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Self-Assembly of Chiral Metallacycles and Metallacages from a Directionally Adaptable BINOL-Derived Donor

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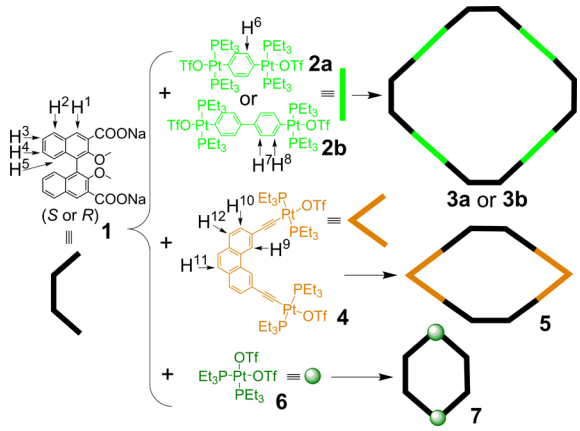
Supporting Information

ABSTRACT: We present the formation of a series of chiral metallacycles and metallacages by the use of a BINOL-derived dicarboxylate as a donor that is capable of affording a variety of coordination angles between its two Lewis basic sites. Two squares, two rhomboids, two tetragonal prisms, and one hexagonal prism were successfully formed when the chiral dicarboxylate donor self-assembled with one of four ditopic Pt(II) complexes, including two bimetallic 180° Pt-based acceptors, a 120° bimetallic Pt-based acceptor, and a 90° mononuclear Pt-based acceptor. Their structures were well characterized by $^{31}P\{^{1}H\}$ NMR, ESI-MS, CD, and optical rotation analyses.

Chiral self-assembly plays important roles in life systems that are essential to many natural processes, including biological recognition and the transmission of biological information.[1,2] Over the past few decades, artificial chiral supramolecules[3] have received intense attention because of both their importance in mimicking biological systems and their extensive applications in chiral recognition, enantiomer separation, asymmetric catalysis, and functional materials.[4] To maintain convenient and efficient self-assembly, synthetic strategies have focused on directly incorporating various nonracemic building blocks into the final discrete supramolecular architectures, which often exhibit characteristic properties that could not be attained by achiral small molecules.[3,4]

Rapid growth in the field of coordination-driven self-assembly during the past three decades has resulted in a variety of 1D, 2D, and 3D finite supramolecular coordination complexes (SCCs) with well-defined shapes and sizes.[5,6] The efficiency and modularity of this self-assembly method has rendered it a powerful tool for the construction of chiral supramolecular architectures. A variety of chiral discrete SCCs have been successfully prepared by self-assembly of enantiomerically pure building blocks into the final discrete self-assemblies.[3,4,7] That said, only a small number of chiral 3D metallacages are known relative to their achiral analogues.[8] This is in part due to the difficulties associated with realizing highly efficient synthetic methodologies for the fabrication of discrete chiral metallacages and finding appropriate chiral building blocks.[8] Furthermore, these structures are often predicated on the use of rigid organic, organometallic, and coordination complexes with controllable directionalities. In contrast, the use of bidentate building blocks capable of varying the angle between their coordination vectors is rare. Such species are intriguing in that they can adjust their binding angles to complement the other partner during the self-assembly of two-component SCCs.

Scheme 1. Self-Assembly of Chiral Squares 3a and 3b and Chiral Rhomboids 5 and 7



In the present work, we utilized (*S*)- or (*R*)-2,2′-dimethoxy-1,1′-binaphthalene-3,3′-dicarboxylate (**1**) as a chiral building block to self-assemble with 180°, 120°, or 90° Pt(II)-based acceptors to form a suite of chiral metallacycles. In addition, a multicomponent approach involving the self-assembly of **1** with a 90° Pt(II) acceptor and tetrapyridyl or hexapyridyl ligands afforded chiral tetragonal and hexagonal prisms, respectively, driven by a preference for Pt−N,O heteroligation. During self-assembly, the angle between the carboxylate coordination vectors, hereafter called the *coordination angle*, of the BINOL-derived dicarboxylate **1** adapted to accommodate the directionalities of the other building blocks used, thus acting as a 90°, 120°, or 180° donor across the architectures.

