

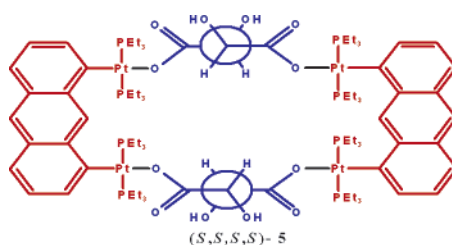
Facile Synthesis of Enantiopure Chiral Molecular Rectangles Exhibiting Induced Circular Dichroism

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ABSTRACT



The facile syntheses of enantiopure molecular rectangles using 1,8-bis(*trans*-Pt(PEt₃)₂(NO₃))anthracene and optically pure D- or L-tartrate are reported in high yields. These self-assembled macrocycles are unique examples where the phenomenon of induced chiral dichroism (ICD) has been observed in chiral metallosupramolecular assemblies.

Coordination-driven self-assembly of discrete nanoscopic structures is an area of intense interest and research activity.^{1–7} As a result, the self-assembly of two- and three-dimensional discrete supramolecular complexes has received considerable attention in recent years.^{2,8–13} Coordination-driven self-assembly utilizes metal systems as key elements in the generation of molecular ensembles.

Square-planar platinum and palladium complexes have been frequently used as acceptor units in this area to synthesize molecular rectangles,^{11,12,14} triangles,^{15–18} squares,^{18–22} hexagons,^{18,23} and higher-order polygons.^{18,24,25}

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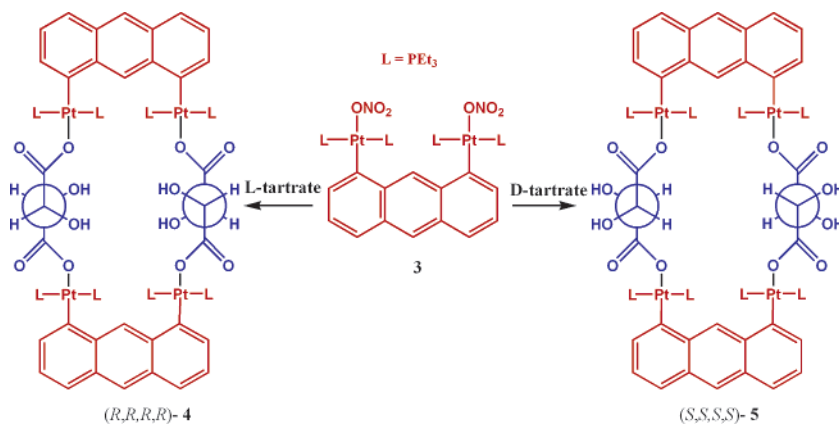
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Scheme 1. Self-Assembly of Chiral Molecular Rectangles (*R,R,R,R*)-**4** and (*S,S,S,S*)-**5**

The design and synthesis of the desired species have mostly focused on the use of rigid, neutral nitrogen donor organic linkers except in a few cases where flexible linkers were used to generate discrete ionic macrocyclic structures.^{26–28} In our previous papers, we have demonstrated the facile self-assembly of pre-designed neutral Pt(II) macrocycles utilizing Pt–oxygen bonding interactions.^{12,29} In this newly developed methodology, Pt(II)-based acceptor linkers were linked with linear or angular dicarboxylate anions (terephthalate, fumarate, isophthalate, muconate, etc.). The efficacy of this newly developed methodology to synthesize neutral two-dimensional nanoscale architectures prompted us to design more complex macrocycles containing 1,1'-ferrocenedicarboxylate³⁰ and carborane dicarboxylates.³¹ However, the neutral assemblies synthesized by this approach were achiral.

Our next objective was to synthesize neutral and at the same time chiral macrocycles. The design and synthesis of chiral supramolecular assemblies is now considered to be an important field of research because chiral macrocycles can be used for enantioselective sensing and asymmetric catalysis.^{32–37}

There are several ways by which one can self-assemble discrete cyclic *chiral* species. One can use intrinsically chiral metallocorners to construct chiral metallocycles. For example, Cotton and co-workers utilized the chiral *cis*-Rh₂(C₆H₄PPh₂)₂²⁺ unit and carboxylate anions to self-assemble molecular triangles.^{1,38} Pure enantiomers of some of these chiral triangles were also prepared, and their catalytic activity was reported.^{35,39} Another means to prepare chiral metallocycles is to use a chiral auxiliary ligand, L' chelated to *cis*-ML₂ units (M = Pt²⁺, Pd²⁺).^{40,41} This metallocorner with its chiral auxiliary subsequently imparts chirality to the final self-assembled macrocyclic species. Finally, one can also synthesize chiral metallocycles using chiral bridging ligands.^{32,36,42–44} This approach is more versatile and popular since it gives an opportunity to incorporate different kinds of chiral bridging ligands. For example, Lin and co-workers have synthesized chiral metallocycles based on atropisomeric linear bridging ligands and angular metallocorners and have shown their use in chiral sensing and asymmetric catalysis.^{32,36,37}

