

Self-Assembly of Chiral Molecular Polygons

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The self-assembly of supramolecular macrocyclic architectures has attracted intense interest in the past decade. Such polygonal structures can be readily synthesized via recognition-driven self-assembly of complementary subunits.¹ With the use of rigid, highly directional multibranching ligands to bind to coordinatively unsaturated metal complexes, numerous metalocycles with triangular and square shapes have been rationally synthesized.² Larger polygonal structures are, however, more scarce, as a direct consequence of their entropic disadvantage. While a few molecular hexagons are known,³ only one example of each is known for molecular pentagon,⁴ heptagon,⁵ and octagon.⁶ We wish to report here the one-pot self-assembly of chiral molecular polygons ranging from triangle to octagon and their purifications by simple column chromatography.

We have recently become interested in the construction of functional chiral metalocycles by using rigid atropisomeric bridging ligands and appropriate metal connectors as the building blocks, with the hope of generating well-defined enzyme-like chiral pockets or functionalities. Our recent work indicated that chiral molecular triangles and squares could be readily synthesized and used for chiral sensing and asymmetric catalysis.⁷ While chiral dinuclear metalocyclophanes were synthesized in high yields when [*cis*-(PEt₃)₂PtCl₂] was reacted with enantiopure 6,6'-bis(alkynyl)-1,1'-binaphthalene,⁸ we have unexpectedly discovered that chiral molecular polygons ranging from triangle to octagon were obtained when [*trans*-(PEt₃)₂PtCl₂] was used as the metal connecting points.⁹

Treatment of 2,2'-diacetyl-1,1'-binaphthyl-6,6'-bis(ethyne), **L-H₂**, with 1 equiv of *trans*-Pt(PEt₃)₂Cl₂ in the presence of catalytic amounts of CuCl in CH₂Cl₂ and HNEt₂ at room temperature afforded a mixture of different sizes of chiral metalocycles [*trans*-(PEt₃)₂Pt(L)]_{*n*} (*n* = 3–8, **1–6**). Each of the chiral molecular polygons **1–6** was purified by silica gel column chromatography, and analytically pure **1–6** was obtained in 5%, 18%, 16%, 10%, 5%, and 4% yield, respectively (Scheme 1).¹⁰ Compounds **1–6** have been characterized by ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy, FAB and MALDI-TOF MS, IR, UV-vis, and circular dichroism (CD) spectroscopies, and microanalysis.

¹H and ¹³C{¹H} NMR spectra of **1–6** indicated a single ligand environment, consistent with the formation of cyclic species. As shown in Figure 1, compounds **1–6** exhibit very similar ¹H NMR spectra with the exception of two doublets around 7 ppm that are assigned to H7 and H8 on the naphthyl ring. The chemical shifts of H7 and H8 are sensitive to the dihedral angle between the naphthyl groups because of the influence of the ring current from the adjacent naphthyl group. The downfield shifts of the H7 and H8 signals observed among **1–4** indicate that the dihedral angle increases on going from **1** to **4**. In contrast, no downfield shifts were observed for the larger cycles **4–6**, suggesting that they exhibit adequate flexibility for the naphthyl groups to adopt similar dihedral angles. Downfield shifts were also observed for the C7 and C8 resonances of **1–4** in their ¹³C{¹H} NMR spectra. ³¹P{¹H} NMR spectra of **1–6** all exhibit a single peak at ~12.5 ppm with a set of

