Impacts of Stereoisomerism on Molecular Packing and Charge Transport of Imide-Fused Corannulene Derivatives


†State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Department of Chemistry, College of Chemistry and Chemical Engineering, ‡Key Laboratory of Chemical Biology of Fujian Province, and §Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Xiamen University, Xiamen 361005, P. R. China

§Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Supporting Information

ABSTRACT: Two chiral tertiary carbon centers bearing one mesityl group at each center are introduced into the molecular backbone of imide-fused corannulene derivatives to produce four stereoisomers (i.e., (S, S), (R, R), (R, S), or (S, R) configurations on two chiral carbons) in one pot, which are separated into two portions through column chromatography over silica gel. Portion 1, containing a pair of enantiomers ((S, S) and (R, R)), adopts layered packing in the crystal. Portion 2, consisting of a pair of mesomers ((R, S) and (S, R)), exhibits columnar packing in their cocystal. Theoretical calculations are performed on these two packing motifs, revealing that Portion 1 displays hole-dominated transport, whereas Portion 2 shows electron-dominated transport.

Corannulene, a curved fragment of C_{60}, has been attracting intense research interest in supramolecular chemistry and organic electronics, owing to its unique bowl-shaped structure and unequal electronic distribution on the concave and convex surfaces. The curvature of corannulene and its derivatives makes their packing in the solid state more variable than their planar analogues, depending on the size and the depths of the bowls as well as on the peripheral substituents. In general, deep bowl depths favor 1D bowl-in-bowl columnar stacking, whereas the π-surface extending and flattening of bowls lead to 2D packing. Such tunable molecular packing of corannulene derivatives provides an excellent molecular platform to investigate charge transport, because molecular arrangement greatly influences intermolecular electronic couplings. Theoretical investigations found that even a small relative translation within a π-stacked dimer leads to large difference in both hole and electron transfer integrals.

Stereoisomerism is common but usually ignored in the organic semiconductors (e.g., the stereoisomers resulting from the configurational variations of chiral branch alkyl chains such as the 2-ethylhexyl and the 2-octyldodecanyl groups). The enantiopure and racemic stereoisomers and their mixtures generally display much different molecular packing motifs from each other as confirmed by nonconjugated compounds. However, only a small amount of work sheds light on how stereoisomerism of the conjugated compounds influences molecular packing and thus charge-transport properties.

For example, Nguyen et al. synthesized diketopyrrolopyrrole (DPP) derivatives bearing two chiral side chains to give three stereoisomers (i.e., (S, S)-isomer, mesomer and (R, R)-isomer). They found that the mesomer had stronger intermolecular π−π interaction and better charge-transport ability than their chiral counterparts. More recently, Fuchter et al. also found that the racemic 1-aza[6]helicene showed a much higher hole mobility than enantiopure 1-aza[6]helicene owing to their different molecular packing. Nonetheless, directly incorporating the chiral centers bearing bulky groups into the conjugated backbone has seldom been employed in the design of organic semiconductors.

Herein, we incorporate two stereogenic carbon centers into imide-fused corannulene derivatives to produce four stereoisomers (Figure 1) arising from the two chiral centers and the absence of σg mirror symmetry of the molecular backbone. These isomers are separated into two portions (Portion 1 and Portion 2) through column chromatography over silica gel. Portion 1 contains a pair of enantiomers and Portion 2 contains a pair of mesomers. The orientation of bulky groups in stereogenic carbon centers together with the bowl-shaped structure effectively alter their molecular packing.
in the corresponding crystals of each portion. The layered packing and the columnar packing are achieved for Portion 1 and Portion 2, respectively. Theoretical calculations demonstrate that Portion 1 shows hole-dominated transport, whereas Portion 2 exhibits electron-dominated transport.

The synthesis was initiated by the Suzuki–Miyaura coupling of compound 1 with 2-formylbenzeneboronic acid to give dialdehyde 2 in 76% yield (Scheme 1). The addition of mesitylmagnesium bromide (MesMgBr) into dialdehyde 2 provided the secondary alcohol 3, which was used without further purification. Compound 4 was produced through a twofold intramolecular Friedel–Crafts alkylation of compound 3 catalyzed by boron trifluoride etherate. Selective formation of five-membered rings was observed, despite the large steric hindrance between the mesityl groups and the imide group. Density functional theory (DFT) calculations were employed to understand such regioselectivity, which suggested that the barrier of forming five-membered rings was lower than that of forming six-membered rings (Figure S1). Four possible stereoisomers (i.e., (S, S), (R, R), (R, S), or (S, R) configurations on two chiral carbons) exist for compound 4 due to the two chiral centers and the lack of $\sigma$$_h$ mirror symmetry of imide-fused corannulene moiety (Figure 1). The dipole moments of the enantiomers are much different from those of the interconvertible mesomers owing to the different orientation of Mes groups. The four isomers were therefore separated by column chromatography over silica gel into two portions. The ratio of [4−1], [4−3]+[4−4], and [4−2] in the crude product was determined to be 1:2:1 (Figure S3) using chiral high-performance liquid chromatography (HPLC). All new compounds were characterized by nuclear magnetic resonance (NMR) spectroscopy and high-resolution mass spectrometry (HRMS).
Table 1. Summary of Optical, Electrochemical, Bowl-Depth, and Calculated Data

<table>
<thead>
<tr>
<th>stereoisomer</th>
<th>HOMO (eV)</th>
<th>HOMOcalc (eV)</th>
<th>LUMO (eV)</th>
<th>LUMOcalc (eV)</th>
<th>$\Delta_{1}/\lambda_{0}$ (meV)</th>
<th>pathway</th>
<th>$V_{F}/V_{H}$ (meV)</th>
<th>$v_{F}/v_{H}$ (cm$^2$ v$^{-1}$ s$^{-1}$)</th>
<th>$\mu_{e}/\mu_{h}$ (cm$^2$ v$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portion 1</td>
<td>$4-1$</td>
<td>$-5.81$</td>
<td>$-5.73$</td>
<td>$-3.34$</td>
<td>$-2.85$</td>
<td>$2.10$</td>
<td>$0.70$</td>
<td>$0.83$</td>
<td>$6.77$</td>
</tr>
<tr>
<td></td>
<td>$4-2$</td>
<td>$-5.73$</td>
<td>$-3.34$</td>
<td>$-2.85$</td>
<td>$2.10$</td>
<td>$0.70$</td>
<td>$0.83$</td>
<td>$6.77$</td>
<td></td>
</tr>
<tr>
<td>Portion 2</td>
<td>$4-3$</td>
<td>$-5.74$</td>
<td>$-3.35$</td>
<td>$-2.91$</td>
<td>$2.10$</td>
<td>$0.78$</td>
<td>$0.85$</td>
<td>$11.3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4-4$</td>
<td>$-5.72$</td>
<td>$-3.35$</td>
<td>$-2.84$</td>
<td>$2.10$</td>
<td>$0.62$</td>
<td>$0.74$</td>
<td>$4.45$</td>
<td></td>
</tr>
</tbody>
</table>

"Calculated data based on the B3LYP/6-311G(d,p) level of theory. Generally, the LUMOs from DFT calculations are 0.3–0.5 eV higher than those from experiments." "Bowl depths from single crystal structures. "Bowl depths from optimized geometries calculated at the B97D/cc-pvdz level of theory.

To elucidate the electronic properties of these two portions, UV–vis absorption and cyclic voltammetry studies were performed (Figure 2, Table 1). Portion 1 and Portion 2 exhibited almost identical absorbance due to their tiny structural difference. The broad peak around 500 nm was attributed to the intramolecular charge transfer transition from HOMO to LUMO, which was confirmed by time-dependent DFT (TD-DFT) calculations (Figure S2). The optical bandgaps were estimated to be 2.10 eV for both Portion 1 and Portion 2 from the absorption onsets. Both portions showed two reversible reduction waves and one reversible oxidation wave in the electrochemical window of the solvent. The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) were estimated to be $-5.81$ eV and $-3.34$ eV for Portion 1 and $-5.78$ eV and $-3.35$ eV for Portion 2 from the potential onsets of oxidation or reduction. The HOMOs of four stereoisomers were distributed on the molecular long axes and LUMOs on imide-fused corannulene moieties (Figure 1).

To confirm the structures and packing motifs of Portion 1 and Portion 2, their single crystals suitable for X-ray analysis were obtained by the phase transfer method. The structures of four possible stereoisomers were all confirmed (Figure S4). Portion 1, consisting of a pair of enantiomers ($S$, $S$) or ($R$, $R$) configurations on two stereogenic carbons, adopted a layered packing mode (Figure 3a). To accommodate each other, intermolecular $\pi$-overlap of compounds $4-1$ and $4-2$ mainly lay on the molecular long axis with a $\pi-\pi$ distance of $\sim 3.45$ Å (Figure 3c). Compound $4-1$ or $4-2$ stacked on top of itself in a layer-by-layer pattern. The $\pi-\pi$ distance of the intralayer adjacent molecules was $\sim 3.43$ Å. The bowl depths of compounds $4-1$ and $4-2$ were 0.70 Å, slightly smaller than those from optimized geometries (0.83 Å). The calculated bowl-to-bowl inversion barriers were 6.77 kcal/mol for both $4-1$ and $4-2$. Portion 2, containing a pair of mesomers,
showed a columnar packing motif (Figure 3b). To accommodate each other, concave-convex stacking dimers of 4−3 and 4−4 were formed with a π−π distance of ