Chiral Conjugated Corrals

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ABSTRACT: We present here a new design motif for strained, conjugated macrocycles that incorporates two different aromatics into the cycle with an −A−B−A−B− pattern. In this study, we demonstrate the concept by alternating electron donors and acceptors in a conjugated cycle. The donor is a bithiophene, and the acceptor is a perylene diimide derivative. The macrocycle formed has a persistent elliptiform cavity that is lined with the sulfur atoms of the thiophenes and the π-faces of the perylene diimide. Due to the linkage of the perylene diimide subunits, the macrocycles exist in both chiral and achiral forms. We separate the three stereoisomers using chiral high-performance liquid chromatography and study their interconversion. The mechanism for interconversion involves an “intra-molecular somersault” in which one of the PDIs rotates around its transverse axis, thereby moving one of its diimide heads through the plane of the cavity. These unusual macrocycles are black in color with an absorption spectrum that spans the visible range. Density functional theory calculations reveal a photoinduced electron transfer from the bithiophene to the perylene diimide.

INTRODUCTION

This article describes the design, synthesis, and study of a new type of conjugated aromatic macrocycle formed from the linkage of donor and acceptor subunits into a strained cycle. These macrocycles are members of an ever-growing class of cyclic, conjugated belts, such as cycloparaphenylenes (CPPs)1−17 and cycloporphyrins (CPs).18−20 CPPs consist of para-connected phenylene rings and possess size-dependent optical and electronic properties.11,21−25 However, CPPs do not absorb at a sufficiently broad part of the visible spectrum for them to be useful in optoelectronic devices.24 The optical gaps for CPs are smaller, but they have not been studied in devices. There are no fully conjugated CPPs or CPs with two different aromatic subunits in an −A−B−A−B− pattern. Alternation of electron-donor and -acceptor subunits is a proven strategy to engineer the energetics of linear, conjugated oligomers and polymers,25−27 but it has not been explored in the context of conjugated, cyclic oligomers. For this study, we designed and synthesized the molecules shown in Figure 1A, comprising two diphenyl perylene diimides (PDIs) and two bithiophenes. Each of these macrocycles has a persistent elliptiform cavity that is lined with electron-deficient π-faces of the PDI and the lone pairs of the sulfur atoms from the thiophene subunits. We have named these macrocycles “conjugated corrals” (abbreviated CC1). The corrals are black in color and have a broad absorption spectrum that spans the entire visible range. The onset of strong absorbance occurs at approximately 700 nm (HOMO-to-LUMO excitation at 1.8 eV), hinting at CC1’s favorable prospects as optical materials. Furthermore, we find that CC1 exists in a dynamical equilibrium between both chiral [(R,R)-CC1 and (S,S)-CC1] and meso [(S,R)-CC1] forms due to the handedness of the helical PDI subunits (Figure 1). The essential point of this study is that this new −A−B−A−B− motif for cyclic conjugated molecules (Figure 1A) provides interesting chiral information and an unusual electronic structure.

RESULTS AND DISCUSSION

We incorporated PDI as the electron acceptor in CC1’s design because PDI derivatives have shown a number of desirable behaviors: (1) they are efficient materials in n-type organic field effect transistors;5a (2) they have high molar absorbivities;5b−5d (3) they are efficient electron acceptors in organic photovoltaics;32−35 (4) they form small band gap polymers with electron-donating moieties; and (5) they are easily

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functionalized from inexpensive starting materials. We employed oligothiophenes as the electron-rich counterpart because they are ubiquitous as electron-donor molecules in electronic materials. Our synthesis is based on the strategies developed by Bauerle and Yamago in the syntheses of conjugated macrocycles via square planar platinum intermediates.