Scheme 1

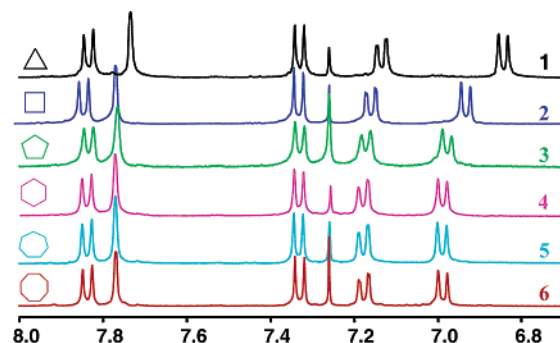
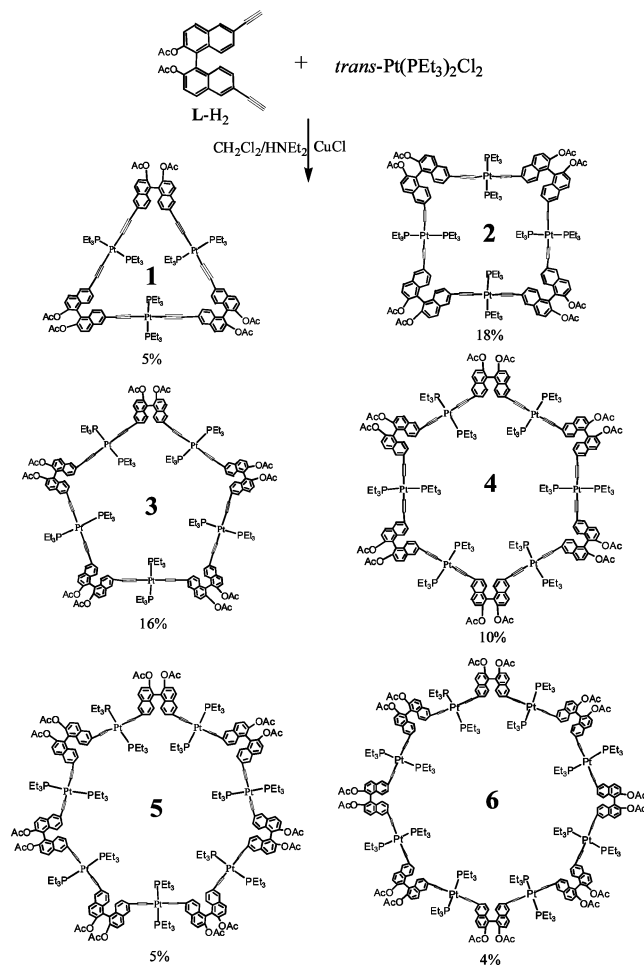


Figure 1. ¹H NMR spectra of **1–6** in CDCl₃. Only the aromatic regions are shown.

¹⁹⁵Pt satellites (*J*_{Pt–P} ≈ 2366 Hz). FAB and MALDI-TOF MS spectra exhibit characteristic peaks due to molecular ions for **1–6**,¹¹ thus confirming their polygonal structures of approximate *D_n*

symmetry. As expected, the terminal acetylenic C–H stretches of L-H₂ at $\sim 3280\text{ cm}^{-1}$ disappeared upon the formation of 1–6. The IR spectra of 1–6 exhibit expected C \equiv C stretches at $\sim 2090\text{ cm}^{-1}$. Numerous attempts have thus far failed to produce X-ray diffraction-quality single crystals of 1–6. Simulated structures using Molecular Mechanics indicated that 1–6 possess open cavities of 1.4–4.3 nm in size (Figure 2).

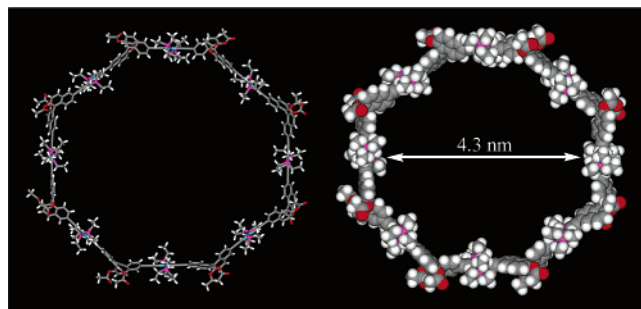


Figure 2. Stick and space-filling presentations of the energy-minimized structure of (S)-6.

The electronic spectrum of L-H₂ shows two peaks at 236 and 250 nm due to the naphthyl $\pi \rightarrow \pi^*$ transitions and a weak peak at 288 nm assignable to the acetylenic $\pi \rightarrow \pi^*$ transition. Upon the formation of metallocycles 1–6, a new intense peak at $\sim 225\text{ nm}$ appeared, which can be assigned to the *trans*-Pt(PEt₃)₂ moiety (Figure 3). The acetylenic $\pi \rightarrow \pi^*$ transitions have significantly

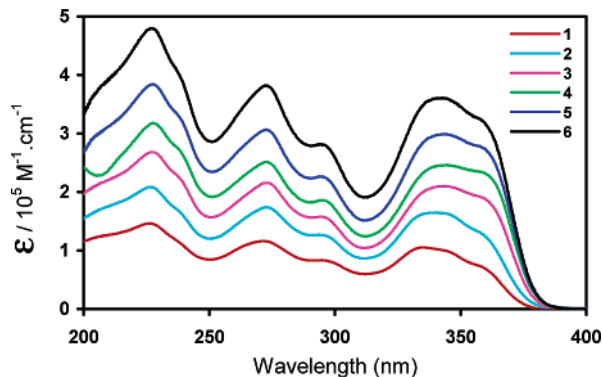


Figure 3. UV-vis spectra of 1–6 in acetonitrile. 0.8% of CH₂Cl₂ (v/v) was added to the solution of 4–6 to enhance the solubility.

