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Unexpected Self-Assembly of Chiral Triangles from 90° Chiral Di-Pt(II) Acceptors

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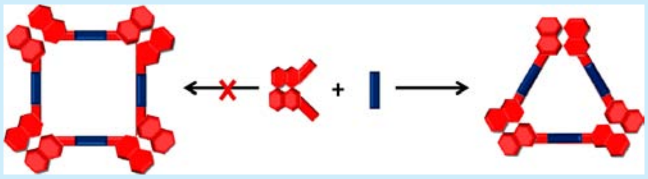
Supporting Information

ABSTRACT: Two unexpected chiral organometallic triangles rather than squares from newly designed 90° chiral di-Pt(II) acceptors were obtained through coordination-driven self-assembly. Their structures were well characterized by multinuclear NMR (^{1}H and ^{31}P) and variable-temperature NMR experiments, ESI-TOF-MS, and elemental analysis. The PM6 semiempirical molecular simulation was employed for the interpretation of the formation and stability of such chiral triangles.



Chiral macromolecules widely existing in nature have proven to play an important role during many biological processes and be essential to some biosomes.[1] Over the years, construction of artificial chiral architectures that could mimic biological systems to realize their functionality has aroused the extensive interest of chemists.[2] Thus, the design and preparation of chiral macromolecules has now represented one of the major frontiers of modern supramolecular chemistry because of their wide applications in the areas of asymmetric catalysis, chiral separation, molecular recognition, etc.[3]

During the past few decades, employing the strategy of coordination-driven self-assembly to build discrete supramolecular two-dimensional (2-D) polygons and three-dimensional (3-D) polyhedra has evolved to be one of the most attractive fields within supramolecular chemistry and materials science.[4] A great number of well-defined discrete 2-D polygons, such as squares, rhomboids, rectangles, and hexagons, etc., have been successfully prepared. With the aim of improving their functionality, recent efforts have focused on incorporating functional groups into the final discrete metallacycles.[5] For example, functional subunits like ferrocene, diarylethene, and Fréchet-type dendrons have been successfully introduced to prepare 2-D functionalized cavity-cored assemblies.[6]

Although a number of functional metallacycles via coordination-driven self-assembly have been reported, only a relatively small number of chiral macrocycles exist in the literature.[7] In particular, the construction of chiral triangles is still a big challenge due to the difficulty in finding the appropriate chiral corner unit and the equilibrium between the triangles and the corresponding squares.[8] Herein, we report the unexpected self-assembly of chiral triangles rather than squares formed from 4,4′-bipyridine and 90° chiral di-Pt(II) acceptors derived from 1,1′-bi-2-naphthol (BINOL). The species of chiral triangles were well confirmed by multinuclear NMR (^{1}H and ^{31}P) and variable-temperature NMR experiments, ESI-TOF-MS, and elemental analysis. The binding energy of chiral triangles was explored by PM6 semiempirical molecular simulation for interpretation of the formation and stability of such chiral triangles.

The chiral acceptors **5a** and **5b** can be easily synthesized in a few steps (see the Supporting Information). Single crystals of **5a** and **5b**, suitable for X-ray diffraction studies, were grown by slow vapor evaporation of a mixed solvent of CH_2Cl_2 and hexane (v/v 1/2) at ambient temperature for 7 days. According to the crystal structure investigation, two binding sites of di-Pt(II) nitrates **5a** and **5b** were found to be 89.0° and 87.3°, respectively (Figure 1). On the basis of the directional-binding approach,[4a] the molecular squares can be logically predicted from the self-assembly of 90° di-Pt(II) nitrates and linear ligands. Nevertheless, the mixtures of triangles and squares were sometimes obtained when the flexible building blocks were utilized. This phenomenon might be attributed to the possible existence of the exchange between triangles and

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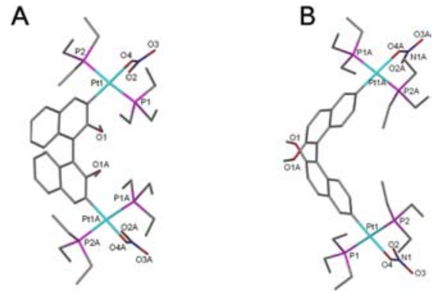


Figure 1. X-ray crystal structures of **5a** (A) and **5b** (B).

