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Self-assembly of coordinative supramolecular polygons with open binding sites

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Dedicated to Professor Harry H. Wasserman on the occasion of his 90th birthday

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ABSTRACT

The design and synthesis of coordinative supramolecular polygons with open binding sites is described. Coordination-driven self-assembly of 2,6-bis(pyridin-4-ylethynyl)pyridine with 60° and 120° organoplatinum acceptors results in quantitative formation of a supramolecular rhomboid and hexagon, respectively, both bearing open pyridyl binding sites. The structures were determined by multinuclear (^{31}P and ^{1}H) NMR spectroscopy and electrospray ionization (ESI) mass spectrometry, along with a computational study.

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Coordination-driven self-assembly, the supramolecular architecture methodology relying on metal–ligand bonding interactions, has proven powerful for accessing well-defined coordinative supramolecules over the past two decades.[1] The rational design of rigid molecular building blocks via coordination-driven self-assembly allows for the formation of discrete supramolecules of variable topologies, as demonstrated by the myriad of metallo-supramolecular grids, polygons, cages, and polyhedra.[1a–l] In general, supramolecules obtained by coordinative self-assembly are fully coordinated, wherein all coordinative binding sites of the building blocks are fully in use upon coordination.[1] Such structures benefit from facile design principles and the potential for isomeric byproducts is minimized. Conversely, reports of coordinative supramolecules containing open binding sites are rare.[2]

Coordinative supramolecules with open binding sites are of interest due to the potential characteristics afforded by open binding sites. Recently, metal-organic frameworks (MOFs) bearing open binding sites have attracted considerable attention in the chemistry and material science literature.[3] These sites enable post-synthetic modification and impart catalytic behavior and gas absorption properties to the MOFs possessing them. A similar effect was observed in a study of coordinative polymers bearing unsaturated metal centers, which could be used as catalysts by exploiting the properties of their open metal coordination sites.[4] For finite coordinative supramolecules, Hupp and coworkers have prepared and studied the catalytic behavior of unsaturated metalloporphyrins.[2a–c] Recently, we presented a coordinative supramolecular rectangle capable of sensing transition metal ions, the key feature being open phenanthroline binding sites.[2d]

The major issue limiting the development of coordinative supramolecules with open binding sites is the synthetic difficulty resulting from open binding sites interrupting the assembly of the structural backbone, resulting in undesirable isomeric supramolecules as well as oligomers. Thus, in the reported examples,[2] the binding moieties used in the self-assembly of the structural backbones are different from the open binding sites, to prevent side product formation. However, this method limits the diversity of potential structures and minimizes the number of usable ligands. In this work, we present the facile synthesis of supramolecular polygons bearing open binding sites, wherein the open substituent is the same species used for self-assembly of the backbone.

2,6-Bis(pyridin-4-ylethynyl)pyridine **1** was prepared by the Sonogashira coupling reaction of 2,6-diacetylenepyridine[5] and 4-bromopyridine (see Supplementary data). Ligand **1** contains two types of pyridyl moieties: terminal pyridine and central pyridine; the terminal pyridines are designed to direct self-assembly of the structural backbone and the central pyridine acts as the open binding site. According to the directional bonding model,[1a] as shown in Scheme 1, donor **1** can undergo [2 + 2] and [3 + 3] self-assemblies with 60° and 120° organoplatinum acceptors **2**[6] and **3**,[7] to form a rhomboid[8] and a hexagon[9] **4** and **5**, respectively. The self-assembly of **1** with **2** or **3** was carried out by mixing the donor and acceptor in a 1:1 ratio in aqueous acetone solution (v/v 1:1). After heating at 75 °C for 5 h, the completed self-assembly was isolated by ion exchange with KPF_6. The product was characterized by ^{31}P and ^{1}H multinuclear NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS), the results of which indicate that rhomboid **4** and hexagon **5**, bearing open pyridyl cores, were formed

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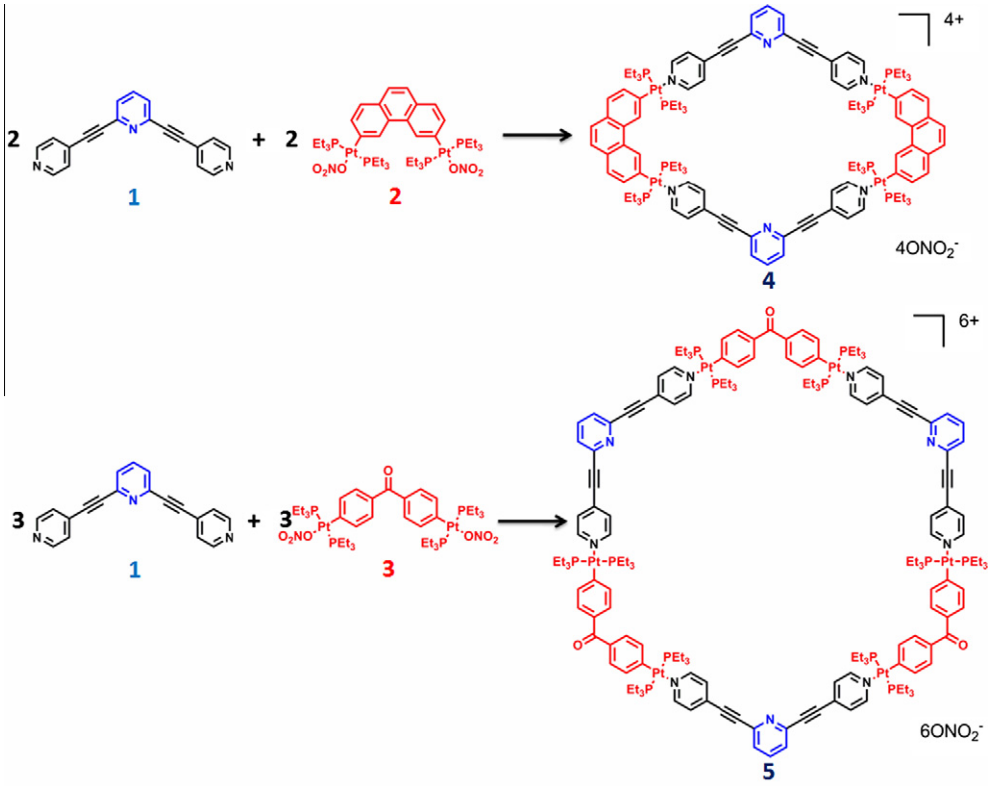