red-shifted and split into two peaks at 335 and 360 nm, a result of mixing of Pt p-orbitals into the acetylenic $\pi \rightarrow \pi^*$ bands.¹² It is

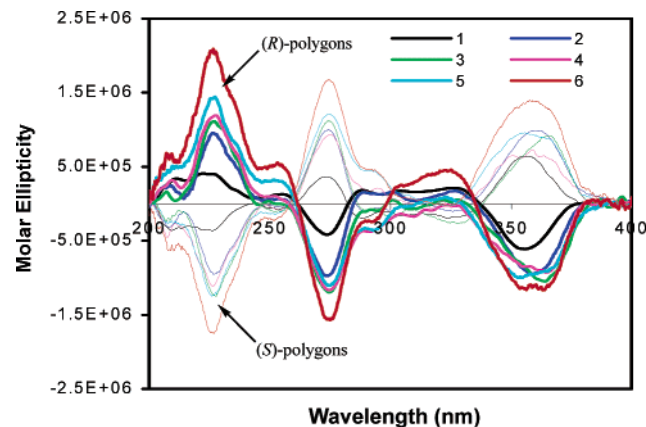


Figure 4. CD spectra of 1–6 in acetonitrile. 0.8% of CH₂Cl₂ (v/v) was added to the solution of 4–6 to enhance the solubility.

also interesting to note that the extinction coefficients increase as the size of the polygons increases, consistent with the presence of more *trans*-Pt(PEt₃)₂ and L building units in larger metallocycles.

CD spectra of 1–6 exhibit a bisignate band at $\sim 260\text{ nm}$ due to the naphthyl $\pi \rightarrow \pi^*$ transitions and an intense band at $\sim 360\text{ nm}$ assignable to the acetylenic $\pi \rightarrow \pi^*$ transitions, along with a strong band at $\sim 225\text{ nm}$ which can be attributed to the chiral arrangement of the PEt₃ groups on the Pt centers (Figure 4). Consistent with an increased number of *trans*-Pt(PEt₃)₂ and L building units, the CD signals also increase steadily as the size of the metallocycle increases.

We believe that limited conformational flexibility of the bridging ligand is key to the facile one-pot self-assembly of chiral molecular polygons 1–6. This work represents a rare example in which multiple products can be readily isolated from a coordination-directed self-assembly process. Tunable cavities and chiral functionalities presented by these molecular polygons promise to make them excellent receptors for a variety of guests.

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Supporting Information Available: Experimental procedures, analytical data, and four figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) These results are in stark contrast with those of previously reported linear polymers which were synthesized under more forcing conditions. See: Onitsuka, K.; Harada, Y.; Takei, F.; Takahashi, S. *Chem. Commun.* **1998**, 643.
- (10) The *R_f* values for 1–6 in hexane/ethyl acetate/CH₂Cl₂ (3:2:2 v/v/v) are 0.63, 0.47, 0.35, 0.31, 0.27, and 0.24, respectively. The yields were calculated on the basis of the starting materials, while linear oligomeric byproducts stay in the baseline.
- (11) FAB-MS: **1**, 2543.9 (calcd 2543.5 for M⁺); **2**, 3392.4 (calcd 3392.3 for [M + H]⁺); **3**, 4239.0 (calcd 4239.1 for M⁺); **4**, 5088.2 (calcd 5087.9 for [M + H]⁺). MALDI-TOF-MS: **5**, 5939.2 (calcd 5935.7 for [M + H]⁺); **6**, 6787.1 (calcd 6782.5 for [M + H]⁺).
- (12) (a) The bathochromic shifts for the acetylenic $\pi \rightarrow \pi^*$ transitions in 1–6 are much more pronounced than those observed in the metallocyclophane built from [*cis*-(PEt₃)₂PtCl₂] and L-H₂, consistent with the more conjugated nature of 1–6. See ref 8. (b) Yam, V. W.-W. *Acc. Chem. Res.* **2002**, *35*, 555.

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