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## Construction of Coordination Driven Self-Assembled [5+5] Pentagons using Metal-Carbonyl Dipyridine Ligands

Liang Zhao<sup>†</sup>, Koushik Ghosh<sup>†</sup>, Yaorong Zheng<sup>†</sup>, Matthew M. Lyndon<sup>§</sup>, Taufika Islam Williams<sup>§</sup>, and Peter J. Stang<sup>†</sup>

<sup>†</sup> Department of Chemistry, University of Utah, 315 South 1400 East, Room 2020, Salt Lake City, Utah 84112

<sup>§</sup> Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695

Pentagonal molecular architectures possessing five-fold ( $C_5$ ) symmetry exist throughout the chemical world from a wealth of inorganic species with pentagonal, pyramidal, bipyramidal, and prismatic geometries,<sup>1</sup> to all-carbon frameworks such as fullerenes and carbon nanotubes bearing curvature-inducing five-membered rings.<sup>2</sup> The unique  $C_5$  symmetry has also been identified in nanoscale materials<sup>3</sup> as well as DNA nanostructures.<sup>4</sup> Moreover, a 2D arrangement of pentagonal structures with  $C_5$  or quasi- $C_5$  symmetry, distinct from the significantly more common  $C_2$ ,  $C_3$ ,  $C_4$  and  $C_6$  periodic symmetries, has been a long-term target pursued by crystal engineers that has been met with limited success.<sup>5</sup> Pentagonal architectures are also attractive because of their potential applications in functional materials such as quasicrystals<sup>6</sup> and discotic liquid crystals.<sup>7</sup>

In light of their potentials, the synthesis of discrete pentagonal architectures has remained a formidable challenge. Only a few discrete  $C_5$ -symmetrical pentagonal organic molecules have been synthesized, generally in low yield and through arduous synthetic work.<sup>8</sup> Coordination-driven self-assembly has been extensively explored in the past few decades and shown to be a powerful synthetic strategy for the construction of metallosupramolecular architectures.<sup>9</sup> By combining specifically designed organic donor building blocks with directional metal acceptors, a plethora of two-dimensional supramolecular structures, including molecular loops,<sup>10</sup> triangles,<sup>11</sup> squares,<sup>12</sup> and hexagons,<sup>13</sup> have been synthesized in high yield. This synthetic methodology provides an efficient and viable means to construct discrete pentagonal structures.

Our group has long endeavored to establish a “molecular library” of metallosupramolecular structures built from the coordination-driven self-assembly of appropriately designed Pt(II) or Pd(II) acceptors and specifically angled donor units in a controllable manner.<sup>9a–d</sup> According to this design concept, discrete pentagonal entities may be exclusively assembled by the incorporation of five  $108^\circ$  building units with five complementary linear units. However, the scarcity of suitable  $108^\circ$  subunits has complicated the realization of such a design concept. In the few reported examples of supramolecular metal-ligand pentagonal architectures,<sup>14</sup> polydentate flexible ligands were used since their coordination to metal centers may lead to a  $108^\circ$  bonding conformation, though an encapsulated anion of specific size must be included to template the assembly process. Furthermore, the difficulty to develop a common methodology to construct a metallosupramolecular pentagon also arises from the internal turning angle of a regular pentagon,  $108^\circ$ , which is close to that of a regular hexagon ( $120^\circ$ ).

Supporting Information Available: Synthetic procedures and spectroscopic characterization of compound **2** and assemblies **4**, **5** and **7**. ESI-TOF-MS of [5+5] pentagon **5**. ESI-MS of [3+3] hexagon **7**. Molecular modeling results of pentagonal and hexagonal structures composed of **1** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

15 The small 12° difference between the 120° angle needed for a hexagonal assembly and the 108° angle needed for an analogous pentagon assembly often leads to an equilibrium mixture of pentagon and hexagon suprastructures.