Chiral BINOL-derived carboxylate donors (*S*)- and (*R*)-**1** were easily synthesized in two steps from a pair of commercially available ester enantiomers (see the Supporting Information (SI)). As shown in Scheme 1, 2D neutral homochiral squares **3a,b** and rhomboid **5** were then prepared in one pot via two-component coordination-driven self-assembly by stirring ligand **1** with either 180° Pt-based acceptor **2a,b** or 60° Pt-based acceptor **4**, respectively, in a 1:1 ratio first in a H_2O/CD_2Cl_2 solution and

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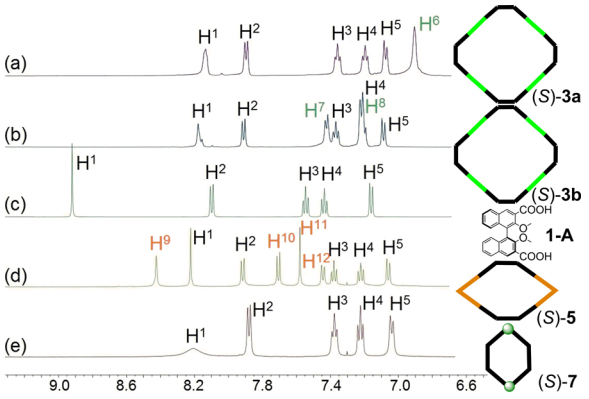


Figure 1. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 22 °C) of (a) chiral square (*S*)-**3a**, (b) chiral square (*S*)-**3b**, (c) BINOL-derived dicarboxylic acid **1-A**, (d) chiral rhomboid (*S*)-**5**, and (e) chiral rhomboid (*S*)-**7**.

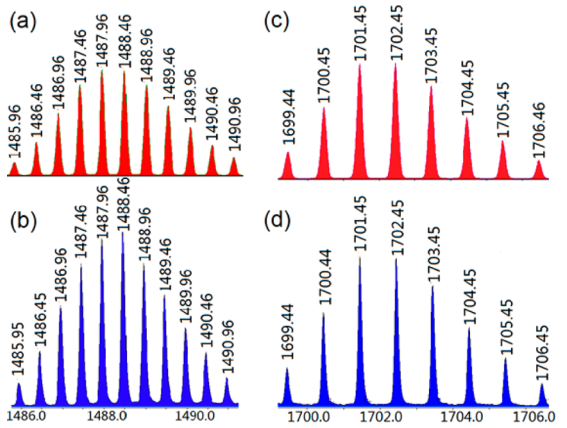


Figure 2. ESI mass spectra of (b) $[(S)\text{-}5{+}2H]^{2+}$ and (d) $[(S)\text{-}7{+}K]^{+}$ and their simulated spectra (a and c, respectively).

then in CD_2Cl_2. Rhomboid **7** was furnished by using the same strategy in a H_2O/CD_3COCD_3 solution and then in CD_3COCD_3. $^{31}P\{^{1}H\}$ and ^{1}H NMR spectroscopy of the reaction solutions supported the formation of single, discrete 2D chiral metallacycles with highly symmetric structures (Figure 1).

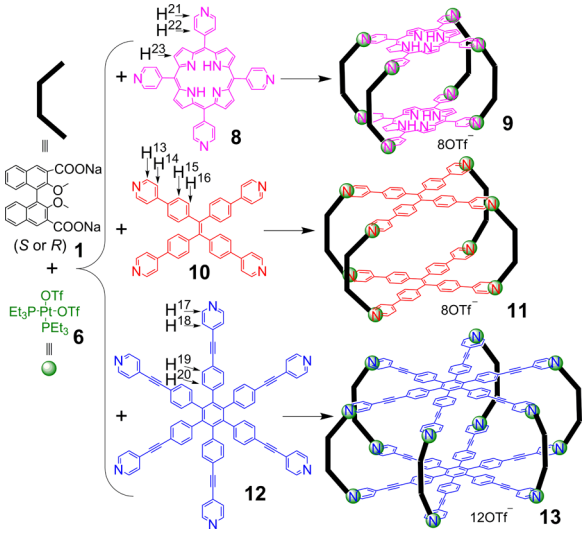
The $^{31}P\{^{1}H\}$ NMR spectra of **3a**,**b**, **5**, and **7** (see the SI) all displayed a singlet peak with two concomitant ^{195}Pt satellites, consistent with the homoligated Pt−O coordination environment. After the self-assembly of chiral metallacycles, the signals in the $^{31}P\{^{1}H\}$ NMR spectra of (*S*)-**3a**, (*S*)-**3b**, (*S*)-**5**, and (*S*)-**7** (SI) shifted upfield from those of the starting Pt acceptors **2a**,**b**, **4**, and **6**, by ∼18.21, 24.79, 21.43, and 7.85 ppm, respectively. Readily apparent shifts were observed for peaks found in the ^{1}H NMR spectra of **3a**,**b**, **5**, and **7** (SI) relative to their analogues in the ^{1}H NMR spectra of **2a**,**b**, **4**, and BINOL-derived dicarboxylic acid **1-A** (Figure 1), respectively. Upon formation of (*S*)-**3a**, (*S*)-**3b**, (*S*)-**5**, and (*S*)-**7**, all the signals associated with the aromatic protons H^1, H^2, H^3, H^4, and H^5 of **1-A** shifted upfield (Figure 1). Similarly, the signals for H^{10} and H^{11} of **4** shifted upfield, while those of H^6 for **2a**, H^7 and H^8 for **2b**, and H^9 and H^{12} for **4** moved downfield (SI).

