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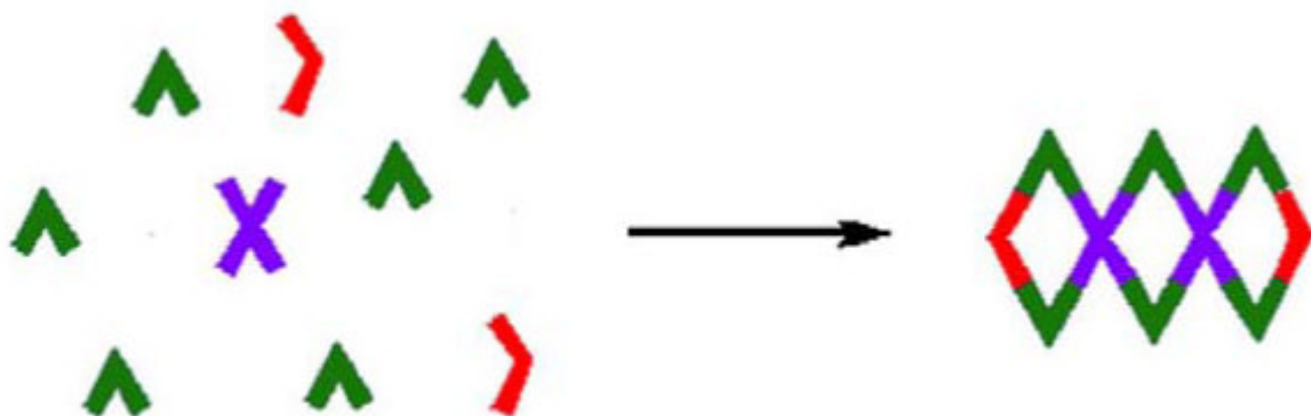
Stoichiometric Control of Multiple Different Tectons in Coordination-Driven Self-assembly:

Preparation of Fused Metallacyclic Polygons

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Abstract



We present a general strategy for the synthesis of stable, multi-component fused polygon complexes where coordination-driven self-assembly allows for single supramolecular species can be formed from multi-component self-assembly and the shape of the obtained polygons can be controlled by simply changing the ratio of individual components. The compounds are characterized by Multinuclear NMR, ESI Mass spectrometry.

From the point of view of the bottom-up strategy of materials self-assembly, it is essential to be able to control the shapes and sizes of supramolecules at the nanoscale precisely and easily.

¹ Over the past two decades, many finite supramolecular two-dimensional (2D) and three-dimensional (3D) structures with well defined and often predetermined shapes, sizes, and geometries have been prepared via the coordination-driven self assembly of simple building blocks.² With the general success and breadth of the coordination-driven approach, some attention has turned toward optimization rather than the discovery of new materials. However, it is often the search for and discovery of new materials that lends considerable insight into their formation and opens the door to many new compounds. Knowing that self assembly involves both self-healing and self-sorting processes to minimize the total free energy (ΔG°) of a given system, the coordination-driven self assembly of supramolecules consisting of multiple components can be a powerful method for controlling the shapes and sizes of new classes of supramolecules. Previously multicomponent species are reported to form discrete structures based on the orthogonality of various weak reversible interactions³; however more than two different donor and acceptor units combined in specific stoichiometric ratios used to self-assemble a single, discrete metallacycle is so far unknown.

We have previously shown that the formation of single discrete species by coordination driven self-assembly can be achieved based on the information encoded within the coordination geometry and directionality of individual donor and acceptor units. We have not only utilized the size and shape of the tectons but also their stoichiometric ratio in order to form single discrete structures. Multi-component mixtures of donor and acceptor units, generally prefer to self-assemble into multiple species through self-recognition processes despite the possibility of oligomer formation.⁴ We envisioned that properly designed multi-component donor and acceptor units combined in designed stoichiometric ratios can lead to a single stable structure rather than multiple discrete metallasupramolecules. Here we have used appropriately designed self-assembly algorithms to form new conjoined supramolecular polygons as single discrete species.

To design the self-assembly of fused polygons, we initially envisioned two or three polygons with overlapping vertexes or sides. From there, one can imagine that conjoined triangle or rhomboid structures can be self-assembled by a vertex-overlapping strategy. By designing multiple donor precursors to function as the overlapped vertex, one can easily synthesize fused supramolecules having different sizes.