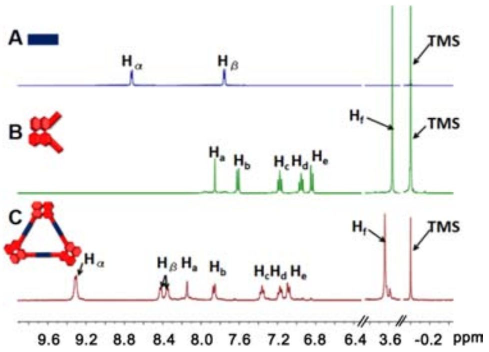


Figure 2. Partial ^1H NMR spectra of the **6** (A), **5a** (B), and **7a** (C).

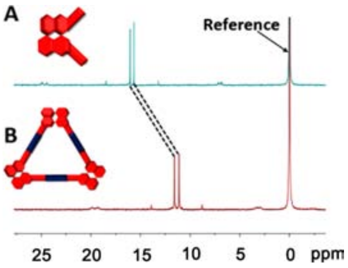


Figure 3. ^{31}P $\{^1H\}$ NMR spectra of **5a** (A) and **7a** (B).

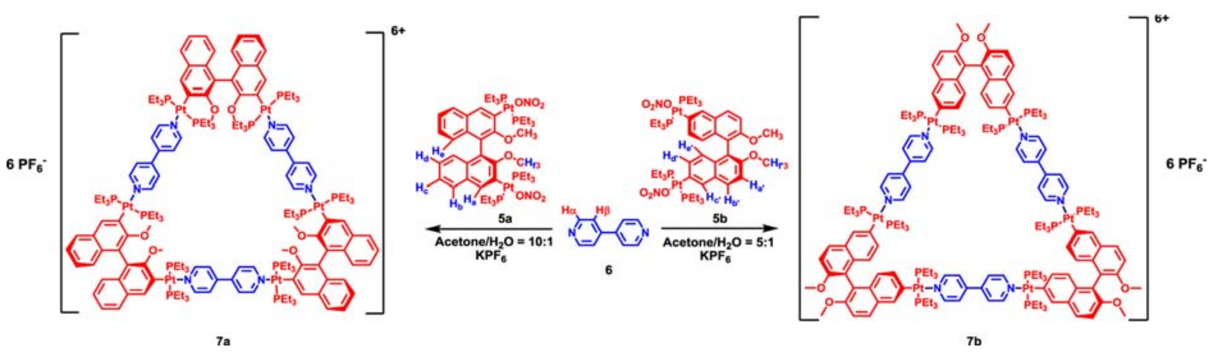
squares or not.[8,9] It is significant, therefore, to explore the specific self-assembly of such newly designed 90° chiral acceptors.

