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Stoichiometric Control of Multiple Different Tectons in Coordination-Driven Self-Assembly: Preparation of Fused Metallacyclic Polygons

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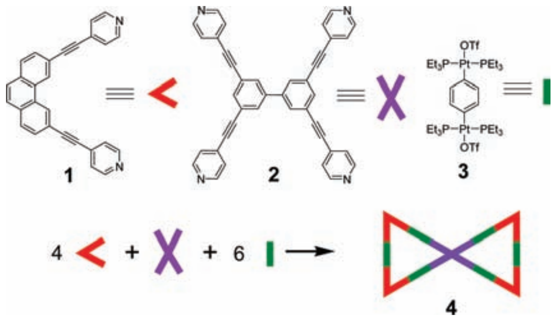
In the bottom-up strategy of materials self-assembly, it is essential to be able to control the shapes and sizes of supramolecules at the nanoscale precisely and easily.[1] Over the past two decades, many finite supramolecular two-dimensional (2D) and three-dimensional (3D) structures with well-defined and often predetermined shapes, sizes, and geometries have been prepared via 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. Since self-assembly involves both self-healing and self-sorting processes to minimize the total free energy ($\Delta G°$) of a given system, 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 have been reported to form discrete structures based on the orthogonality of various weak reversible interactions;[3] however, more than two different donor and acceptor units combined in specific stoichiometric ratios used to self-assemble a single, discrete metallacycle is unknown to date.

We have previously shown that the formation of single discrete species by coordination-driven self-assembly can be achieved from the information encoded within the coordination geometry and directionality of individual donor and acceptor units. We have utilized not only the size and shape of the tectons but also their stoichiometric ratio to form single discrete structures. Multicomponent 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 multicomponent donor and acceptor units combined in designed stoichiometric ratios could 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 could 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 twofold-symmetric tetrapyridyl donor. Because the bridging component should have similar connectivity to the tecton located in the opposite vertex, we designed the bridging donor 3,5,3′,5′-tetrakis(pyridylethynyl)biphenyl (**2**), which is similar to donor **1**. The tetrapyridine donor **2** can be easily prepared via Sonogashira coupling of 3,5,3′,5′-tetrabromobiphenyl[5] and 4-ethynylpyridine hydrochloride.

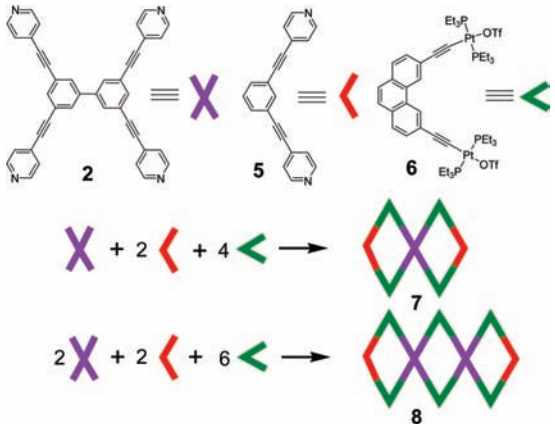
Scheme 1. Synthesis of Double Triangle **4**



Stirring a mixture of donors **1** and **2** and 180° di-Pt(II) acceptor **3** in a 4:1:6 ratio resulted in the formation of double triangle **4** (Scheme 1). Multinuclear (^{1}H and ^{31}P) NMR analysis of the reaction mixture indicated the formation of a discrete supramolecule with high symmetry. The ^{31}P{^{1}H} NMR spectrum 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 phosphorus signals expected for **4**. The appearance of a single peak with a shoulder in the ^{31}P NMR spectrum implies that the chemical environment around the P atoms varies little for the 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 mass spectrometry (ESI-MS) provided further evidence for the formation of the new fused triangle **4**. The ESI mass spectrum for double triangle **4** revealed peaks at m/z 2225.07 and 1749.50, corresponding to $[\mathrm{M} - 4\mathrm{OTf}]^{4+}$ and $[\mathrm{M} - 5\mathrm{OTf}]^{5+}$, respectively [Figure 1 and Figure S7 in the Supporting Information (SI)]. Both peaks were isotopically resolved and agreed very well with the theoretical distribution. The full spectrum indicated that no other products existed in the solution of double triangle **4**. Consequently, it is possible to synthesize a discrete fused metallacycle structure via multicomponent self-assembly.

Scheme 2. Synthesis of Fused Rhomboids **7** and **8**



10.1021/ja903330j CCC: $40.75

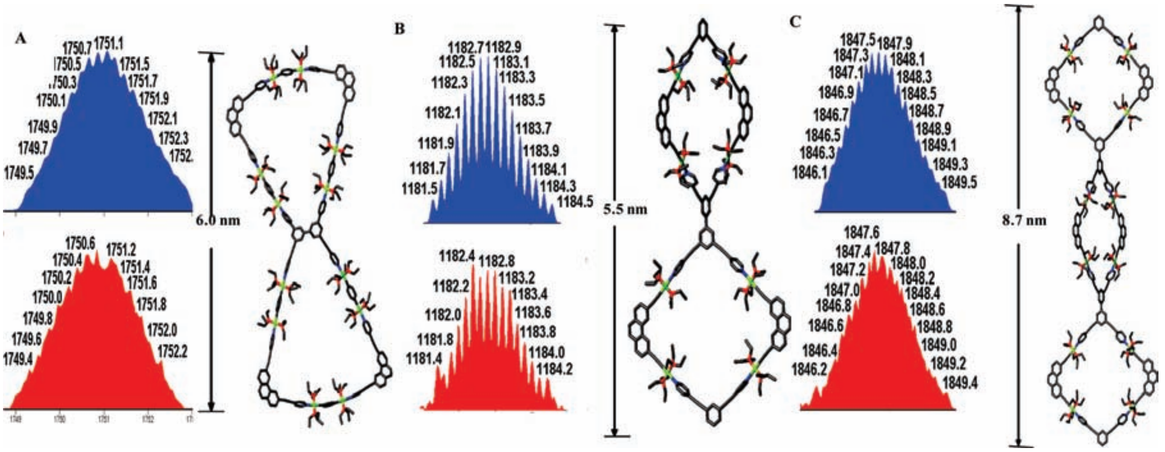


Figure 1. Calculated (top, blue) and experimental (bottom, red) ESI-MS spectra (5+) and molecular force field models of (A) double triangle **4**, (B) double rhomboid **7**, and (C) triple rhomboid **8**.