Therefore we chose a strategy for self-assembling a double triangle that uses a 2-fold symmetric tetrapyridyl donor. Because the bridging component should have similar connectivity to the tecton located in the opposite vertex, we designed 3,5,3',5' tetrapyridylethynyl-biphenyl as donor **2**, which is similar to **1**. The tetra-pyridine donor **2** can be easily prepared via a Sonogashira coupling reaction of 3,5,3',5'-tetrabromo-biphenyl⁵ and 4-ethynylpyridine hydrochloride.

Stirring a mixture of donor **1**, **2** and 180 ° di-Pt(II) acceptor **3** in a 4 : 1 : 6 ratio resulted in the formation of the double-triangle **4** (Scheme 1). Multinuclear NMR (¹H and ³¹P) analysis of the reaction mixture indicates the formation of a discrete supramolecule with high symmetry. The ³¹P {¹H} NMR displayed a singlet with a shoulder (13.8 ppm) shifted 8.4 ppm upfield from the peak of the starting platinum acceptor **3**, for the two different phosphorous signals expected for **4**. The appearance of one single peak with a shoulder in ³¹P NMR implies that the chemical environment around the phosphorous varies little with two similar types of donors. Additionally, the protons of the pyridine rings exhibited 0.2 ~ 0.4 ppm downfield shifts, resulting from the loss of electron density upon coordination of the pyridine-N atom with the Pt(II) metal center.

Electrospray ionization (ESI) mass spectrometry provides further evidence for the formation of the new fused triangle **4**. The ESI mass spectra for double triangle **4** revealed peaks at *m/z* = 2225.07 and 1749.50, corresponding to [M - 4OTf]⁴⁺ and [M - 5OTf]⁵⁺, respectively (Figure 1 & Figure S7 in Supporting Information). Both peaks were isotopically resolved, and they agree very well with the theoretical distribution. The full spectrum indicates that no other products exist in the solution of double triangle **4**. Consequently, it is possible to synthesize discrete fused metallacycles structure via multicomponent self-assembly.

We then tried to extend this protocol from triangular to rhomboidal systems. Tetra-pyridine donor **2** can also be used as a linker in the formation of double- and triple-rhomboid structures. Whereas donor **1**, with two pyridine arms angled 60° from each other, was used in the formation of double triangle **4**, a different bispyridine (**5**) with an angle of 120° between coordination sites is required for the formation of multi-rhomboid polygons such as **7** and **8**. Reacting a mixture of donors **2** and **5** with 180° di-Pt(II) acceptor **6** in a 1 : 2 : 4 gave double-rhomboid **7**. Moreover, when the ratio was changed to 1 : 1 : 3, triple-rhomboid **8** was readily obtained (Scheme 2).

A single set of signals from the donor and acceptor units in the ^1H NMR of **7** and **8** indicates the formation of a single, discrete, highly symmetric supramolecular assembly for each reaction. For both **7** & **8** two ^{31}P signals are predicted, however, for **7** only a single signal was observed, whereas for **8** two overlapping signals were observed, indicating as expected a close similarity of the two phosphorous environments in both **7** & **8**. (See Supporting Information) In the ESI mass spectra of double rhomboid **7**, peaks at $m/z = 2070.5$ and $m/z = 1182.3$ attributable to $[\text{M} - 3\text{OTf}]^{3+}$ and $[\text{M} - 5\text{OTf}]^{5+}$, respectively, were observed (Figure 1 & Figure S8 in Supporting Information). The full spectrum showed that no other products exist in the solution of double rhomboid **7**. Furthermore, the ESI mass spectra for triple rhomboid **8** revealed a peak at $m/z = 1847.6$ and $m/z = 3179.3$, corresponding to $[\text{M} - 5\text{OTf}]^{5+}$ and $[\text{M} - 3\text{OTf}]^{3+}$, respectively (Figure 1 & Figure S9 in Supporting Information). The full spectrum of triple-rhomboid **8** indicates that there are no other products in the complex mixture and no evidence of the smaller double-rhomboid **7**. Further, PGSE experiments were used to find the diffusion coefficient. The ratio of the diffusion coefficients of rhomboid **7** and **8** is 1.6:1, indicating that their hydrodynamic diameters lie in the inverse ratio of 1:1.6, since D is inversely proportional to the molecular size. Molecular force field simulations showed outer diameters of about 5.5 and 8.6 nm for **7** and **8**, respectively, which are in relative, qualitative agreement with the experimentally determined ratio. (See Supporting Information) Consequently, we have demonstrated that it is possible to control the shape and size of supramolecules by simply tuning the relative ratio of multi-component donor/acceptor mixtures.