Heating the mixtures of 4,4-bipyridine **6** and the corresponding chiral di-Pt(II) nitrates **5a** or **5b** in a stoichiometric ratio in aqueous acetone for 12 h resulted in self-assemblies **7a** and **7b**, respectively (Scheme 1). The self-assemblies **7a** and **7b** were dissolved in acetone-d_6 for ^1H and ^{31}P NMR studies. In the ^1H NMR spectrum of each assembly, the hydrogen atoms of the pyridine rings exhibited downfield shifts (α-H, 0.50–0.58 ppm; β-H, 0.57–0.64 ppm) resulting from the transition of electron from the pyridine-N atom to the Pt(II) metal center (Figure 2 and Figure S8, Supporting Information). Moreover, the pyridine protons displayed two sets of doublets in the ^1H NMR spectrum, which might be caused by the hindered rotation of Pt–N bonds in a small-sized triangle, thus leading to the different chemical environments between the inner and outer triangles.[10] The $^{31}P\{^1H\}$ NMR spectrum of **7a** displayed two doublets (ca. 11.59 ppm and 11.13 ppm) shifted upfield from the starting platinum acceptor **5a** by approximately 4.45 and 4.52 ppm (Figure 3). This change, as well as the decrease in coupling of flanking ^{195}Pt satellites (ca. $\Delta^1J_{\mathrm{PPt}} = -48.71$ Hz), was consistent with back-donation from the platinum atoms. Moreover, the presence of the two-spin AB-type system resulted from the existence of an A doublet and a B doublet with a common coupling constant J_{AB} in **7a**. Likewise, the signals in the $^{31}P\{^1H\}$ NMR spectrum of **7b** shifted upfield from the starting platinum acceptors by approximately 4.06 ppm (Figure S9, Supporting Information). However, only the sharp singlet with a set of ^{195}Pt satellites on the either side was observed in the $^{31}P\{^1H\}$ NMR spectrum of **7b**, which indicated that the two phosphorus atoms were equivalent in **7b**. The abnormal phenomenon of **7a** might be attributed to the ortho-effect of methoxyl groups.[11] The sharp NMR signals in both ^1H and ^{31}P NMR spectra along with the solubility of these species ruled out the formation of oligomers.

The obtained result of one set of signals observed in the ^1H and ^{31}P $\{^1H\}$ NMR spectra could be traced back to the single species or the fast exchange process between both squares and triangles. If such an exchange process between chiral triangles and squares existed, upon reducing the temperature, the exchange process would become slower, and the separation of ^1H NMR signals would be observed.[12] Therefore, variable-temperature NMR spectra of **7a** and **7b** for a given concentration (0.09 mM) in acetone-d_6 were recorded over the temperature range of 223–323 K (Figures S11 and S12, Supporting Information), respectively. Variable-temperature ^1H NMR spectra showed that the signals of **7a** and **7b** stayed almost the same upon reducing the temperature from 323 to 223 K, and nearly no separation of signals was observed, which suggested the formation of sole, discrete, and stable chiral macrocycles.

In order to confirm which species was achieved, an ESI-TOF-MS technique was further utilized to explore mass spectra of the chiral self-assemblies **7a** and **7b**. In the ESI-TOF-MS spectrum of **7a**, a peak at m/z = 1070.85, corresponding to the

Scheme 1. Self-Assembly of Chiral Macromolecules 7a and 7b via Coordination-Driven Self-Assembly



charge state $[M - 4\ PF_6]^{4+}$ of the chiral triangles, was found. Likewise, the ESI-TOF-MS spectrum of **7b** exhibited the signal at m/z = 1070.85, related to $[M - 4\ PF_6]^{4+}$ of the chiral triangles. Their isotopic distributions were in excellent agreement with the theoretical distributions of the triangles (Figure 4). Close examination of the ESI-TOF mass spectra of **7a** and **7b** revealed that only the signals derived from triangles agreed well with their theoretical distributions (Figure S10, Supporting Information). The multinuclear NMR (^{1}H and ^{31}P) and variable-temperature NMR experiments and mass spectra ensured that chiral triangles rather than chiral squares were obtained exclusively.

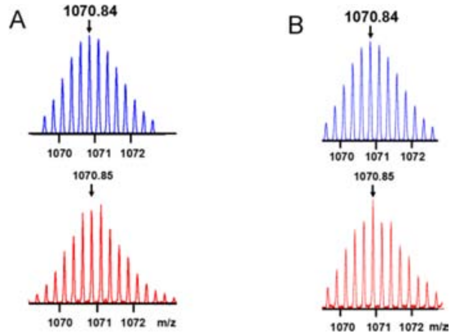


Figure 4. Calculated (top) and experimental (bottom) ESI-TOF-MS of **7a** $[M - 4\ PF_6]^{4+}$ (A) and **7b** $[M - 4\ PF_6]^{4+}$ (B).