Acetylene units (C≡C) are extensively incorporated into many donor and acceptor building blocks due to their rigid linear conformation. In view of the ready reactivity<sup>16</sup> of a wide range of metal carbonyl cluster complexes with acetylene moieties, we envisioned that the steric bulk of a metal carbonyl cluster species adhered to the acetylene moiety may be used as a control factor to adjust the bonding angle of the building block in order to exclusively form a pentagon self-assembly. Two metal carbonyl dipyrindine adduct ligands, (4-C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>C≡CCo<sub>2</sub>(CO)<sub>6</sub> (**1**) and (4-C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>C≡CMo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub> (**2**), were synthesized and were combined with a linear acceptor ligand bis[1,4-(*trans*-Pt(PET<sub>3</sub>)<sub>2</sub>OTf)]ethynylbenzene (**3**) to investigate the possibility of constructing [5+5] pentagonal metallocsupramolecules (Scheme 1).

Crystallographic studies have shown that the acetylene moiety adducted by Co<sub>2</sub>(CO)<sub>6</sub> can form a tetrahedral Co<sub>2</sub>C<sub>2</sub> core,<sup>16b</sup> thus making an angle of 120° between the two pyridine rings in **1**. Self-assembly between this 120° donor with the complementary linear acceptor **3** is assumed to construct a [6+6] hexagon. The reaction of **1** with **3** in a 1:1 ratio in CD<sub>2</sub>Cl<sub>2</sub> gave a wine-colored homogeneous solution of **4**, whose <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed a single peak at 16.5 ppm with concomitant <sup>195</sup>Pt satellites, upfield shifted by roughly 6.4 ppm compared with **3** (δ = 23.0 ppm) as a result of the coordination of the pyridine rings (Figure S2 in Supporting Information). However, the proton NMR of **4** displayed broad signals in contrast to the sharp peaks of previously reported for discrete hexagon structures,<sup>17</sup> implying the possible existence of several species in the mixture (Figure S2). The ESI-TOF mass spectrum indicated that two self-assembled polygons – [5+5] pentagon and [6+6] hexagon – do indeed co-exist in self-assembly **4**. Two charge states at m/z = 2040.0 and 1310.3 corresponding to [pentagon – 4CF<sub>3</sub>SO<sub>3</sub>]<sup>4+</sup> and [pentagon – 6CF<sub>3</sub>SO<sub>3</sub>]<sup>6+</sup>, respectively, were observed and were in good agreement with their theoretical isotopic distributions. The isotopically well-resolved mass peak at m/z = 1952.8, resulting from [hexagon – 5CF<sub>3</sub>SO<sub>3</sub>]<sup>5+</sup>, was found in the mass spectrum as well (Figure 1a).

Mixing molybdenum cluster donor ligand **2** in a 1:1 stoichiometric ratio with **3** generated a homogeneous dark-red solution of **5**. A single sharp peak at 16.7 ppm with two <sup>195</sup>Pt flanking satellites were observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **5** (Figure S3). The proton NMR spectrum of **5** displayed sharp signals with differentiable coupling constants (Figure S3). The signals of the pyridine ring α-protons experienced a small upfield shift of 0.03 ppm, but the β-protons and the hydrogen nuclei on the Cp ring undergo approximately 0.2–0.3 ppm downfield shifts, suggestive of the strong back-donation effect of the molybdenum carbonyl cluster to the pyridine ring.

The ESI-TOF mass spectrum of **5** displayed four peaks corresponding to four charge states of the [5+5] pentagon, including [M – 3CF<sub>3</sub>SO<sub>3</sub>]<sup>3+</sup> (m/z 3016.6), [M – 4CF<sub>3</sub>SO<sub>3</sub>]<sup>4+</sup> (m/z 2225.0), [M – 5CF<sub>3</sub>SO<sub>3</sub>]<sup>5+</sup> (m/z 1750.2, overlapping with the 1+ fragment) and [M – 6CF<sub>3</sub>SO<sub>3</sub>]<sup>6+</sup> (m/z 1433.5), which were all isotopically well-resolved and agree very well with their respective theoretical distributions (the 4+ and 6+ charge state are illustrated in Figure 1b and the full spectrum is shown in Figure S5). No evidence for any other species such as a [4+4] square, [6+6] hexagonal, or [7+7] heptagonal assembly was found. The exclusive formation of a [5+5] pentagon is also supported by comparing the proton NMR spectrum of pentagon-hexagon mixture **4** and that of **5**, wherein the peaks of the former are much broader than the latter (Figure S6).

