attained an orange color. The orange solution was then transferred to an NMR tube for analysis. The product thus obtained was precipitated with KPF_6, collected on a frit, washed with excess water, and dried in vacuo. Yield: 95%. ^1H NMR (acetone-d_6/D_2O 5:1, 300 MHz): δ 9.52 (d, $J = 6.6$ Hz, 8H, H_α2-Py), 9.32 (d, $J = 6.0$ Hz, 4H, H_α1-Py), 9.24 (d, $J = 5.4$ Hz, 4H, H_α1-Py), 8.85 (m, 8H, H_β2-Py), 8.72 (s, 4H, H_1), 8.48−8.52 (m, 8H, H_β1-Py), 7.72 (d, $J = 8.1$ Hz, 4H, H_3), 7.61−7.65 (m, 8H, H_4 and H_5), 5.88−5.93 (m, 4H), 3.44−3.56 (m, 8H), 2.56 (m, 12H), 1.41 (m, 48H, PCH_2CH_3), 1.02−1.20 (m, 72H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (acetone-d_6/D_2O 5:1, 121.4 MHz): δ 18.77 (s, $^1J_{Pt-P} = 2683.9$ Hz). Anal. Calcd for $C_{132}H_{192}F_{48}N_8P_{16}Pt_4S_2$: C, 38.27; H, 4.67; N, 2.70. Found: C, 38.18; H, 4.84; N, 2.58.

Self-Assembly of Hexagon 7. To 0.5 mL of acetone-d_6 solution containing 5.51 mg (0.0041 mmol) of triflate salt **4** was added 0.5 mL of acetone-d_6 solution of **2** (3.04 mg, 0.0041 mmol) drop by drop with continuous stirring (10 min). The reaction mixture was stirred overnight at room temperature. The solution was then transferred to an NMR tube for analysis. The product thus obtained was precipitated with KPF_6, collected on a frit, washed with excess water, and dried in vacuo. Yield: 96%. ^1H NMR (acetone-d_6, 300 MHz): δ 9.62 (d, $J = 6.3$ Hz, 12H, H_α2-Py), 9.34 (d, $J = 6.0$ Hz, 12H, H_α1-Py), 8.80 (d, $J = 6.3$ Hz, 12H, H_β2-Py), 8.48 (d, $J = 6.0$ Hz, 12H, H_β1-Py), 7.73 (d, $J = 7.8$ Hz, 12H, Ph*H*), 7.59 (d, $J = 7.8$ Hz, 12H, Ph*H*), 6.03 (m, 6H), 3.64 (br, 12H), 2.59 (m, 18H), 1.51 (m, 72H, PCH_2CH_3), 1.15−1.29 (m, 108H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (acetone-d_6, 121.4 MHz): δ 9.25 (s, $^1J_{Pt-P} = 2647.1$ Hz). Anal. Calcd for $C_{195}H_{288}F_{72}N_{12}O_3P_{24}Pt_6S_3$: C, 37.62; H, 4.66; N, 2.70. Found: C, 37.82; H, 4.88; N, 2.55.

Self-Assembly of Hexagon 8. To 0.5 mL of CD_2Cl_2 solution containing 5.92 mg (0.0055 mmol) of triflate salt **5** was added 0.5 mL of acetone-d_6 solution of **2** (4.08 mg, 0.0055 mmol) drop by drop with continuous stirring (10 min). The reaction mixture was stirred overnight at room temperature. The orange solution was then transferred to an NMR tube for analysis. The product was precipitated with KPF_6, collected on a frit, washed with excess water, and dried in vacuo. Yield: 95%. ^1H NMR (acetone-d_6/CD_2Cl_2 1:1, 300 MHz): δ 9.58 (d, $J = 5.7$ Hz, 24H, H_α2-Py), 9.25 (d, $J = 5.7$ Hz, 24H, H_α1-Py), 8.75 (d, $J = 5.7$ Hz, 24H, H_β2-Py), 8.42 (d, $J = 5.4$ Hz, 24H, H_β1-Py), 7.46−7.54 (m, 48H, Ph*H*), 6.01 (br, 12H), 3.60 (br, 24H), 2.57 (m, 36H), 1.47 (m, 144H, PCH_2CH_3), 1.13−1.27 (m, 216H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (acetone-d_6/CD_2Cl_2 1:1, 121.4 MHz): δ 19.0 (s, $^1J_{Pt-P} = 2686.3$ Hz). Anal. Calcd for $C_{384}H_{576}F_{144}N_{24}P_{48}Pt_{12}S_6$: C, 37.54; H, 4.73; N, 2.74. Found: C, 37.54; H, 4.96; N, 2.57.

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Supporting Information Available: ^{31}P and ^1H NMR spectra of all assemblies **6**−**8**, ESI/MS of **6** and **7**, ESI-FTI-CR/MS of **7** and **8**, and crystallographic file (in CIF format) of linker **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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