To build on our newly developed self-assembly paradigm that utilizes Pt–oxygen bonding interactions, we became interested in incorporating chiral tartrate anions to synthesize chiral assemblies. The advantage of using tartrates is that these ligands are readily available from commercial sources in pure enantiomeric forms. Herein, we report the facile synthesis of chiral molecular rectangles (Scheme 1) using

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tartrate as the donor/bridging ligand in high yields. We have characterized these chiral molecular rectangles with a variety of techniques such as NMR, UV-vis and CD spectroscopy, and elemental analysis.

Enantiopure neutral supramolecular assemblies **4** and **5** were synthesized as shown in Scheme 1. Addition of an aqueous solution of disodium L-(+)-tartrate **1** to an acetone solution of anthracene-based diplatinum clip **3** in a 1:1 molar ratio resulted in immediate precipitation of chiral supramolecular rectangle **4** in 93% isolated yield. The yellow product, which precipitated, was centrifuged and washed several times with water. The yellow powder was then dissolved in CDCl₃ for ¹H and ³¹P NMR studies. Similar treatment of disodium D-(−)-tartrate **2** with clip **3** produced **5** in 94% isolated yield.

The ³¹P{¹H} NMR (121.4 MHz) spectrum of chiral molecular rectangle (*R,R,R,R*)-**4** is shown in Figure 1.

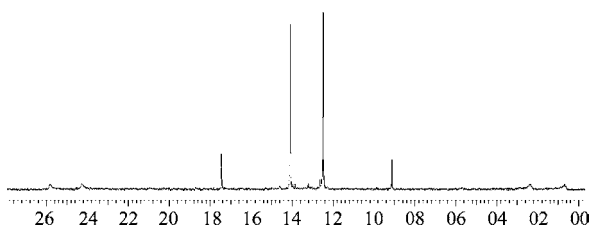


Figure 1. ³¹P{¹H} NMR (121.4 MHz) spectra of molecular rectangles (*R,R,R,R*)-**4** in CDCl₃.

The spectrum indicates the presence of a two-spin system of *AB* type due to the existence of an *A* doublet and a *B* doublet with a common coupling constant J_{AB} . The two doublets are centered at 15.8 and 10.8 ppm. The coupling constant J_{AB} is 408.3 Hz. The *A* and *B* doublets are accompanied with a set of ¹⁹⁵Pt satellites on either side.

In the case of the platinum-based neutral rectangular macrocycles that we have reported in our previous papers,^{12,29–31} the presence of a sharp singlet in the ³¹P{¹H} NMR with concomitant ¹⁹⁵Pt satellites indicated that all phosphorus atoms are equivalent. However, since the ³¹P{¹H} NMR spectrum in the case of macrocycle (*R,R,R,R*)-**4** resembles an *AB* system, we can conclude that the two phosphorus atoms connected to a particular platinum atom are magnetically nonequivalent. We believe that the magnetic nonequivalence of the PEt₃ groups attached to a particular platinum atom, in the case of (*R,R,R,R*)-**4**, is imparted because of the presence of chiral centers of the tartrate bridging ligand.

The ¹H NMR (300 MHz) spectrum of (*R,R,R,R*)-**4** also indicates the incorporation of tartrate in the macrocycles due to the presence of two doublets centered at 4.44 and 3.72 ppm. The coupling constant ($^3J_{CH-OH}$) due to the C–H and O–H protons of tartrate is 5.15 Hz. Upon exchanging the protons of the hydroxy groups in (*R,R,R,R*)-**4** with deuterium, there was a considerable decrease in the doublet signal at 3.72 ppm. This clearly indicated that the doublet centered

at 4.44 ppm corresponds to the set of C–H protons, whereas the doublet centered at 3.72 ppm corresponds to the set of O–H protons. The presence of two magnetically inequivalent PEt₃ groups attached to a particular platinum atom was also evident from the ¹H NMR (300 MHz) spectrum of (*R,R,R,R*)-**4** as indicated by the presence of two sets of multiplet signals for both CH₂ and CH₃. The other chiral macrocycle (*S,S,S,S*)-**5**, prepared by reacting disodium D-(−)-tartrate **2** with clip **3**, exhibits ³¹P{¹H} and ¹H NMR spectra identical to (*R,R,R,R*)-**4**. The inherent chirality of (*R,R,R,R*)-**4** and (*S,S,S,S*)-**5** was demonstrated by their CD spectrum. (*2R,3R*)-(+)-Tartaric acid **1** exhibits only one negative Cotton effect at 214 nm and is CD-inactive in the long wavelength (Figure 2).