According to the previously reported crystal structures of similar compounds, the coordination angle of free dicarboxylate ligand **1** was estimated to be ∼90°.[7e,9] If this angle were assumed to be static, the self-assembly of **1** with either **2** or **6** would be expected to afford normal square metallacycles. However, the binding angle of **1** would not match with the directionality of **4**, a common 60° rigid acceptor. Despite this mismatch, an unexpected [2+2] self-assembly occurred in mixtures of **1** and **4**. Both an axial rotation within the BINOL-based ligand and the ability of carboxylate donors to approach a metal along a variety of orientations contribute to a coordination angle expansion to ∼120°, enabling the assembly of chiral rhomboid **5**.

Electrospray ionization mass spectrometry (ESI-MS) provided clear evidence for the formation stoichiometry of the assembled 2D chiral metallacycles. In the ESI mass spectrum for (*S*)-**5** (see the SI), all of the main peaks supported the [2+2] rhomboid structural assignment, including four peaks at *m*/*z* 1487.46, 1498.45, 1509.43, and 1517.45 attributed to $[(S)\text{-}5{+}2H]^{2+}$ (Figure 2b), $[(S)\text{-}5{+}Na{+}H]^{2+}$, $[(S)\text{-}5{+}2Na]^{2+}$, and $[(S)\text{-}5{+}K{+}Na]^{2+}$, respectively. No peaks consistent with self-assemblies formed with other stoichiometries were found. In the ESI mass spectra for chiral squares (*S*)-**3a** and (*S*)-**3b** (SI), three and four related peaks were observed that supported the (*S*)-**3a** and (*S*)-**3b** structural assignments, respectively. For (*S*)-**7** (SI), three peaks were found that supported the (*S*)-**7** structural assignment, including a peak at *m*/*z* 1701.45 attributed to $[(S)\text{-}7{+}K]^{+}$ (Figure 2d). All these peaks were isotopically resolved and agreed very well with their calculated theoretical distributions.

Three 3D chiral metallacages, tetragonal prisms **9** and **11** and hexagonal prism **13**, were constructed using a selective multicomponent self-assembly strategy (Scheme 2). An initial self-assembly of (*S*)-**1** with 90° Pt(II)-based acceptor **6** and 5,10,15,20-tetra(4-pyridyl)porphyrin (**8**) in a 4:8:2 ratio in a $CD_2Cl_2/CD_3CN/CD_3NO_2$ solution and then CD_2Cl_2 furnished tetragonal prism (*S*)-**9**. The other two chiral metallacages, (*S*)-**11** and (*S*)-**13**, were self-assembled in H_2O/CD_3COCD_3 followed by CD_3COCD_3. Tetragonal prism **11** was obtained from **1**, **6**, and tetrapyridyl compound **10** in a 4:8:2 ratio, while hexagonal prism **13** was prepared from **1**, **6**, and hexapyridyl compound **12**[10] in a 6:12:2 ratio. $^{31}P\{^{1}H\}$ and ^{1}H NMR analyses of the reaction solutions supported the formation of these discrete chiral metallacages (Figures 3 and 4). The $^{31}P\{^{1}H\}$ NMR spectra of **9**, **11**, and **13** (SI) displayed two coupled doublets of approximately equal intensity with concomitant ^{195}Pt satellites, consistent with the multicomponent Pt−N,O heteroligated

Scheme 2. Self-Assembly of Chiral Tetragonal Prisms 9 and 11 and Chiral Hexagonal Prism 13