Our attempts to crystallize the polygonal structures **4** (pentagon and hexagon mixture) and **5** (exclusively pentagon) have so far been unsuccessful. We have therefore used molecular force

field simulations to investigate the structural details of the supramolecular pentagon and hexagon composed of cobalt donor **1** and linear di-Pt(II) acceptor **3**, as well as the [5+5] pentagon formed by the self-assembly of molybdenum donor **2** with **3**. In the case of the pentagonal and hexagonal supramolecules that incorporate **1** with **3**, the energies of the two different polygon structures are nearly identical with the [6+6] hexagon being slightly more stable. In the self assembly between **2** and **3**, modeling suggests the pentagonal structure is more stable than the hexagon. The modeled suprastructures show that the linear acceptor units in the hexagonal structure must distort away from a 180° orientation in order to fit the complementarity requirement of a [6+6] hexagon whereas the acceptors retain their 180° geometry in the modeled [5+5] pentagonal structure (Figure 2). The formation of a discrete [5+5] pentagon in **5**, derived from **2**, can also be rationalized by the fact that the primary steric effect of the Cp rings in building block **2** forces the two pyridine rings closer to each other, thus forming a smaller bonding angle than in the related donor **1**.

We also investigated the self-assembly of **1** and **2** with the 120° ferrocenyl acceptor **6** in order to construct a Fe<sub>3</sub>-Co<sub>6</sub>-Pt<sub>6</sub> and a Fe<sub>3</sub>-Mo<sub>6</sub>-Pt<sub>6</sub> trimetal [3+3] hexagons, respectively, and substantiate the effects of the bonding angle difference between **1** and **2** in self-assembly (Scheme 1). Preparation of the novel trimetal Fe<sub>3</sub>-Co<sub>6</sub>-Pt<sub>6</sub> [3+3] hexagon **7** was successfully achieved by mixing **1** with ferrocenyl acceptor **6** in a 1:1 ratio in dichloromethane. The resulting red solution was characterized by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, with the latter displaying a single sharp peak (Figure S4). The ESI mass spectrum exhibited two charge states of the Fe<sub>3</sub>-Co<sub>6</sub>-Pt<sub>6</sub> hexagon **7** (m/z = 1335.1 and 1038.3 for +4 and +5, respectively), which were isotropically resolved and were in good agreement with theoretical isotopic distributions (Figure S7). However, our attempt to produce a Fe<sub>3</sub>-Mo<sub>6</sub>-Pt<sub>6</sub> trimetal [3+3] hexagon using a similar synthetic protocol employing **2** instead of **1** was unsuccessful. This differing reactivity of related donor ligands **1** and **2** further confirms that the bonding angles of the two pyridine rings of each metal carbonyl donor ligand are measurably dissimilar in coordination-driven self assembly because of the difference in the steric bulk of Co<sub>2</sub>(CO)<sub>6</sub> and Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>.

In conclusion, we have successfully prepared a [5+5] supramolecular pentagon by the self-assembly of a molybdenum carbonyl cluster dipyridyl donor ligand (**2**) with a linear di-Pt(II) acceptor (**3**). The roughly 108° bonding angle encoded within **2** directs this coordination-driven self-assembly process to form a single pentagonal metallocsupramolecule rather than a pentagon-hexagon mixture, implying that the generality of this method can be extended to construct other pentagonal structures with a variety of functional groups for even more advanced multifunctional materials.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