We then tried to extend this protocol from triangular to rhomboidal systems. Tetrapyridine 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 at an angle of 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 was required for the formation of multirhomboid 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 ratio 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 ^{1}H NMR spectra of **7** and **8** indicated the formation of a single, discrete, highly symmetric supramolecular assembly for each reaction. For both **7** and **8**, two ^{31}P signals are predicted, but only a single signal was observed for **7**, whereas two overlapping signals were observed for **8**, indicating as expected a close similarity of the two phosphorus environments in both **7** and **8** (see the SI). In the ESI mass spectrum of double rhomboid **7**, peaks at *m*/*z* 2070.5 and 1182.3 attributable to $[M - 3OTf]^{3+}$ and $[M - 5OTf]^{5+}$, respectively, were observed (Figure 1 and Figure S8 in the SI). The full spectrum showed that no other products existed in the solution of double rhomboid **7**. Furthermore, the ESI mass spectrum for triple rhomboid **8** revealed peaks at *m*/*z* 1847.6 and 3179.3, corresponding to $[M - 5OTf]^{5+}$ and $[M - 3OTf]^{3+}$, respectively (Figure 1 and Figure S9 in the SI). The full spectrum of triple rhomboid **8** indicated that there were no other products in the complex mixture, including the smaller double rhomboid **7**. Furthermore, pulsed-gradient spin-echo experiments were used to find the diffusion coefficients, *D*. The ratio of *D* values for **7** and **8** was 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 ~5.5 and ~8.6 nm for **7** and **8**, respectively, which are in relative, qualitative agreement with the experimentally determined ratio (see the SI). Consequently, we have demonstrated that it is possible to control the shape and size of supramolecules simply by tuning the relative ratio of multicomponent donor/acceptor mixtures.

All attempts to obtain the crystal structure of higher-order polygons **4**, **7**, and **8** were unsuccessful. Therefore, molecular force field simulations were used to gain further insight into their structural characteristics (Figure 1 and Figure S10 in the SI). A 1.0 ns molecular dynamics simulation (MMFF force field) was used to equilibrate the supramolecules, and then the energies of the resulting structures were minimized to full convergence. 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 multicomponent mixtures of different pyridyl donors and platinum acceptors. These studies have revealed that single supramolecular species can be formed from multicomponent self-assembly and that the shape of the product polygons can be controlled simply by changing the ratio of individual components, thus demonstrating that various multisupramolecular 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.

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Supporting Information Available: Synthesis and analytical data for **2**, ESI mass spectra, and molecular modeling procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Li, S.-S.; Yan, H.-J.; Wan, L.-J.; Yang, H.-B.; Northrop, B. N.; Stang, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 9268. (b) Seeman, N. C.; Belcher, A. M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 6451. (c) Balzani, V.; Credi, A.; Venturi, M. *Chem.—Eur. J.* **2002**, *8*, 5524.

(2) (a) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (c) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972. (d) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863. (e) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022. (f) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759. (g) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369. (h) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349. (i) Ward, M. D. *Chem. Commun.* **2009**, 4487.

(3) (a) Stulz, E.; Ng, Y.-F.; Scott, S. M.; Sanders, J. K. M. *Chem. Commun.* **2002**, 524. (b) Schmittel, M.; Mahata, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 5284. (c) Schmittel, M.; Kalsani, V.; Kishore, R. S. K.; Cölfen, H.; Bats, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 11544. (d) Schmittel, M.; Mahata, K. *Inorg. Chem.* **2009**, *48*, 822. (e) Yang, H.-B.; Ghosh, K.; Northrop, B. H.; Zheng, Y.-R.; Lyndon, M. M.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 14187. (f) Ghosh, K.; Yang, H.-B.; Northrop, B. H.; Lyndon, M. M.; Zheng, Y.-R.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 5320. (g) Baxter, P.; Lehn, J.-M.; DeCian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 69. (h) Chichak, K. S.; Cantrill, S. J.; Pease, A. R.; Chiu, S.-H.; Cave, G. W. V.; Atwood, J. L.; Stoddart, J. F. *Science* **2004**, *304*, 1308. (i) Cho, Y. L.; Uh, H. S.; Chang, S.-Y.; Chang, H.-Y.; Choi, M.-G.; Shin, I.; Jeong, K.-S. *J. Am. Chem. Soc.* **2001**, *123*, 1258.

(4) (a) Yang, H.-B.; Ghosh, K.; Northrop, B. H.; Stang, P. J. *Org. Lett.* **2007**, *9*, 1561. (b) Addicott, C.; Das, N.; Stang, P. J. *Inorg. Chem.* **2004**, *43*, 5335. (c) Northrop, B. H.; Yang, H.-B.; Stang, P. J. *Inorg. Chem.* **2008**, *47*, 11257. (d) Zheng, Y.-R.; Yang, H.-B.; Northrop, B. H.; Ghosh, K.; Stang, P. J. *Inorg. Chem.* **2008**, *47*, 4706.

(5) Yamanoi, Y.; Sakamoto, Y.; Kusukawa, T.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 980.

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