Influence of Molecular Conformation on Electron Transport in Giant, Conjugated Macrocycles

Melissa L. Ball,† Boyuan Zhang,† Qizhi Xu,†‡ Daniel W. Paley,† Virginia Cary Ritter,† Fay Ng,*† Michael L. Steigerwald,*† and Colin Nuckolls*†‡

†Department of Chemistry, Columbia University, New York, New York 10027, United States
‡Wuhan University of Science and Technology, Wuhan, Hubei 430072, People’s Republic of China

ABSTRACT: We describe here the direct connection between the molecular conformation of a conjugated macrocycle and its macroscopic charge transport properties. We incorporate chiral, helical perylene diimide ribbons into the two separate macrocycles as the n-type, electron transporting material. As the macrocycles’ films and electronic structures are analogous, the important finding is that the macrocycles’ molecular structures and their associated dynamics determine device performance in organic field effect transistors. We show the more flexible macrocycle has a 4-fold increase in electron mobility in field effect transistor devices. Using a combination of spectroscopy and density functional theory calculations, we find that the origin of the difference in device performance is the ability of more flexible isomer to make intermolecular contacts relative to the more rigid counterpart.

This Communication describes the direct connection between the molecular conformation of a macrocycle and its macroscopic charge transport properties. The macrocycles studied here are the merger of two classes of electronic materials: conjugated macrocycles1−27 and electron transporting helical perylene diimide (hPDI) ribbons.28−30 Conjugated macrocycles are emerging as efficacious materials for electron transport in organic field effect transistors (OFETs), photovoltaics (OPVs), and sensors.19,31−33 Thus, the most successful conjugated macrocycles in devices consist of multiple copies of PDI monomers with various spacers that are wound into a macrocycle. Our goal here is to substitute monomeric PDI subunits with oligomeric hPDI subunits. The hPDI nanoribbons are known to have extraordinary properties in devices requiring efficient charge transport, such as solar cells and photodetectors,34−38 making them exciting candidates for incorporation into a conjugated macrocycle construction.

Here we reveal the first of new, giant macrocycles that incorporate hPDI ribbons (Figure 1). Each of these macrocycles comprises a macrocycle building block with a phenyl-bithiophene-phenyl linker (B) and an hPDI dimer (D). The macrocycles are formed from these two molecular components wrapped into a -D-B-D-B- arrangement.
in a pronounced difference in the conductance of the films: the electron mobility of cis-cDBDB is over 4-times greater than that of trans-cDBDB. The difference in mobility is a direct consequence of the different molecular conformations available to the two isomers: the cis isomer’s more flexible structure is better able to make intermolecular contacts than the trans isomer’s more rigid structure.

Scheme 1 displays the synthesis of cis-cDBDB and trans-cDBDB. Both syntheses begin from the cis and trans dibrominated dimers (hPDI-Br2, 1a and 2a) that are formed as a 1:1 mixture in the bromination of the parent hPDI dimer.28 The separation of 1a and 2a proved to be a challenging step in part because the two regioisomers are indistinguishable by 1H NMR or UV/vis spectroscopy. Moreover, we were unable to extract the mobility or use the more modern methods developed by McCulloch39 and Choi.40 The cis-cDBDB based transistor has a mobility of ~4.1 × 10⁻³ cm²/(V·s) relative to ~9.9 × 10⁻⁴ cm²/(V·s) for trans-cDBDB (Figure 2). The devices in Figure 2 are the highest mobility for each isomer. To confirm the statistical relevance of this data, we measured seven devices and averaged the data for both trans-cDBDB and cis-cDBDB. The averaged data, too, showed the cis isomer has a 4-fold increase in electron mobility. Details for the device fabrication and output curves can be found in the Supporting Information (Figure S6, Table S2). We tested 1a and 2a, too, to see if there was a difference in mobility within the acyclic fragments, and found that the mobilities of the two are essentially identical (Figure S7).

To understand why cis-cDBDB’s mobility is much greater than trans-cDBDB, we consider two factors that have a significant and general impact on charge transport in thin films: (1) the film morphology and (2) the molecular and electronic structure of the molecule. We conclude that the films as we have prepared them are amorphous, and the electronic structures of the two macrocycles are essentially identical. These points suggest that it is the molecular structures and their associated dynamics that determine device performance.

We next explore how the connectivity of the macrocycles influences charge transport in thin films. From the potential of the first reduction peak in the cyclic voltammogram, we estimate the lowest unoccupied molecular orbital (LUMO) energy level to be −3.80 and −3.82 eV for trans-cDBDB and cis-cDBDB (Figure S5), respectively. These values are similar to the parent hPDI dimer and common n-type semiconductors like [6,6]-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM).28 This data suggests both macrocycles are promising n-type semiconductors.