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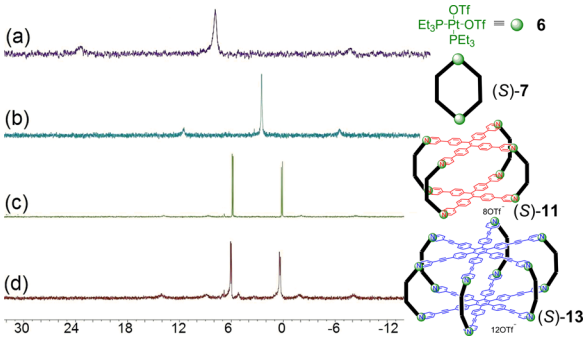

Figure 3. Partial $^{31}P\{^{1}H\}$ NMR spectra (500 MHz, CD_3COCD_3, 22 °C) of (a) **6**, (b) chiral rhomboid (*S*)-**7**, (c) chiral tetragonal prism (*S*)-**11**, and (d) chiral hexagonal prism (*S*)-**13**.

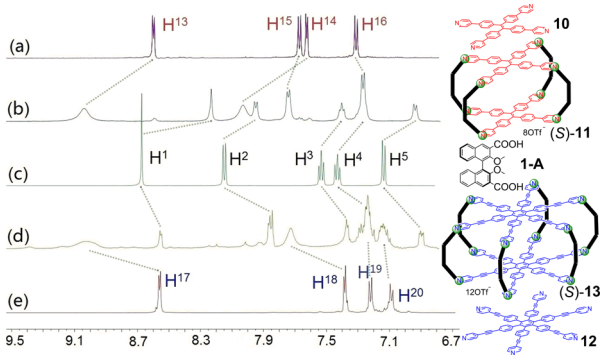

Figure 4. Partial ^{1}H NMR spectra (500 MHz, CD_3COCD_3, 22 °C) of (a) **10**, (b) chiral tetragonal prism (*S*)-**11**, (c) BINOL-derived dicarboxylic acid **1-A**, (d) chiral hexagonal prism (*S*)-**13**, and (e) **12**.

coordination environment in which the Pt(II) centers of **9**, **11**, and **13** coordinated with one pyridyl moiety and one carboxylate moiety per metal center. Unlike the angles predicted in the metallacycles discussed above, the formation of these multicomponent prisms necessitates a ∼180° coordination angle for ligand **1**, a large deviation from its 90° nature in the square metallacycles.

The ^{1}H NMR spectra also supported the formation of **9**, **11**, and **13** (SI). For (*S*)-**9**, the signals associated with aromatic protons H^1, H^2, H^3, H^4, and H^5 of **1-A** moved upfield. The peaks for pyridinium protons H^{21} and H^{22} of **8** split into two doublets and moved downfield. The signal of porphyrin protons H^{23} for **8** split into two singlet peaks with one shifted downfield and the other shifted upfield (SI). Clear shifts were observed for the peaks in the ^{1}H NMR spectra of (*S*)-**11** and (*S*)-**13** relative to those found in the ^{1}H NMR spectra of **10** and **12**, respectively, as well as the ^{1}H NMR spectrum of BINOL-derived dicarboxylic acid **1-A** (Figure 4). All the aromatic proton peaks of **1-A** (H^1, H^2, H^3, H^4, and H^5) moved upfield. The peaks for pyridinium protons H^{13} and H^{14} and aromatic proton H^{15} of **10** shifted downfield upon the formation of (*S*)-**11**, while that of aromatic protons H^{16} on **10** shifted upfield. Upon the formation of (*S*)-**13**, the signals of pyridinium protons H^{17} and H^{18} and aromatic protons H^{19} and H^{20} of **12** shifted downfield.

ESI-MS studies provided further evidence for the formation stoichiometry of the assembled 3D chiral metallacages. In the ESI mass spectrum for (*S*)-**9** (SI), four related peaks were observed that supported the (*S*)-**9** structural assignment. For chiral tetragonal prism (*S*)-**11** (SI), four peaks were found that supported the (*S*)-**11** structural assignment, including a peak at