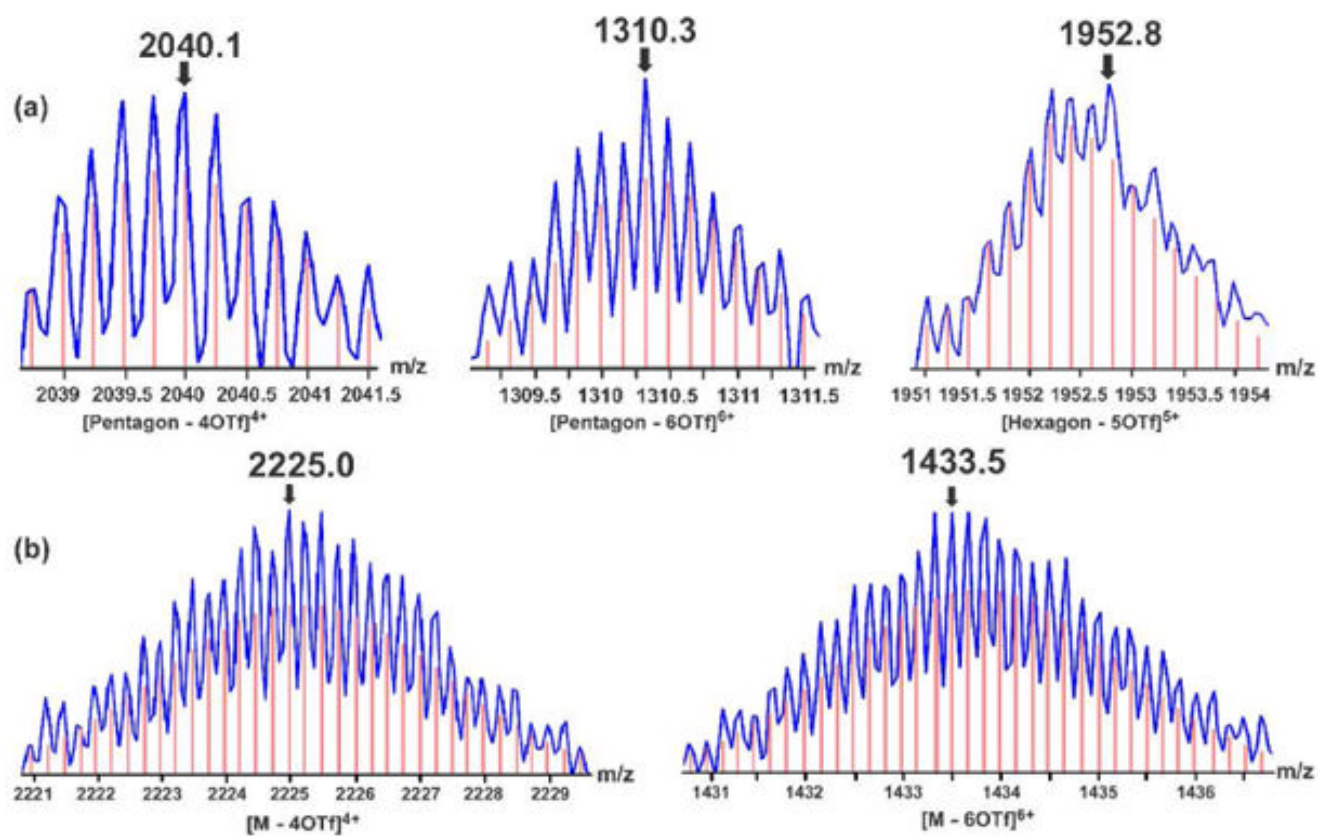
## Acknowledgments

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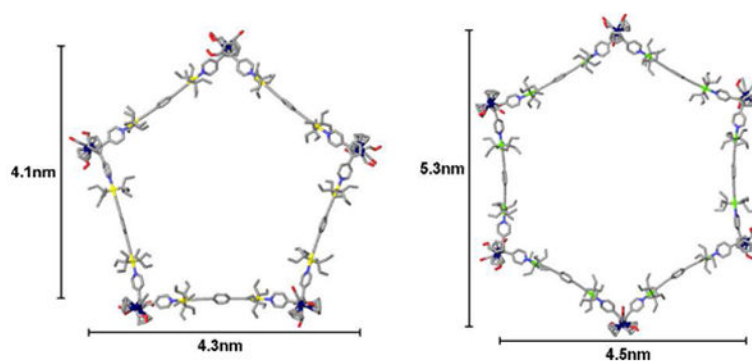
## References