Scheme 1. Synthesis of (a) cis-cDBDB and (b) trans-cDBDB**

```
```

关键：(a) 1,4-二(tributylstannyl)苯，P-(2-呋喃)₃Pd₂dba₄，THF，55 °C，12 h；(b) Pt(COD)Cl₂，toluene，100 °C，12 h；(c) 5,5'-二(tributylstannyl)-2,2'-bithiophene，THF，55 °C，40 h；(d) PPh₃，toluene，100 °C，12 h.

Figure 2. (a) Schematic of the OFET device and (b) transfer characteristics for trans-cDBDB and cis-cDBDB, showing a 4-fold increase in electron mobility for the latter.

cis-cDBDB. The remarkable finding is cis-cDBDB shows a 4-fold increase in mobility relative to trans-cDBDB. The conclusion is the same whether we use traditional methods to extract the mobility or use the more modern methods developed by McCulloch39 and Choi.40 The cis-cDBDB based transistor has a mobility of ~4.1 × 10⁻³ cm²/(V·s) relative to ~9.9 × 10⁻⁴ cm²/(V·s) for trans-cDBDB (Figure 2). The devices in Figure 2 are the highest mobility for each isomer. To confirm the statistical relevance of this data, we measured seven devices and averaged the data for both trans-cDBDB and cis-cDBDB. The averaged data, too, showed the cis isomer has a 4-fold increase in electron mobility. Details for the device fabrication and output curves can be found in the Supporting Information (Figure S6, Table S2). We tested 1a and 2a, too, to see if there was a difference in mobility within the acyclic fragments, and found that the mobilities of the two are essentially identical (Figure S7).

To understand why cis-cDBDB’s mobility is much greater than trans-cDBDB, we consider two factors that have a significant and general impact on charge transport in thin films: (1) the film morphology and (2) the molecular and electronic structure of the molecule. We conclude that the films as we have prepared them are amorphous, and the electronic structures of the two macrocycles are essentially identical. These points suggest that it is the molecular structures and their associated dynamics that determine device performance.

It is well-established that a thin film’s crystallinity and morphology will influence the charge transport characteristics,
and thus we first investigated the film morphology under device fabrication for each macrocycle. We used a combination of differential scanning calorimetry (DSC), powder/thin-film X-ray diffraction (PXRD), and atomic force microscopy (AFM) to investigate the film morphology and crystallinity. Broad and featureless transitions in the DSC occur below 160 °C for both trans-cDBDB and cis-cDBDB (Figure S8). Thus, we anneal the macrocyclic films to this temperature, and then allow the films to cool to room temperature. PXRD of both films suggests that both films are amorphous, lacking any obvious signs of crystallinity for both trans-cDBDB and cis-cDBDB, (Figure S9). The AFM images, too, showed both films possess a smooth surface, with a root-mean-square roughness of 1.39 and 1.36 nm for trans-cDBDB and cis-cDBDB, respectively (Figure S10). The essential point is that the origin of the difference in device performance cannot be due to the molecular structure of the molecules as a source of the difference.

Density functional theory (DFT) calculations reveal that there is a marked difference between the lowest energy structures of both macrocycles. Trans-cDBDB possesses an upright conformation (Figure 3a), where the hPDI dimer subunits are vertically arranged with respect to the macrocyclic plane. In contrast, cis-cDBDB adopts a tent shape (Figure 3b), where the hPDI dimer subunits collapse across the macrocycle. The two macrocycles show a pronounced difference in their shapes: while both are elliptical, the eccentricity of trans-cDBDB is greater than that of cis-cDBDB (Figure 3c).

From the elongation and the upright structure for trans-cDBDB, we reasoned that it was more strained than cis-cDBDB. Calculations using a homodesmotic6,42–44 series reveal that the strain energy difference between trans-cDBDB and cis-cDBDB is 9 kcal/mol, with the former structure possessing 18.6 kcal/mol of strain relative to just 9.5 kcal/mol for cis-cDBDB (Table S3). To put this number into context, trans-cDBDB contains a similar amount of strain to the smaller PDI macrocycle,19 highlighting cis-cDBDB’s conformational flexibility. We can visualize the strain in the two isomers from the difference in their tetracyclic linkers (phenyl-bithiophene-phenyl) connecting the hPDI subunits (Figure 3d). It is apparent from the overlay that the tetracyclic linker bows in order to accommodate the rigidity of the trans-cDBDB macrocycle (blue model). This is not the case for the cis isomer (red model) where the tetracyclic linker is essentially flat and less strained relative to trans-cDBDB.

