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

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The coordination-driven self-assembly of two metal−carbonyl-cluster-coordinated dipyridyl donors, $(4\text{-}C_5H_4N)_2C{\equiv}CCo_2(CO)_6$ (**1**) and $(4\text{-}C_5H_4N)_2C{\equiv}CMo_2Cp_2(CO)_4$ (**2**), with a linear diplatinum (II) acceptor ligand was investigated. The structures of the resulting self-assembled polygons were found to be controlled by the steric bulk of the metal−carbonyl cluster adduct. The use of a sterically less imposing ligand **1** resulted in a pentagon−hexagon mixture, which was characterized by electrospray ionization time-of-flight mass spectroscopy. The exclusive formation of a [5 + 5] pentagon was achieved by the self-assembly of the bulkier molybdenum donor ligand **2** with a linear organoplatinum(II) acceptor ligand. Molecular force field modeling was used to study the structural details of the pentagonal and hexagonal architectures. The first Fe_3−Co_6−Pt_6 trimetal [3 + 3] hexagon was also synthesized via the combination of **1** with a 120° ferrocenyldiplatinum(II) acceptor.

Pentagonal molecular architectures possessing 5-fold (C_5) symmetry exist throughout the chemical world from a wealth of inorganic species with pentagonal, pyramidal, bipyramidal, and prismatic geometries[1] to all-carbon frameworks such as fullerenes and carbon nanotubes bearing curvature-inducing five-membered rings.[2] The unique C_5 symmetry has also been identified in nanoscale materials[3] as well as DNA nanostructures.[4] Moreover, a two-dimensional 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 met with limited success.[5] Pentagonal architectures are also attractive because of their potential applications in functional materials such as quasicrystals[6] and discotic liquid crystals.[7]

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.[8] 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.[9] By

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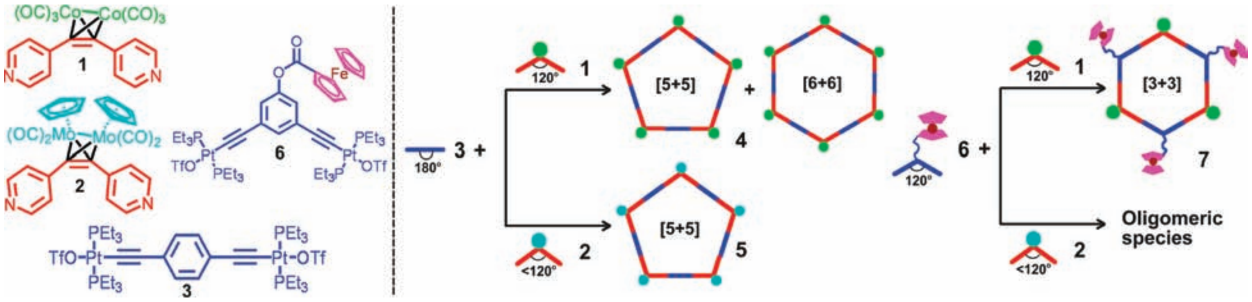
Scheme 1. Molecular Structures of Donor (Red) and Acceptor (Blue) Building Blocks and Their Self-Assembly into Metallacyclic Supramolecules



combining specifically designed organic donor building blocks with directional metal acceptors, a plethora of two-dimensional supramolecular structures, including molecular loops,[10] triangles,[11] squares,[12] and hexagons,[13] 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 platinum(II) or palladium(II) acceptors and specifically angled donor units in a controllable manner.[9a−9d] According to this design concept, discrete pentagonal entities may be exclusively assembled by the incorporation of five 108° building units with five complementary linear units. However, the scarcity of suitable 108° subunits has complicated the realization of such a design concept. In the few reported examples of supramolecular metal−ligand pentagonal architectures,[14] polydentate flexible ligands were used because their coordination to metal centers may lead to a 108° 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°, which is close to that of a regular hexagon (120°).[15] The small 12° difference between the 120° angle needed for a hexagonal assembly and the 108° angle needed for an analogous pentagonal assembly often leads to an equilibrium mixture of pentagonal and hexagonal suprastructures.

Acetylene units (C≡C) are extensively incorporated into many donor and acceptor building blocks because of their rigid linear conformation. In view of the ready reactivity[16] 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 pentagonal self-assembly. Two metal−carbonyl dipyridine adduct ligands, $(4\text{-}C_5H_4N)_2C{\equiv}CCo_2(CO)_6$ (**1**) and $(4\text{-}C_5H_4N)_2C{\equiv}CMo_2Cp_2(CO)_4$ (**2**; Cp = Cyclopentadienyl), were synthesized and were combined with a linear acceptor ligand bis[1,4-(*trans*-$Pt(PEt_3)_2OTf$)]ethynylbenzene (**3**) to investigate the possibility of constructing [5 + 5] pentagonal metallosupramolecules (Scheme 1).