All attempts to obtain the crystal structure of higher order polygons **4**, **7** & **8** have so far been unsuccessful. Therefore, molecular force-field simulations were used to gain further insight into the structural characteristics of supramolecular complexes **4**, **7** & **8** (Figure 1 and Figure S10 in Supporting Information). A 1.0 ns molecular dynamics simulation (MMFF force field) was used to equilibrate the supramolecules, followed by energy minimization of the resulting structures to full convergence. The rotation around the single bond of the biphenyl moiety of **2** makes **4**, **7** and **8** nonplanar.

In conclusion, new self-assembled fused metallacyclic polygons have been synthesized through stoichiometric and structural control of multi-component mixtures of different pyridyl donors and platinum acceptors. These studies have revealed that single supramolecular species can be formed from multi-component self-assembly and the shape of the product polygons can be controlled by simply changing the ratio of individual components, thus demonstrating that various multi supramolecular architectures can be synthesized from multiple diverse tectons via a dynamic coordination-driven self-assembly process when appropriate components are mixed in a controlled ratio. To the best of our knowledge this represents the first report of the formation of predesigned, discrete products using multiple different tectons via the coordination driven methodology.

Supplementary Material

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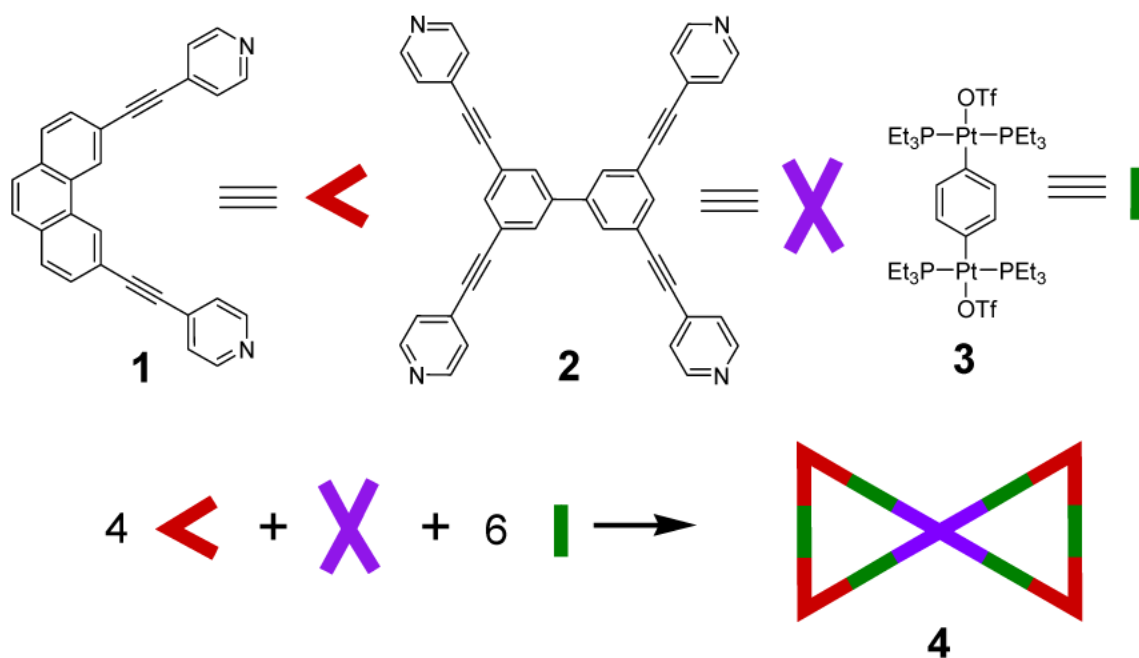
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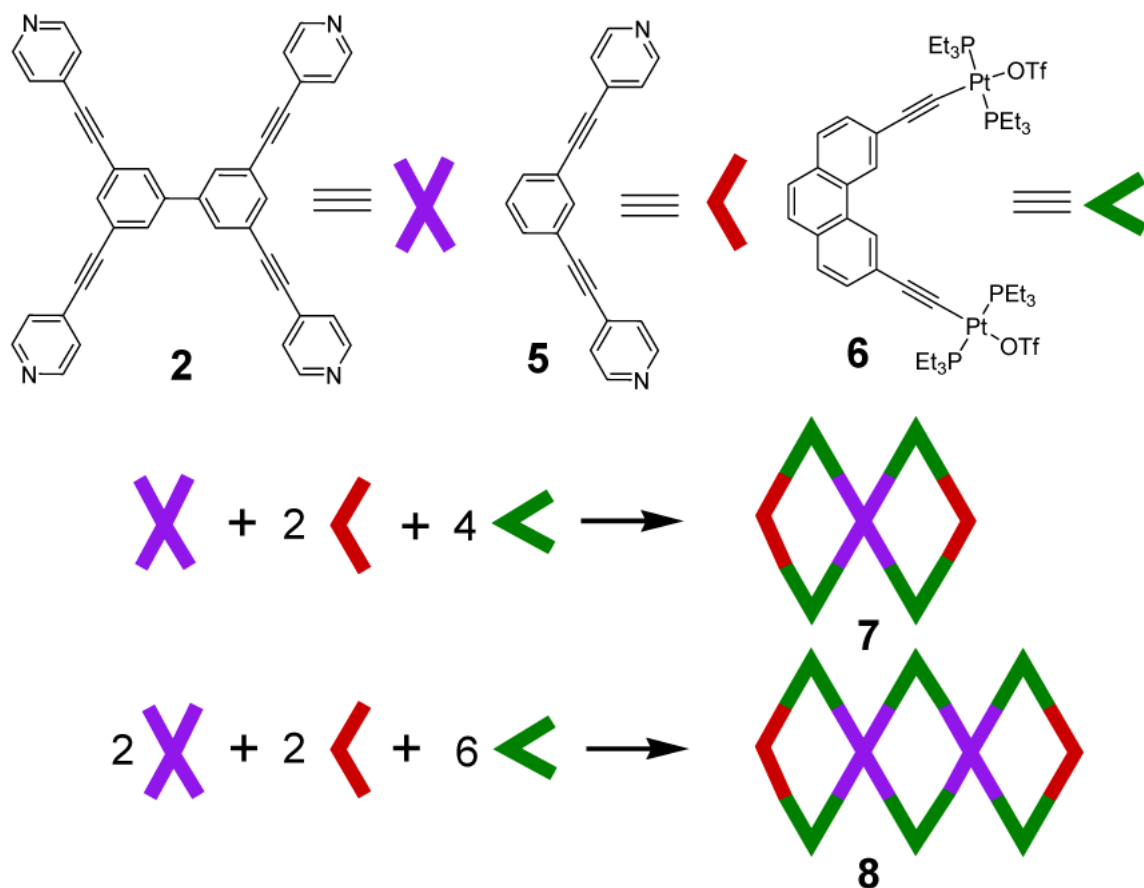
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Scheme 1.
Synthesis of Double Triangle 4.