1. For some selected samples: (a) Davidovich RL, Stavila Vi, Marinin DV, Voit EI, Whitmire KH. *Coord Chem Rev* 2009;253:1316. (b) Zhou B, Denning MS, Kays DL, Goicoechea JM. *J Am Chem Soc* 2009;131:2802.
2. Fowler, P.; Manolopoulos, D. *An Atlas of Fullerenes*. 2. Dover Publications; Mineola, NY: 2006.
3. (a) Eskandari S, Kreman M, Kavanaugh MP, Wright EM, Zampighi GA. *Proc Natl Acad Sci USA* 2000;97:8641. [PubMed: 10900021] (b) Pivetta M, Blüm MC, Patthey F, Schneider WD. *Angew Chem Int Ed* 2008;47:1076.

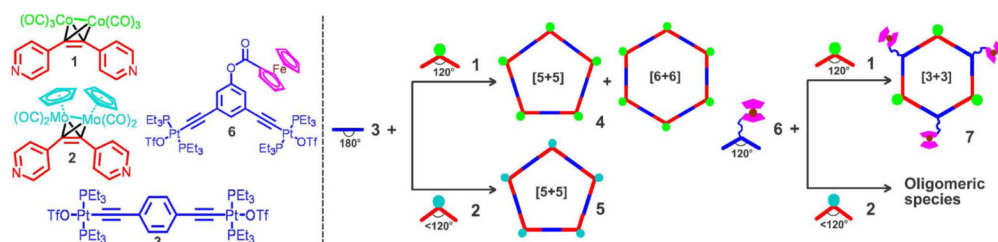
4. Chaput JC, Switzer C. *Proc Natl Acad Sci USA* 1999;96:10614. [PubMed: 10485874]
5. (a) Keller SW, Lopez S. *J Am Chem Soc* 1999;121:6306. (b) Moulton B, Lu J, Zaworotko MJ. *J Am Chem Soc* 2001;123:9224. [PubMed: 11552856] (c) Thakuria R, Sarma B, Nangia A. *Cryst Growth Des* 2008;8:1471.
6. Man WN, Megens M, Steinhardt PJ, Chaikin PM. *Nature* 2005;436:993.
7. (a) Block MAB, Kaiser C, Khan A, Hecht S. *Top Curr Chem* 2005;245:89. (b) Sergeev S, Pisula W, Geerts YH. *Chem Soc Rev* 2007;36:1902. [PubMed: 17982517]
8. (a) Wu YT, Siegel JS. *Chem Rev* 2006;106:4843. [PubMed: 17165677] (b) Sessler JL, Anzenbacher P Jr, Shriver JA, Jursikova K, Lynch V, Marquez M. *J Am Chem Soc* 2000;122:12061. (c) Zhang W, Moore JS. *J Am Chem Soc* 2004;126:12796. [PubMed: 15469273] (d) Qin B, Chen X, Fang X, Shu Y, Yip YK, Yan Y, Pan S, Ong WQ, Ren C, Su H, Zeng H. *Org Lett* 2008;10:5127. and references therein. [PubMed: 18928289]
9. (a) Stang PJ, Olenyuk B. *Acc Chem Res* 1997;30:502. (b) Leininger S, Olenyuk B, Stang PJ. *Chem Rev* 2000;100:853. [PubMed: 11749254] (c) Seidel SR, Stang PJ. *Acc Chem Res* 2002;35:972. [PubMed: 12437322] (d) Northrop BH, Yang HB, Stang PJ. *Chem Commun* 2008:5896. (e) Holliday BJ, Mirkin CA. *Angew Chem, Int Ed* 2001;40:2022. (f) Cotton FA, Lin C, Murillo CA. *Acc Chem Res* 2001;34:759. [PubMed: 11601960] (g) Fujita M, Tominaga M, Hori A, Therrien B. *Acc Chem Res* 2005;38:371. (h) Fiedler D, Leung DH, Bergman RG, Raymond KN. *Acc Chem Res* 2005;38:351. (i) Severin K. *Chem Commun* 2006:3859. (j) Pitt MA, Johnson DW. *Chem Soc Rev* 2007;36:1441. [PubMed: 17660877]
10. (a) Sun SS, Stern CL, Nguyen ST, Hupp JT. *J Am Chem Soc* 2004;126:6314. [PubMed: 15149229] (b) Ghosh S, Mukherjee PS. *Organometallics* 2008;27:316.
