Conjugated Macrocycles in Organic Electronics

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CONSENSUS: This Account describes a body of research on the design, synthesis, and application of a new class of electronic materials made from conjugated macrocycles. Our macrocyclic design takes into consideration the useful attributes of fullerenes and what properties make fullerenes efficient n-type materials. We identified four electronic and structural elements: (1) a three-dimensional shape; (2) a conjugated and delocalized \( \pi \)-space; (3) the presence of an interior and exterior to the \( \pi \)-surface; and (4) low-energy unoccupied molecular orbitals allowing them to accept electrons. The macrocyclic design incorporates some of these properties, including a three-dimensional shape, an interior/exterior to the \( \pi \)-surface, and low-lying LUMOs maintaining the n-type semiconducting behavior, yet we also install synthetic flexibility in our approach in order to tune the properties further. Each of the macrocycles comprises perylenediimide cores wound together with linkers. The perylenediimide building block endows each macrocycle with the ability to accept electrons, while the synthetic flexibility to install different linkers allows us to create macrocycles with different electronic properties and sizes. We have created three macrocycles that all absorb well into the visible range of the solar spectrum and possess different shapes and sizes. We then use these materials in an array of applications that take advantage of their ability to function as n-type semiconductors, absorb in the visible range of the solar spectrum, and possess intramolecular cavities.

This Account will discuss our progress in incorporating these new macrocycles in organic solar cells, organic photodetectors, organic field effect transistors, and sensors. The macrocycles outperform acyclic controls in organic solar cells. We find the more rigid macrocyclic structure results in less intrinsic charges and lower dark current in organic photodetectors. Our macrocycle-based photodetector has the highest detectivity of non-fullerene acceptors. The macrocycles also function as sensors and are able to recognize nuanced differences in analytes. Perylenediimide-based fused oligomers are efficient materials in both organic solar cells and field effect transistors. We will use the oligomers to construct macrocycles for use in solar energy conversion. In addition, we will incorporate different electron-rich linkers in our cycles in an attempt to engineer the HOMO/LUMO gap further. Looking further into the future, we envision opportunities in applying these conjugated macrocycles as electronic host/guest materials, as concatenated electronic materials by threading the macrocycles with electroactive oligomers, and as a locus for catalysis that is driven by light and electric fields.

INTRODUCTION

In this Account, we describe our efforts to design and synthesize a new class of conjugated macrocycles and test their usefulness in electronic devices. Conjugated macrocycles have several potential advantages as organic electronic materials in recent years. In order to create electronic materials that complement fullerenes as n-type electron transporting electronic materials, we must first understand what makes fullerenes effective, and then use the power of synthetic chemistry to try to install these features into new materials. Fullerenes present four useful structural and electronic properties: (1) a three-dimensional shape; (2) a conjugated and fully delocalized \( \pi \)-space; (3) the presence of an interior and exterior to the \( \pi \)-surface; and (4) low-energy unoccupied molecular orbital(s) allowing them to accept electrons. While designing the macrocycles, we wondered how “fullerene-like” the macrocycles needed to be in order to remain “fullerene-like” electronic materials. We synthesized the macrocycles to mimic the three-dimensional (3D) shape of fullerenes, yet our design offers several advantages: synthetic flexibility (allowing us to control the electronic properties of the macrocycles); extensive, but not “whole-molecule” \( \pi \)-conjugation; and intramolecular cavities that facilitate guest incorporation and sensing. Figure 1 shows the three main macrocycles studied. The three differ in the number of perylenediimide (PDI) groups and linking groups that wind them into macrocycles.