Scheme 2.
Synthesis of Fused Rhomboid 7 & 8.

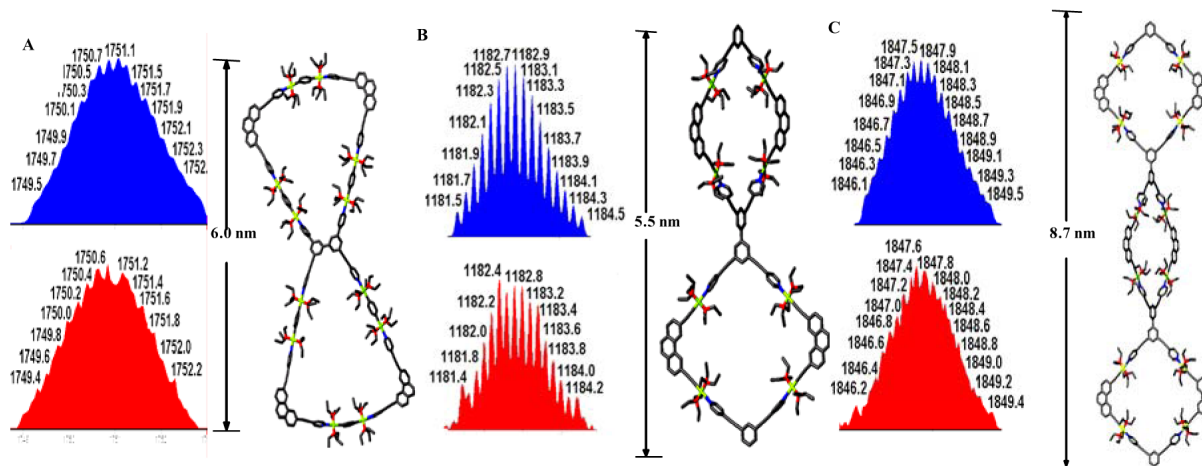


Figure 1. Calculated (top, blue) and experimental (bottom, red) ESI-MS spectrum (5+) and molecular force field model of double triangle 4 (A), double rhomboid 7 (B) and triple rhomboid 8 (C).