11. (a) Qin Z, Jennings MC, Puddephatt RJ. *Inorg Chem* 2002;41:3967. [PubMed: 12132923] (b) Cotton FA, Lin C, Murillo CA. *Proc Natl Acad Sci USA* 2002;99:4810. [PubMed: 11891273] (c) Kryschenko YK, Seidel SR, Arif AM, Stang PJ. *J Am Chem Soc* 2003;125:5193. [PubMed: 12708871] (d) Martin-Redondo MP, Scoles L, Sterenberg BT, Udachin KA, Carty AJ. *J Am Chem Soc* 2005;127:5038. [PubMed: 15810836] (e) Weilandt T, Troff RW, Saxell H, Rissanen K, Schalley CA. *Inorg Chem* 2008;47:7588. [PubMed: 18680283] (f) Ghosh S, Mukherjee PS. *Inorg Chem* 2009;48:2605. [PubMed: 19267506]
12. (a) Angaridis P, Berry JF, Cotton FA, Murillo CA, Wang X. *J Am Chem Soc* 2003;125:10327. [PubMed: 12926957] (b) Caskey DC, Shoemaker RK, Michl J. *Org Lett* 2004;6:2093. [PubMed: 15200293] (c) Ni ZH, Tao J, Wernsdorfer W, Cui AL, Kou HZ. *Dalton Trans* 2009:2788. [PubMed: 19333502] (d) Theilmann O, Saak W, Haase D, Beckhaus R. *Organometallics* 2009;28:2799.
13. (a) Coronado E, Galan-Mascaros JR, Gavina P, Marti-Gastaldo C, Romero FM, Tatay S. *Inorg Chem* 2008;47:5197. [PubMed: 18479127] (b) Ghosh K, Zhao Y, Yang HB, Northrop BH, White HS, Stang PJ. *J Org Chem* 2008;73:8553. [PubMed: 18841907]
14. (a) Hasenknopf B, Lehn JM, Kneisel B, Baum G, Fenske D. *Angew Chem Int Ed Engl* 1996;35:1838. (b) Hasenknopf B, Lehn JM, Boumediene N, Dupontgervais A, Vandorselaer A, Kneisel B, Fenske D. *J Am Chem Soc* 1997;119:10956. (c) Campos-Fernandez CS, Clerac R, Koomen JM, Russell DH, Dunbar KR. *J Am Chem Soc* 2001;123:773. [PubMed: 11456607] (d) Campos-Fernández CS, Schottel BL, Chifotides HT, Bera JK, Bacsá J, Koomen JM, Russell DH, Dunbar KR. *J Am Chem Soc* 2005;127:12909. [PubMed: 16159285] (e) Satake A, Tanak H, Hajjaj F, Kawai T, Kobuke Y. *Chem Commun* 2006:2542.
15. Caulder DL, Raymond KN. *Acc Chem Res* 1999;32:975.
16. (a) Abel, EW.; Stone, FGA.; Wilkinson, G. *Comprehensive Organometallic Chemistry II*. Vol. 8. Pergamon; Oxford: 1995. (b) Song LC, Jin GX, Wang HT, Zhang WX, Hu QM. *Organometallics* 2005;24:6464.
17. Yang HB, Das N, Huang F, Hawkrigde AM, Díaz DD, Arif AM, Finn MG, Muddiman DC, Stang PJ. *J Org Chem* 2006;71:6644. [PubMed: 16901162]



**Figure 1.** ESI-TOF-MS spectra of (a) self assembly **4** containing both pentagon and hexagon, and (b) two charge states of [5+5] pentagon **5**. Red vertical lines are the theoretical abundances.



**Figure 2.** Pentagonal and hexagonal structures composed of molybdenum donor ligand **2** and linear acceptor **3** as obtained from molecular force field modeling.



**Scheme 1.**

Molecular structures of donor (red) and acceptor (blue) building blocks and their self-assembly into metallacyclic supramolecules.