Scheme 1 displays the synthesis of CC1 that employs a four-cornered tetraplatinum macrocycle. The key intermediate is the bisplatinated diphenyl-PDI. We synthesize this important building block by a double Stille coupling of 1,4-bis(tributylstannyl)benzene with the 1,7-dibromo-PDI to afford the bis-tributyltin-substituted aromatic. Transmetalation of 2 with dichloro(1,5-cyclooctadiene)platinum(II) provides 3. We heat equimolar amounts of 3 and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene for 40 h to yield 4. This organometallic macrocycle proved difficult to isolate, so we carried the crude material onto the ultimate product by heating it with excess triphenylphosphine. This initiates the 4-fold reductive elimination that forms CC1. Preparative high-performance liquid chromatography (HPLC) gives pure CC1 in an 8% yield from 3. This yield is exceptional given that it incorporates two steps and provides such a complex strained macrocycle.

Figure 1. (A) Schematic structure of the –A–B–A–B– pattern encoded in CC1. (B) Stereoisomerism of CC1 results from the chirality of the (R)- and (S)-1,7-diphenyl-PDI subunits. (C) Molecular, conjugated corals (CCs) exist in chiral [(R,R)-CC1 and (S,S)-CC1] and meso [(S,R)-CC1] forms.

Scheme 1. Synthesis of CC1

Key: (a) Pt(COD)Cl2, toluene, 100 °C, 24.5 h, 45% yield; (b) 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, THF, 50 °C, 40 h; (c) PPh3, toluene, 100 °C, 24 h, 8% yield (2 steps).
possessed electron-withdrawing substituents. We sought to circumvent this scrambling by performing transmetalation on the PDI (2 to 3) prior to adding the electron-rich bithiophene subunit. In fact, upon isolating 3, we find no evidence of scrambling of the Pt–phenyl bond when heated to 50 °C with tributyltin chloride for 48 h. This lack of reversibility is a new design feature that allows the synthesis, for the first time, of conjugated macrocycles with an alternating −A−B−A−B− pattern.

The branched undecyl side chains and the molecular dynamics of the PDIs in CC1 (vide infra) hinder formation of crystals suitable for single-crystal X-ray diffraction. High-resolution mass spectrometry (Supporting Information Figure S1A,B) confirms a cyclic structure that consists of two bithiophenes and two diphenyl-PDIs. The 1H NMR spectrum of CC1 contains several broad peaks in the aromatic region at room temperature, suggesting that the dynamical processes (rotation of the phenyl rings and the undecyl side chains) occur on the NMR time scale (Figure S1C). Acquiring the NMR data at 87 °C (in 1,1,2,2-tetrachloroethane-d2), however, provides a well-resolved 1H NMR spectrum (Figure S1D). In the downfield region of the spectrum (Figure 2A), we observe resonances consistent with the macrocycle alongside a smaller set of resonances that have analogous splitting and multiplicity. This pattern suggests that CC1 exists as two closely related isomers, and integration of the resonances reveals that the two isomers occur in a ratio of approximately 6:1 (at 87 °C). The gas-phase calculations provide a ratio of 316:1 at 87 °C (see the Supporting Information for details). The effects of the medium, solvation, guest inclusion, and dielectric constant must account for the difference between calculated and observed ratios. We also performed variable-temperature NMR and did not observe coalescence up to 147 °C.

The two sets of resonances we observe in the NMR in Figure 2A are a result of stereoisomerism. The diphenyl-PDI moiety, when linked in the 1,7-position and constrained in a macrocycle, introduces chirality (Figure 1B). We were able to grow crystals of N,N′-di(6-undecyl)-1,7-di(4-bromophenyl)-perylen-3,4,9,10-tetracarboxylic diimide that revealed that the PDI core is highly contorted such that the long axis of the PDI is twisted into a helix, with a 22° dihedral angle between the two naphthalene subunits of the perylene. This contorted core places each of the pendant aromatic rings on the same face of the PDI (Figure S2). This structural feature was observed previously in crystallography of PDIs substituted with ferrocene groups in the 1,7-positions. With this information in hand, we used density functional theory (DFT) to determine energy-optimized structures for the stereoisomers, and these are represented in Figure 2B,C. When linked together by a pair of bithiophenes, two diphenyl-PDI subunits possessing the same chirality produce a pair of enantiomers [(R,R)-CC1 and (S,S)-CC1, Figure 2B]. Alternatively, linking two PDI subunits with opposite chirality produces an achiral, meso form [(R,S)-CC1, Figure 2C]. The enantiomeric forms of CC1 have an approximate C3 axis that relates the two PDIs in the macrocycle. The achiral, meso isomer contains a mirror plane between the two PDIs. Both the chiral and meso forms of CC1 have PDI core structures that resemble the diphenyl-PDI conformation. The twist of the PDI core in the meso isomer is the same as that of the diphenyl-PDI derivative, 22° (Figure S2), whereas the chiral isomer has a larger twist in its PDI subunit (25°, shown in Figure 2B). We believe that this twist and orientation of the phenyls facilitates formation of CC1 by giving curvature to the otherwise flat PDI.