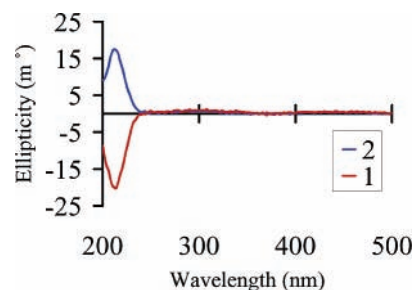


Figure 2. Circular dichroism spectra of L-tartaric acid **1** (concn 2.25×10^{-4} M) and D-tartaric acid **2** (concn 2.16×10^{-4} M).

On the other hand, macrocycle (*R,R,R,R*)-**4** is CD-active and exhibits at least three negative Cotton effects above 350 nm (Figure 3).

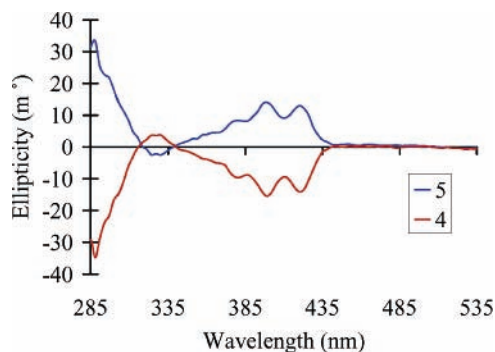


Figure 3. Circular dichroism spectra of (*R,R,R,R*)-**4** (concn 1.1×10^{-4} M) and (*S,S,S,S*)-**5** (concn 1.3×10^{-4} M) in CHCl₃.

The bands in the CD spectrum of (*R,R,R,R*)-**4** centered at 288, 381, 399, and 420 nm correspond to the transitions at 270, 382, 400, and 422 nm observed in the electronic spectrum of **4** due to the anthracene moiety. The electronic spectrum of metallacycle (*R,R,R,R*)-**4** is shown in Figure 4.

This result clearly shows the presence of induced circular dichroism (ICD) in the anthracene moiety of (*R,R,R,R*)-**4**.

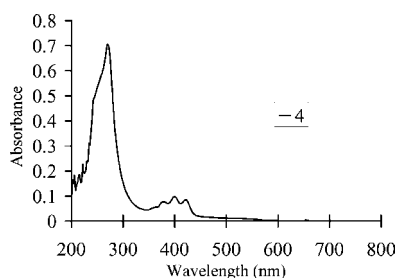


Figure 4. Electronic (UV-vis) spectrum of (R,R,R,R) -**4** (concn 1.3×10^{-5} M) in CHCl_3 .

According to Hill, “ICD is realized when an achiral molecule(s) displays CD signals within their absorbing regions on association with a chiral inducer”.⁴⁵ In our case, upon association of two $(2R,3R)$ -(+)-tartarate dianions (**1**) (chiral inducer) with two anthracene-based diplatinum clips **3** (achiral unit) to yield **4**, ICD appears within the absorption bands of **3** which is otherwise CD-inactive.

Similarly, the phenomenon of ICD is also observed in the case of macrocycle (S,S,S,S) -**5** as indicated from its CD

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spectrum (Figure 3). Though the phenomenon of ICD is well-known, (R,R,R,R) -**4** and (S,S,S,S) -**5** are the only examples where it has been observed and discussed in self-assembled metallacycles.

In summary, the facile syntheses of two novel chiral molecular rectangles have been described. Enantiopure metallacycles (R,R,R,R) -**4** and (S,S,S,S) -**5** were self-assembled in high yields using 1,8-bis(*trans*-Pt(PEt₃)₂(NO₃))-anthracene **3** and commercially available $(2R,3R)$ -(+)-tartarate and $(2S,3S)$ -(-)-tartarate, respectively. Assemblies (R,R,R,R) -**4** and (S,S,S,S) -**5** are the first examples where the phenomenon of induced circular dichroism (ICD) has been observed in chiral metallosupramolecular assemblies. We are currently investigating the catalytic potentials of these macrocycles.

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Supporting Information Available: Experimental details, ³¹P{¹H} and ¹H NMR data for (S,S,S,S) -**5**, ¹H NMR data for (R,R,R,R) -**4**, and electronic (UV-vis) spectrum of (S,S,S,S) -**5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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