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These conjugated macrocycles are electronic and optoelectronic materials, and these “pseudo-fullerenes” are useful in an array of devices. We demonstrate that the macrocycles are effective n-type semiconductors in organic field-effect transistors (OFETs),\textsuperscript{10,32,35} and that the macrocycles can act as the electron-accepting materials in a bulk heterojunction.\textsuperscript{10} Moreover, we find that the internal cavity within the macrocycle can be used as a locus of guest binding to create sensors and nanoscale reaction chambers.\textsuperscript{32}

\section*{SYNTHESIS AND MOLECULAR STRUCTURE}

\subsection*{Synthesis}
We based our synthetic strategy on the pioneering studies by Yamago and Bäuerle employed for cycloparaphenylenes (CPPs) and cyclothiophenes (CTs).\textsuperscript{21,36,37} The strategy utilizes stannylated aromatics to create multinuclear platinum macrocycles, which ultimately yield the conjugated macrocycles. Inspired by this approach, we created stannylated and platinated perylenediimide (PDI) moieties as our key intermediates (Scheme 1). PDIs are ubiquitous as electron acceptors and useful in many electronic and optoelectronic applications.\textsuperscript{38–47}

Our syntheses start with 1,7-dibromo-PDI building blocks (1, 2, and 3, in Scheme 1) that we substitute with different linkers to create the three target molecules. A multinuclear platinum macrocycle is an intermediate in each synthesis: \((\text{PDI-BBr}_4)_3^−\) is reductively eliminated from a trimeric platinum intermediate, while \((\text{PDI-Ph-B-Ph})_2^−\) and \((\text{PDI-BP})_4^−\) each derive from a tetraplatinum intermediate. We isolate \((\text{PDI-Ph-B-Ph})_2^−\) as a black solid, \((\text{PDI-BP})_4^−\) as a purple solid, and \((\text{PDI-BBr}_4)_3^−\) as a deep red solid.

\subsection*{Molecular Structure}
The macrocycles possess interesting structural features that affect their electronic properties. One of the most obvious differences among the macrocycles is the size of their intramolecular cavities. According to structures determined using density functional theory (DFT), the cavity is smallest in \((\text{PDI-BBr}_4)_3^−\) (1.1 nm from PDI to thiophene), largest in \((\text{PDI-BP})_4^−\) (\(\sim 2\) nm across its transannular axis from PDI to PDI), and intermediate (1.6 nm) in \((\text{PDI-Ph-B-Ph})_2^−\) (Figure 2a–c). We also found that the intramolecular fractional behavior is influenced by the size of the cavity with the larger cavities allowing for easier interconversion between accessible conformations.\textsuperscript{4,10,32}

\section*{ELECTRICAL TRANSPORT AND SELF-ASSEMBLY}

\subsection*{Electrical Transport}
The synthetic flexibility within our approach allows us to incorporate subunits with the desired electronic properties within our macrocycles. The first indication that the macrocycles could be efficient optoelectronic materials was their color. DFT calculations and estimates from electrochemistry reveal that each molecule possesses a low-energy lowest unoccupied molecular orbital (LUMO) that can accept at least two electrons due PDI’s efficient electron accepting ability (Table 1). From the potential of the first reduction peak in the cyclic voltammogram, we estimate the LUMO energy levels to be approximately \(-3.9\) eV for the three macrocycles. These values are similar to the common n-type semiconductors like [6,6]-phenyl-C\textsubscript{61}-butyric acid methyl ester (PC\textsubscript{60}BM), whose LUMO is also \(-3.9\) eV, and an unsubstituted PDI at \(-3.89,48,49\)
The linker groups influence the electronic properties of each macrocycle. The highest occupied molecular orbitals (HOMOs) reside on the electron-rich phenyl-bithiophene-phenyl belt for \(-(\text{PDI-Ph-B-Ph})_2^-\). Figure 3a,b shows the calculated frontier orbitals for \(-(\text{PDI-Ph-B-Ph})_2^-\). The HOMO energy is higher in \(-(\text{PDI-Ph-B-Ph})_2^-\) than in the other two macrocycles, and since the LUMO energies of the three are the same, this results in a reduction in its HOMO/LUMO gap and a bathochromic shift in its UV-vis absorption spectrum (Figure 3c).\(^4\) For both \(-(\text{PDI-BP})_4^-\) and \(-(\text{PDI-BBr}_4)^3^-\), the linker groups function as electronically inert struts for the frontier orbitals. Both the HOMO energy levels, in addition to the LUMOs, reside on the PDI moieties in these macrocycles. All three macrocycles function as efficient n-type semiconductors.\(^{10,32}\) Figure 3d displays the transfer curves for the three macrocyclic devices. Films of \(-(\text{PDI-BBr}_4)^3^-\) have an electron mobility of \(\sim 1.5 \times 10^{-2} \text{ cm}^2/(\text{V} \cdot \text{s})\) and those from \(-(\text{PDI-Ph-B-Ph})_2^-\) and \(-(\text{PDI-BP})_4^-\) have an electron mobility of \(\sim 1.5 \times 10^{-3} \text{ cm}^2/(\text{V} \cdot \text{s})\).