Scheme 1. Representation of the self-assembly of supramolecular rhomboid **4** and hexagon **5** bearing open pyridyl binding sites.

quantitatively in the mixtures. No isomeric byproducts resulting from the coordination of the central pyridine of ligand **1** to Pt was observed in either case.

As shown in Figure 1, the $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixtures show only one singlet signal at 14.3 ppm for **4** and 13.9 ppm for **5** with contaminant ^{195}Pt satellites, indicating that one highly symmetrical assembly was formed in each mixture. Likewise, in the ^{1}H NMR spectra (Fig. 2b and Fig. S2 in Supplementary data), signals attributed to the terminal pyridyl protons of **1** can be found at 8.98 ppm ($H_{Py\text{-}\alpha}$) and 7.93 ppm ($H_{Py\text{-}\beta}$) for rhomboid **4** and at 8.90 ppm ($H_{Py\text{-}\alpha}$) and 7.88 ppm ($H_{Py\text{-}\beta}$) for hexagon **5**. A comparison with the spectrum of **1** (Fig. 2a) indicates that these signals are downfield shifted ($\Delta\delta$ = 0.2–0.3 ppm) upon coordination to the Pt metal centers. In contrast, the central pyridyl protons exhibit only minor shifts ($\Delta\delta$ = 0.01 ppm for $H_{Py\text{-}\gamma\text{-}Core}$; $\Delta\delta$ = 0.05 ppm for $H_{Py\text{-}\beta\text{-}Core}$). These results are consistent with the terminal pyridines of **1** being involved in coordination-driven self-assembly, resulting in the formation of one discrete supramolecular polygon bearing open pyridyl cores.

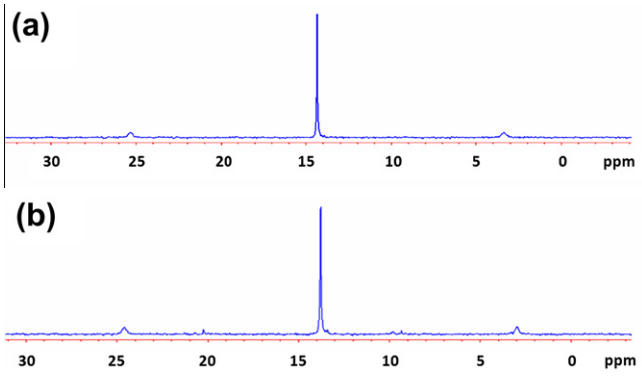

Figure 1. $^{31}P\{^{1}H\}$ NMR spectra (121.4 MHz) of the coordinative supramolecular rhomboid (a) and hexagon (b) in acetone-d_6/D_2O (v/v 1:1).

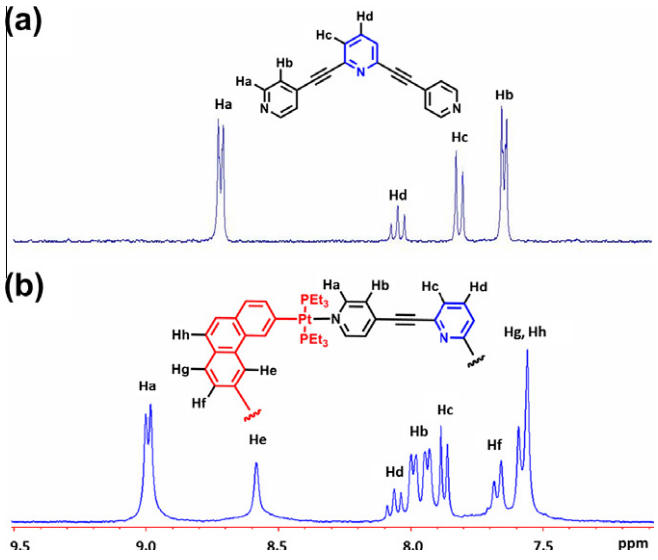

Figure 2. ^{1}H NMR spectra (300 MHz) of free ligand **1** in acetone-d_6 (a) and the coordinative supramolecular rhomboid **4** in acetone-d_6/D_2O (v/v 1:1) (b).

ESI mass spectral analysis further supports the formation of rhomboid **4** and hexagon **5**. As shown in Figure 3 and Figure S3 in the Supplementary data, the ESI mass peaks corresponding to the consecutive loss of nitrate anions from rhomboid **4**: m/z = 1382.3 $[M-2NO_3^-]^{2+}$ and m/z = 900.5 $[M-3NO_3^-]^{3+}$ are