In both stereoisomers of CC1, the macrocycle has a persistent elliptiform cavity, measuring 1.6 nm from PDI to PDI and 1.0 nm from bithiophene to bithiophene. One striking difference between these two stereoisomers is the apparent strain in the tetracyclic linkers connecting the PDIs. The meso isomer forces the linkers to bow in order to accommodate the rigidity of the cycle (Figure 2C), which make the chiral isomer appear less strained. In both isomers, the sulfur atoms of the four thiophenes point into the cavity, while the diphenyl-PDIs cap the ends of the macrocycle. Oligothiophenes typically possess an antigemetry of their sulfur atoms rather than syn orientation, reflecting decreased steric repulsion in the former. However, this is not the case for CC1. The bithiophene orientation plays a crucial role in the assembly of CC1 by relieving strain. In order to quantify this effect, we modeled the syn and anti conformers of simple bithiophene, C6H7S2. The angle between the two terminal C–H bond vectors defines the curvature supported by the bithiophene. This angle is 117° in the syn geometry and 180° in the anti geometry. Thus, the syn orientation of the bithiophene promotes the formation and stabilization of CC1. Conversely, the incorporation of the bithiophenes into CC1 promotes the otherwise unfavorable syn orientation in the bithiophenes. Reports from Bäuerle and Itami describe a similar conformation preference in macroyclic, 2,5-linked oligothiophenes. Calculations using a homodesmotic reaction reveal that the strain energy is ∼20 kcal/mol for the chiral isomers of...
CC1 and 22 kcal/mol for the meso isomer. The Supporting Information contains the details of these calculations.

Chiral HPLC allowed us to separate and characterize the stereoisomers of CC1. The chromatogram of CC1 (Figure 3A) shows both the pair of enantiomers and the meso isomer. In the chromatogram, peaks A and C have equal integrated intensity and therefore represent the enantiomeric pair. A third peak, B, corresponds to the meso stereoisomer. Using HPLC with a circular dichroism (CD) detector, we were able to confirm this assignment (Figure 3B). The two peaks in the chromatogram assigned to the two enantiomers gave opposite CD signals (225–800 nm, Figure 3B,C). As anticipated, the peak assigned to the meso compound had no detectable CD signal.

It is interesting that A and C interconvert at room temperature, albeit not directly; the interconversion requires the intermediacy of B, the meso compound. To confirm the intermediacy of B, we used preparative HPLC. We obtained a pure fraction of C and immediately reinjected it into the HPLC and monitored for appearance of the A and B stereoisomers.

![Figure 3](https://jacs.org/jacs/5b05698.jpg)

**Figure 3.** (a) HPLC chromatogram of CC1 using a CHIRALPAK IA-3 column. (b) HPLC-CD chromatogram of CC1 showing that peaks A and C exhibit opposite optical activity (270–410 nm). (c) CD spectra for both enantiomers of CC1. (D) Interconversion of the stereoisomers of CC1 by sequential rotation of one PDI subunit through the macrocycle and then rotation of the other PDI to convert between enantiomers. The hydrocarbon side chains have been replaced with a methyl group. Carbon = gray, nitrogen = blue, oxygen = red, sulfur = yellow. Hydrogen atoms have been removed to clarify the view.
Within 20 min, the concentration of B had already reached 62% of its equilibrium value, yet that of A had reached only 8% of its equilibrium value. After 2 h at room temperature, all peaks had reached their equilibrium intensities. This result is remarkable because it suggests the mode of isomerization is a PDI “intramolecular somersault” in which one of the PDIs rotates around its transverse axis, thereby moving one of its diimide heads through the plane of the cavity. This somersault converts a chiral molecule into an achiral one and vice versa. Figure 3D shows a schematic of this conversion process between A and B.