**Self-Assembly**

The solid-state structures for both \(-(\text{PDI-Ph-B-Ph})_2^-\) and \(-(\text{PDI-BBr}_4)^3^-\) help elucidate their behavior as n-type semiconductors. The self-assembly process results in close PDI–PDI contact in the solid-state structure of \(-(\text{PDI-Ph-B-Ph})_2^-\).

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**Scheme 1. Synthesis of Conjugated Macrocycles\(^a\)**

\[\text{C}_n\text{H}_{2n+2}\text{O}_x\text{N}_y\text{SnMe}_3\]

\[\text{Me}_3\text{SnS}\]

\[\text{Bu}_3\text{Sn}\]

\[\text{Gr} \text{PtCl}_2\]

\[\text{Pt}(\text{COD})\text{Cl}_2\, 1,2\text{dichloroethane, 85 °C, 72 h, (b) DPPF, CHCl}_3\rt, 24 h, (c) PPh}_3, \text{PhMe, 110 °C, 48 h, 15% yield; (d) Br}_2, \text{I}_2, \text{CH}_2\text{Cl}_2, \text{rt, 24 h, (e) Pt}(\text{COD})\text{Cl}_2, \text{Br}_2, \text{I}_2, \text{CH}_2\text{Cl}_2, \text{rt, 27 h, 8% yield. Synthesis of (PDI-BP)_4^-: (f) Br}_2, \text{I}_2, \text{CH}_2\text{Cl}_2, \text{rt, 27 h, 8% yield. Synthesis of (PDI-BBr}_4)^3^-: (g) Pt}(\text{COD})\text{Cl}_2, \text{toluene, 100 °C, 12 h, (h) 5,5'}\text{'bis}(\text{tributylstannyl})-2,2'-bithiophene, \text{THF, 50 °C, 48 h, (i) PPh}_3, \text{toluene, 100 °C, 12 h, 48% yield.}

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**Table 1. Electrochemistry, UV/vis, and FET Data for Conjugated Macrocycles**

<table>
<thead>
<tr>
<th>(PDI-Ph-B-Ph)_2^-</th>
<th>(E_{\text{LUMO}}) (eV)</th>
<th>(E_{\text{HOMO}}) (eV)</th>
<th>(E_{\text{gap}}) (eV)</th>
<th>(\mu) (cm² V⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-(\text{PDI-Ph-B-Ph})_2^-)</td>
<td>-3.87</td>
<td>-5.39</td>
<td>1.52</td>
<td>1.79</td>
</tr>
<tr>
<td>(-(\text{PDI-BP})_4^-)</td>
<td>-3.90</td>
<td>-6.06</td>
<td>2.16</td>
<td>2.00</td>
</tr>
</tbody>
</table>

\(^a\)HOMO and LUMO levels were estimated from onset of the first oxidation and reduction peaks. \(^b\)Optical band gaps were estimated from the onset of absorption.

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**Figure 2.** Side-on and face-on views of the lowest energy geometries from DFT calculations for (a) \(-(\text{PDI-BBr}_4)^3^-\), (b) \(-(\text{PDI-Ph-B-Ph})_2^-\), and (c) \(-(\text{PDI-BP})_4^-\). DFT calculations carried out at 6.31G* /B3LYP level of theory.
Figure 4a shows the relationship between two adjacent diphenyl-PDI subunits. The π-faces are spaced by ∼3.7 Å between neighboring diphenyl-PDIs of adjacent macrocycles (Figure 4a). This packing is similar to that observed in crystals and aggregates of PDI derivatives. The core of the PDI molecules is polarized by the imide positions, which makes π−π overlap favorable. Sequential π−π interaction creates a one-dimensional wire down the b axis (Figure 4b,c); each of the PDIs is a link in an electronic chain (Figure 4d).