The geometrical structures of **7a** and **7b** were optimized by PM6 semiempirical molecular orbital methods (Figure 5), which indicated that the internal radii of chiral triangles **7a** and **7b** were 1.1 and 1.4 nm, respectively. Moreover, this simulation method was further employed to explore the formation of triangles and squares in term of energy. The simulations of the self-assemblies unambiguously revealed that the formation of triangles was much easier than the squares in aspect of energy. The binding energy of **7a** was −6.547 eV under solution conditions, which was lower than that of the squares by 5.84 eV. In the case of **7b** and the corresponding squares, the energy difference was of 85.55 eV favorable to the triangles. The calculation results strongly supported that the formation of chiral triangles was more favorable, which agreed well with the results observed in the NMR spectra, variable-temperature NMR experiments, and ESI-TOF-MS spectra.

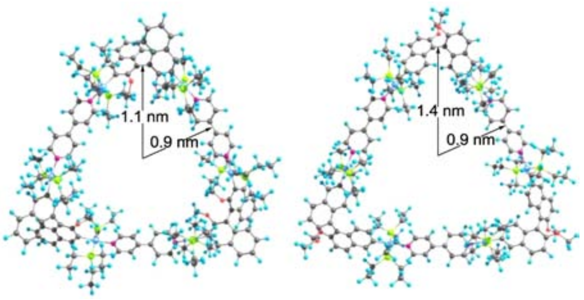


Figure 5. Optimized structures of **7a** (left) and **7b** (right).

As mentioned above, according to the directional-bonding approach,[4] the self-assembly of rigid linear linkers and 90° building blocks is expected to yield a molecular square. Moreover, the equilibrium between triangles and squares sometimes exists when 90° precursors are applied.[13] However, in this study, the chiral triangles were exclusively obtained, which might be mainly caused by the flexibility of chiral di-Pt(II) acceptors **5a** and **5b** based on BINOL.[14] Usually less rigid building blocks are believed to induce relative less strain in the triangular structure compared to the corresponding square structures, which makes the molecular triangles more favorable.[15] Furthermore, the entropic preference for the small ring might be another controlling thermodynamic factor that led to the selective formation of chiral triangles in this case.[9]

The investigation of inherent chirality of **5a**, **5b**, **7a**, and **7b** was performed by using circular dichroism (CD) spectra. The CD spectrum of **7b** exhibited one major single band at ~340 nm corresponding to the electronic spectrum of **7b** (Figure S7, Supporting Information) due to the ligand (naphthyl)-to-metal Pt(II)) charge transfer (LMCT), which was similar to **5b**, but with higher intensity. This observation suggested that the enhancement of CD signals in **7b** was consistent with the presence of multiple ligands in the metallocycle (Figure 6).[16] But the CD signals of **5a** and **7a** were too low to be clearly observed, which might be related to the relatively low optical rotation of di-Pt(II) nitrate **5a** ($[\alpha]_{25°C}(CH_2Cl_2)$ = +4.9) and triangle **7a** ($[\alpha]_{25\ °C}$(acetone) = +24.2), compared to that of **5b** and **7b** (see the Supporting Information).

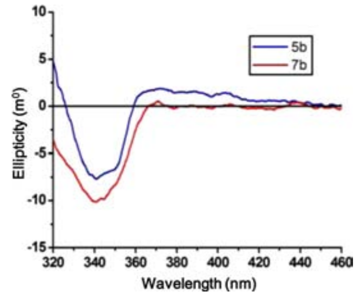


Figure 6. CD spectra of **5b** and **7b** in acetone.

In summary, a novel family of chiral triangles rather than squares has been obtained unexpectedly from the newly designed 90° chiral di-Pt(II) acceptors via coordination-driven self-assembly. It was one of few examples where chiral triangles were exclusively obtained from 90° building blocks. The chiral triangles were determined by multinuclear NMR, ESI-TOF-MS, variable-temperature NMR experiments, and elemental analysis. PM6 semiempirical molecular simulation was employed for the interpretation of the formation and stability of chiral triangles. This phenomenon might be attributed to a combination of the flexibility of di-Pt(II) acceptors in solution and entropic advantage of forming triangles. This work thus not only enriched the library of chiral macromolecules but also provided an enhanced understanding of the formation of chiral triangles. Further investigation on the breadth and scope of these newly designed chiral triangles is underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, characterization, and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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