We were also interested in the rate of interconversion, and we used variable-temperature HPLC to study this process. Maintaining the temperature of both the HPLC column and the sample at 0 °C, we analyzed the freshly isolated meso isomer, B, monitoring its conversion to both of the enantiomers (A/C) over time. Figure S4B shows the natural log of the diastereomeric excess as a function of time. If we assume that this process is a simple first-order reaction, the rate constant was \(10^{-3} \text{s}^{-1}\) at 0 °C. It is difficult to relate this rate to other macrocycles, given there have been just a few kinetic studies concerning the racemization of conjugated belt-like compounds. Yet, we see experimentally that equilibrium is reached within 2 h at room temperature as discussed above.

The electronic properties of CC1 can be appreciated by consideration of its UV–vis absorption spectrum (Figure 4), particularly when compared to the spectra of its constituent parts, viz., a helically deformed PDI (2) and a bithiophene derivative. CC1 retains the shorter-wavelength absorptions (300–400 nm) characteristic of bithiophene and the intermediate-wavelength absorptions (450–550 nm) characteristic of PDIs, but a new, strong absorption band appears at longer wavelength (∼550–700 nm). The optical gap is estimated to be 1.8 eV from the absorption band edge. It is the addition of this latter band that completes the absorption of the visible and renders CC1 black in color.

We used quantum chemical calculations (time-dependent DFT) to characterize the low-lying excited states of CC1 and found that while there is little charge transfer from the electron-rich thiophenes to the electron-accepting PDIs in the ground state of the molecule, there is such charge transfer in the lowest-energy excited states: the long-wavelength absorptions are best viewed as forming bithiophene-to-PDI charge transfer states (Figure S5). We also studied the energetics of the frontier orbitals of CC1 using electrochemistry (see Figure S6). The onset of the first oxidation (0.58 V) and reduction (−1.07 V) peaks relative to Fc/Fc + provides an estimate of the HOMO–LUMO gap (1.6 eV). Similar to other aryl-substituted PDI compounds, CC1 has one oxidation and two one-electron reductions, revealing that the PDIs within CC1 retain their ability to accept two electrons.

**CONCLUSIONS**

In this study, we have described a new class of fully conjugated macrocycles that incorporate donor and acceptor subunits to form a chiral conjugated corral. CC1 is the first example of a conjugated macrocycle with alternating aromatic subunits in an −A−B−A−B− pattern. These new macrocycles possess an interesting topology and useful electronic properties that are a result of the pattern written into the cycle. The corral’s unusual electronic structure provides a small HOMO/LUMO gap and broad absorbance across the entire visible light spectrum. Excited-state DFT calculations reveal intramolecular charge transfer in the frontier orbitals. Not only does the corral’s rich conformational dynamics allow for the interconversion of this macrocycle between chiral and achiral forms, but this easy propensity for shape-shifting offers the appealing opportunity for sterically forgiving host–guest chemistry. This unusual set of properties makes the corrals exciting new candidates for use in energy applications such as photovoltaics.

**ASSOCIATED CONTENT**

3 Supporting Information

Experimental procedures for the synthesis and characterization of CC1 and precursors. UV–vis spectroscopy, cyclic voltammetry, VT-NMR, HPLC, crystallographic data (CIF), and computational details. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05698.

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Notes

The authors declare no competing financial interest.

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**Figure 4.** UV–vis absorption spectrum of CC1 (black line), 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (blue), and 2 (red) in CH2Cl2 (concentration = 1.6 × 10⁻⁵, 1.3 × 10⁻⁴, and 1.8 × 10⁻⁵ M, respectively, path length = 1.0 cm). The blue trace is plotted with respect to the right ordinate, and the black and red traces are plotted with respect to the left ordinate.
REFERENCES

(24) The smallest HOMO/LUMO gap in a CPP is seen in [5]-CPP, the smallest CPP synthesized to date. The HOMO/LUMO gap from calculations is 2.34 eV. See refs 2 and 12.