Both enantiomers are also present in crystals of (PDI-BBr4)$_3^−$, yet while PDI-to-PDI interactions dominate (PDI-Ph-B-Ph)$_2^−$, they are absent in (PDI-BBr4)$_3^−$. Instead the 2D assembly process results in halogen bonding between the neighboring brominated thiophene rings and π−π contacts between the same rings (Figure 5c). These interactions create two-dimensional sheets comprised of hexameric arrangement of the cyclic structures (Figures 5a,d). The sheets create a 2D network for charge transport, contributing to the more efficient charge mobility (∼1.5 × 10$^{-2}$ cm$^2$/Vs). We performed powder X-ray diffraction (PXRD) on powders of both (PDI-Ph-B-Ph)$_2^−$ and (PDI-BBr4)$_3^−$ and found their powder patterns matched the pattern calculated for their solid-state structures. This suggests the self-assembly motifs described above are robust and influence their transport properties in thin films.

The macrocycles retain the 3D molecular design principle from fullerenes, yet our synthetic flexibility allows us to tune the electronic properties of the macrocycles to a much greater degree. While the “pseudo-fullerenes” possess different electronic structures tuned by the linking groups, they each function as efficient n-type semiconductors. The following sections detail our efforts to use these new materials in optoelectronic and sensing applications.

### FUNCTIONAL PORES

One of the useful new design elements of the “pseudo-fullerenes” is the ability to create porous, hollow semiconductors, a new motif within molecular electronics. Using Brunauer–Emmett–Teller (BET) analysis, powders of (PDI-BBr4)$_3^−$ showed a surface area of 20 m$^2$/g. Figure 6 shows the van der Waals surfaces of (PDI-BBr4)$_3^−$: the structure possesses a cavity, as best viewed in Figure 6c,f, that could serve as a potential host for guest analytes. Since thin films of this material showed higher conductivity, we tested films of (PDI-BBr4)$_3^−$ as electrical sensing media.

Thin-films of (PDI-BBr4)$_3^−$ show current modulation depending on what, if anything, resides in the intramolecular cavities. We studied a variety of guest molecules, and every guest molecular design principle from fullerenes, yet our synthetic flexibility allows us to tune the electronic properties of the macrocycles to a much greater degree. While the “pseudo-fullerenes” possess different electronic structures tuned by the linking groups, they each function as efficient n-type semiconductors. The following sections detail our efforts to use these new materials in optoelectronic and sensing applications.

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had a measurable effect on the drain current in the device. Figure 7a displays transfer curves from an OFET constructed using a self-assembled thin film of $-(\text{PDI-BBr}_4)_3-$ and the cavity formed by the packing of $-(\text{PDI-BBr}_4)_3-$, respectively. The remaining sulfur atoms are colored in yellow to provide a marker to identify the macrocycle cavities. Highlighted in green are the inside side chains (some of the side chains have been removed to clarify the view of the cavity). In red are the thiophene rings likely involved in holding the macrocycles together. The vertical stacking follows the c axis. The alkyl side chains of the imide are shown in green. Hydrogen atoms have been removed to clarify the view.

1-Hexyne behaves differently than each of the other guests. For the devices in an atmosphere of 1-hexyne, the current continues to drop and does not reach a plateau even after 2 h of exposure. The 1-hexyne device did not recover current to its original level when placed in vacuum. We believe the terminal alkyne participates in a process that is not possible for the internal alkyne or the alkane. We hypothesize that the electric field in the device is inducing chemical reactions in the cellular semiconductor. This reaction could be a homocoupling of two terminal alkynes, and we are currently investigating this hypothesis. The ability of $-(\text{PDI-BBr}_4)_3-$ to detect nuanced differences in small molecule guests demonstrates the utility of the new class of hollow, porous semiconductors as sensors and nanoreactors.

## OPTOELECTRONIC MATERIALS

Due to their broad absorption in the visible range and ability to function as n-type semiconductors, both $-(\text{PDI-Ph-B-Ph})_2-$ and $-(\text{PDI-BP})_4-$ are good candidates for optoelectronic applications such as organic photovoltaics (OPVs) and organic photodetectors (OPDs).