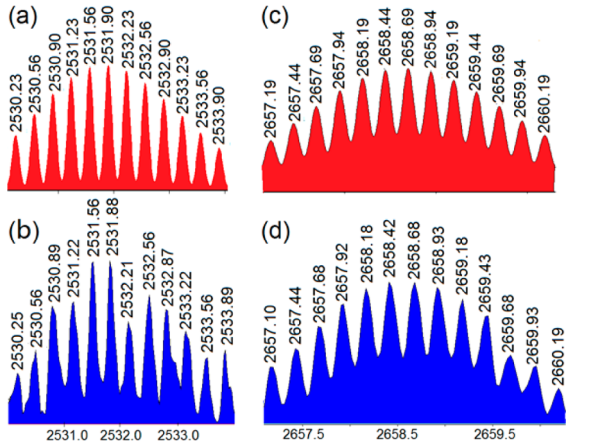

Figure 5. ESI mass spectra of (b) $[(S)\text{-}\mathbf{11}+K+2NH_4]^{3+}$ and (d) $[(S)\text{-}\mathbf{13}-7HOTf+K+3H]^{4+}$ and their simulated spectra (a and c, respectively).

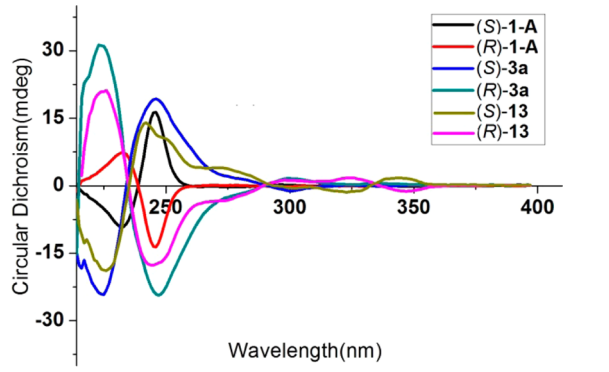

Figure 6. CD spectra of BINOL-derived dicarboxylic acids (*S*)- and (*R*)-**1-A**, 2D chiral metallacycles (*S*)- and (*R*)-**3a**, and 3D chiral metallacages (*S*)- and (*R*)-**13** in CH_2Cl_2.

m/*z* 2531.88 attributed to $[(S)\text{-}\mathbf{11}+K+2NH_4]^{3+}$ (Figure 5b). For chiral hexagonal prism (*S*)-**13** (SI), five peaks were found that supported the (*S*)-**13** structural assignment, including a peak at *m*/*z* 2658.68 attributed to $[(S)\text{-}\mathbf{13}-7HOTf+K+3H]^{4+}$ (Figure 5d). All these peaks were isotopically resolved and agreed very well with their calculated theoretical distributions.

Self-assembly of the other enantiomer (*R*)-**1** acting as an adaptable building block with the suite of acceptors described above similarly yielded the corresponding chiral metallacycles (*R*)-**3a**, (*R*)-**3b**, (*R*)-**5**, and (*R*)-**7** and metallacages (*R*)-**9**, (*R*)-**11**, and (*R*)-**13**. Similar chemical shifts were found in both the $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of these *R*-configured self-assemblies. ESI-MS also supported their formation.

The inherent chirality of the obtained enantiomeric metallacycles and metallacages was investigated by circular dichroism (CD) experiments. The CD spectra (see the SI) of pairs of enantiomeric self-assemblies, e.g., (*S*)- vs (*R*)-**3a** and (*S*)- vs (*R*)-**13**, showed mirrored responses (Figure 6 and SI). Enhancements of the CD signals in **3a** and **13** compared with the CD spectrum of ligand **1-A** were consistent with the presence of multiple ligands in the metallacycles and metallacages. The CD spectrum of **3a** exhibited two major single bands at ∼220 and ∼245 nm, while that of **13** exhibited two major single bands at ∼225 and ∼240 nm (Figure 6), due to ligand-to-Pt(II) charge transfer.[2b,3b,c] The chirality of these self-assemblies was further confirmed by optical rotation analysis (SI).

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In summary, we have described the highly efficient construction of chiral metallacycles and chiral metallacages by coordination-driven self-assembly of a chiral BINOL-derived dicarboxylate possessing an adaptive coordination angle. *S* and *R* pairs of two squares, two rhomboids, two tetragonal prisms, and one hexagonal prism were formed when the chiral BINOL-derived dicarboxylate self-assembled with selected Pt(II)-based acceptors, wherein the dicarboxylate donor changed its directionality to match the requirements of each architecture. These chiral metallacycles and metallacages were well characterized by ^{1}H and ^{31}P NMR, ESI-MS, CD, and optical rotation analyses. The present studies not only provide convenient pathways to new chiral supramolecules with interesting structures but also offer an enhanced understanding of selective self-assembly.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07529.

Experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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