Crystallographic studies have shown that the acetylene moiety adducted by $Co_2(CO)_6$ can form a tetrahedral Co_2C_2 core,[16b] 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_2Cl_2 gave a wine-colored homogeneous solution of **4**, whose $^{31}P\{^1H\}$ NMR spectrum showed a single peak at 16.5 ppm with concomitant ^{195}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 the Supporting Information, SI). However, the ^1H NMR of **4** displayed broad signals, in contrast to the sharp peaks previously reported for discrete hexagonal structures,[17] implying the possible existence of several species in the mixture (Figure S2 in the SI). The electrospray ionization time-of-flight mass spectroscopy (ESI-TOF-MS) spectrum indicated that two self-assembled polygons, [5 + 5] pentagon and [6 + 6] hexagon, do indeed coexist in self-assembly **4**. Two charge states at *m*/*z* 2040.0 and 1310.3 corresponding to $[\text{pentagon} - 4CF_3SO_3]^{4+}$ and $[\text{pentagon} - 6CF_3SO_3]^{6+}$, 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 $[\text{hexagon} - 5CF_3SO_3]^{5+}$, was found in the MS 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 ^{195}Pt flanking satellites was observed in the $^{31}P\{^1H\}$ NMR spectrum of **5** (Figure S3 in the SI). The ^1H NMR spectrum of

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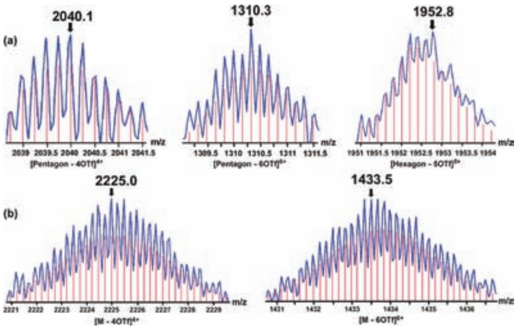

Figure 1. ESI-TOF-MS spectra of (a) self-assembly **4** containing both pentagon and hexagon and (b) two charge states of [5 + 5] pentagon **5**. Red vertical lines are the theoretical abundances.

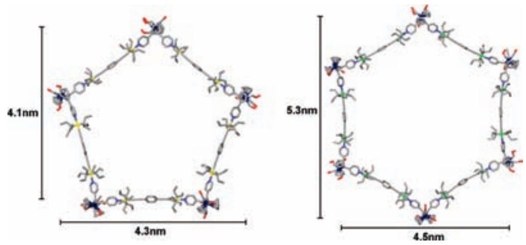

Figure 2. Pentagonal and hexagonal structures composed of molybdenum donor ligand **2** and linear acceptor **3** as obtained from molecular force field modeling.

5 displayed sharp signals with differentiable coupling constants (Figure S3 in the SI). 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-MS spectrum of **5** displayed four peaks corresponding to four charge states of the [5 + 5] pentagon, including $[M - 3CF_3SO_3]^{3+}$ (*m*/*z* 3016.6), $[M - 4CF_3SO_3]^{4+}$ (*m*/*z* 2225.0), $[M - 5CF_3SO_3]^{5+}$ (*m*/*z* 1750.2, overlapping with the 1+ fragment), and $[M - 6CF_3SO_3]^{6+}$ (*m*/*z* 1433.5), which were all isotopically well-resolved and agree very well with their respective theoretical distributions (the 4+ and 6+ charge states are illustrated in Figure 1b, and the full spectrum is shown in Figure S5 in the SI). 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 a comparison of the ^{1}H NMR spectrum of pentagon−hexagon mixture **4** and that of **5**, wherein the peaks of the former are much broader than those of the latter (Figure S6 in the SI).

Our attempts to crystallize the polygonal structures **4** (pentagon−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 diplatinum(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 that the pentagonal structure is more stable than the hexagonal structure. 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 that 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 $Fe_3{-}Co_6{-}Pt_6$ and $Fe_3{-}Mo_6{-}Pt_6$ 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 $Fe_3{-}Co_6{-}Pt_6$ [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 ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy, with the latter displaying a single sharp peak (Figure S4 in the SI). The ESI-MS spectrum exhibited two charge states of the $Fe_3{-}Co_6{-}Pt_6$ hexagon **7** (*m*/*z* = 1335.1 and 1038.3 for 4+ and 5+, respectively), which were isotopically resolved and were in good agreement with theoretical isotopic distributions (Figure S7 in the SI). However, our attempt to produce a $Fe_3{-}Mo_6{-}Pt_6$ 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 $Co_2(CO)_6$ and $Mo_2Cp_2(CO)_4$.

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 diplatinum(II) acceptor (**3**). The roughly 108° bonding angle encoded within **2** directs this coordination-driven self-assembly process to form a single pentagonal metallosupramolecule 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.

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Supporting Information Available: Synthetic procedures and spectroscopic characterization of compound **2** and assemblies **4**, **5**, and **7**, ESI-TOF-MS spectrum of [5 + 5] pentagon **5**, ESI-MS spectrum of [3 + 3] hexagon **7**, and 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.