The difference in strain for the two macrocycles affects the dynamics in solution. From variable temperature 1H NMR measurements, we observe trans-cDBDB is much less floppy than cis-cDBDB. Both macrocycles possess different conformers that are able to interconvert through an “intramolecular somersault” process, where a hPDI subunit rotates through the center of the cavity (denoted with green arrows in Figure 4b,c),19 Yet the intramolecular somersault dynamics differ for trans-cDBDB and cis-cDBDB. Whereas the 1H NMR resonances for cis-cDBDB’s two conformers fully coalesce at 380 K, the NMR shows the presence of both diastereomers for trans-cDBDB (denoted with gray circles in Figure 4d). Figure S11 contains further coalescence details. This suggests the activation barrier for the somersault process is higher for trans-cDBDB than for cis-cDBDB. We postulate this reflects the geometries of each macrocycle: the cis isomer’s “tent” shape is less rigid, and the hPDI subunits are more able to rotate through the cavity relative to the trans isomer’s upright, rigid scaffold.

The floppiness of the cis-cDBDB relative to trans-cDBDB is evident in both their UV–vis and fluorescence spectra. While trans-cDBDB retains features of a vibrational progression, characteristic of the unsubstituted PDI dimer,28 cis-cDBDB possesses a broadened spectrum. Trans-cDBDB’s lowest energy transition, too, is bathochromically shifted relative to cis-cDBDB by approximately 20 nm. Both structural features reflect trans-cDBDB’s more rigid, strained conformation (Figures S12 and S13). Cis-cDBDB’s fluorescence spectrum is more broadened relative to trans-cDBDB (Figures S12 and S13).

As both films are amorphous with no crystalline features, the disparity in transport properties reflects the differences in molecular structure between trans-cDBDB and cis-cDBDB geometries. The cis isomer’s “tent” shape is conformationally flexible, aiding its ability to transport charge more effectively than the more rigid trans isomer. cis-cDBDB’s less strained and floppy structure allows it to make better intermolecular contacts with neighboring molecules, resulting in higher mobility. We tested this hypothesis using temperature dependent transport measurements on films of pure cis-cDBDB and trans-cDBDB to temperatures as low as 250 K. We find that the mobility of cis-cDBDB films is much more sensitive to temperature than is that of the trans isomer (Figure S14). The slope of the change in current in the device with decreasing temperature is an order of magnitude steeper for the cis isomer relative to a shallow slope for the trans isomer (Figure S14). When we plot electron mobility, extracted using the techniques of McCulloch39 and Choi40 versus temperature, we find the slope is more steep for cis-cDBDB, although the difference is less pronounced due to the higher threshold voltage for trans-cDBDB. The structure of cis-cDBDB, which is quite flexible at room temperature, stiffens as the temperature decreases; in contrast, the trans isomer is already rigid, making it less susceptible to temperature changes.
In summary, we describe two n-type, electronic materials made from giant conjugated macrocycles comprising hPDI dimers and bithiophenes in an alternating pattern. We find that there is a marked difference in the electron transporting properties of the two macrocycles. Creating amorphous films of both macrocycles, we were able to probe the effects of conformation on transport and find that the cis-cDBDB’s conformational flexibility enhances its ability to transport charge relative to trans-cDBDB. These materials will serve as the electron accepting semiconducting material in organic photovoltaics, taking advantage of their ability to transport electrons and open cavities.

**ASSOCIATED CONTENT**

* Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b06565.

  Experimental procedures for the synthesis and characterization of 1a-c, 2a-c, cis-cDBDB, and trans-cDBDB, UV−vis spectroscopy, fluorescence, cyclic voltammetry, field effect transistor fabrication, characterization methods, device performance, AFM images, and computational details (PDF)
  Crystallographic data (CIF)

**AUTHOR INFORMATION**

**Corresponding Authors**
* fwn2@columbia.edu
* mls2064@columbia.edu
* cn37@columbia.edu

**ORCID**
Colin Nuckolls: 0000-0002-0384-5493

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
We are thankful to Sebastian Russell for the helpful assistance and conversations on the DSC experiments. C.N. thanks Sheldon and Dorothea Buckler for their generous support. Primary support for this project was provided by the Office of Naval Research, under award no. N00014-17-1-2205. Support for the preparative chemistry was provided by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE), under award number DE-FG02-01ER15264. The Columbia University Shared Materials Characterization Laboratory (SMCL) was used extensively for this research. We are grateful to Columbia University for support of this facility.

**REFERENCES**