### Organic Photovoltaics (OPVs)

We used the “pseudo-fullerene” acceptors in solar cells to better understand how, if at all, the macrocyclic design impacted device performance. For comparison to $-(\text{PDI-Ph-B-Ph})_2-$ and
we synthesized acyclic control molecules (shown in Figure 8a) of various fragments and electronic character to understand the effects of a cyclic geometry in bulk heterojunctions. Devices using either -(PDI-Ph-B-Ph)$_2$ or -(PDI-BP)$_4$ outperformed similar devices that used the associated acyclic molecules. The power conversion efficiencies (PCEs) of the two macrocycles were at least twice those of the acyclic controls. Figure 8b,c contains a schematic of a solar cell, and the $J$−$V$ curve for -(PDI-Ph-B-Ph)$_2$. An analogous study was performed on -(PDI-BP)$_4$ and showed similar results.

The photocurrent generation in cyclic-based devices is much larger than the acyclic-based devices. These results indicate that the cyclic acceptors have enhanced photocarrier generation and better charge transport. We observed several trends from this study: (1) acyclic oligomeric molecules and the polymers (Figure 8a) show decreased $J_{sc}$ relative to the cyclic compounds; (2) the acyclic molecules also show higher $V_{oc}$ values as compared to the cyclic acceptors; and (3) the poor PCEs in the devices from acyclic molecules are primarily attributed to the reduced $J_{sc}$ and FFs relative to the cyclic ones. To better understand the performance difference between the cyclic and acyclic molecules, we examined the electrochemistry, UV−vis absorption, electron mobility, and morphology of the films. In each of these areas, the properties were found to be more efficacious for photovoltaics for the macrocyclic-based devices than acyclic-based devices.

For example, the energy offset between the donor’s HOMO and acceptor’s LUMO is one of the factors that determines the $V_{oc}$ in BHJ solar cells. The values obtained from CV results are in good agreement with the $V_{oc}$ trend from the devices. Previous studies show a direct correlation between relatively large $V_{oc}$ values coupled with low $J_{sc}$ when the band offset does not provide sufficient driving force for exciton dissociation at the donor/acceptor interfaces. Here, the trend observed suggests that the high LUMO levels, particularly in the short acyclic compounds, result in a higher occurrence of recombination and lower $J_{sc}$. Greater visible light absorption contributes to the more efficient solar cells for the cyclic molecules, providing the higher $J_{sc}$ parameter for the cyclic molecules relative to the acyclic molecules.
Two additional factors that are critical for efficient OPV device performance are electron transport through the acceptor phase and film morphology. The average mobility in $-(PDI-Ph-B-Ph)_2-$ is a factor of 5 higher than that in its acyclic counterparts, while that in $-(PDI-BP)_4-$ is nearly 2 orders of magnitude higher than its acyclic controls. Atomic force microscopy (AFM) images showed clear ideal phase separation for both $-(PDI-Ph-B-Ph)_2-$ and $-(PDI-BP)_4-$; either over-aggregation or very large domain sizes occurred in the acyclic controls, with the former resulting in carrier recombination and poor device performance.33,57

Organic Photodetectors (OPDs)
We also found that $-(PDI-BP)_4-$ performed well as an electron acceptor in an OPD device.7 The electron donors used are the commercially available polymers poly[4,8-bis(5-(2-ethylhexyl)-thiophen-2-yl)benzo[1,2-b:4,5-b’]-dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene)-2-carboxylate-2,6-diyl] (PTB7-Th).58,59 The devices are fabricated in an inverted structure with a configuration of ITO/ZnO(20 nm)/PTB7-Th: $-(PDI-BP)_4-$/MoOx(10 nm)/Al(100 nm) without extra carrier blocking layers (Figure 9a).

Previous studies suggest that the intrinsic conductivity of organic semiconductors is dominated by free carriers that are usually generated from charged defects from photo- or thermoactivation60–62 or deformed $sp^3$ bonds.63–65 For example, covalent defects formed upon photo- or thermoactivation and mechanically deformed $sp^3$ carbon–carbon bonds in $\pi$-conjugated molecules are known to produce charged defects that introduce carriers.64 High levels of intrinsic charge carriers limit the sensitivity of organic photodetector devices, and a high dark current determines the noise current level and sensitivity of an OPD.

We designed $-(PDI-BP)_4-$ to mitigate some of these challenges: (1) The rigid structure, constrained in a ring, minimizes the number of charged defects originating from deformed $sp^3$ carbons. This reduces the number of intrinsic carriers in the film; calculations reveal that although $-(PDI-BP)_4-$ is rigid, the molecule possesses no strain. (2) No covalent defects are formed upon photo- or thermoactivation. This, too, reduces the number of free carriers, reducing the dark current level. (3) It transports electrons well, and (4) it has high visible light absorption that yields significant photocurrent in a bulk heterojunction photodiode. These design principles result in an excellent macrocyclic-based photodetector by decreasing the dark current in the film. The highest detectivity in our device approaches $10^{14}$ Jones at near zero bias voltage and is comparable to the best fullerene-based photodetectors (Figure 9b–d).

Figure 9. (a) Device structure for the inverted OPD. (b) Current density–voltage curves under dark conditions and simulated AM1.5 G irradiation (100 mW cm$^{-2}$). (c) External quantum efficiency and specific detectivity spectra calculated at $-0.1$ V bias voltage (black = EQE and blue = detectivity). (d) Comparison of detectivity and working voltage in reported OPDs and this work.

Figure 10. hPDI oligomers based on PDI: hPDI$_2$, hPDI$_3$ and hPDI$_4$. 

<table>
<thead>
<tr>
<th>hPDI$_2$</th>
<th>hPDI$_3$</th>
<th>hPDI$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE = 6.1%</td>
<td>7.9%</td>
<td>8.3%</td>
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</table>
We also assessed the importance of the cyclic design by comparing \((\text{PDI-BP})_4\) OPDs with an acyclic, polymeric control that linked PDI and biphenyl moieties and found the polymer-based OPD has a dark current 10-fold higher and lower responsivity than that of the \((\text{PDI-BP})_4\) based device. \((\text{PDI-BP})_4\) possesses a relatively locked conformation and is more rigid, creating fewer locally charged defects relative to the acyclic polymeric counterpart.

■ OUTLOOK AND FUTURE DIRECTIONS

This Account describes our efforts using conjugated macrocycles as "pseudo-fullerenes" within a variety of device structures that require efficient electron transport. We sought to expand on this theme by using the helical perylenediimide (hPDI) oligomers to prepare the next-generation macrocycles (Figure 10). The hPDI oligomers are efficient n-type materials in both OFETs and OPVs: the performance in solar cells rises with increasing oligomer length. We synthesized two different macrocycles, each of which contains two hPDI dimers and two phenyl-bithiophene-phenyl (Ph-B-Ph) units wrapped into a cyclic, \(-a-b-a-b-\), pattern (Figure 11). The difference between the two is in the regiochemistry of the hPDI attachments: one of the macrocycles has Ph-B-Ph belts connected to the hPDI dimers in a cis orientation; in the other macrocycle these attachments are in a trans orientation. We call these \(-\text{cis-(hPDI})_2\text{-Ph-B-Ph})_2\) and \(-\text{trans-(hPDI})_2\text{-Ph-B-Ph})_2\), respectively. This change in the regiochemistry results in a pronounced difference in the conductance of the films: the OFET electron mobility of \(-\text{cis-(hPDI})_2\text{-Ph-B-Ph})_2\) is more than four-times greater than that of \(-\text{trans-(hPDI})_2\text{-Ph-B-Ph})_2\).

This Account demonstrates the power of bottom-up synthesis as a synthetic tool to create conjugated macrocycles with varying electronics. We have begun our studies with the hPDI oligomers and have shown how the ability to introduce nuanced differences into the molecular structure is an advantage to fullerenes: it allows us to probe on a fundamental level how conformation affects charge mobility. We will continue using the oligomers to construct macrocycles for use in solar energy conversion. In addition, we will incorporate different electron-rich linkers in our cycles in an attempt to engineer the HOMO/LUMO gap further. Looking further into the future, we envision opportunities in applying these conjugated macrocycles as electronic host/guest materials, as concatenated electronic materials by threading the macrocycles with electroactive oligomers, and as a locus for catalysis that is driven by light and electric fields.

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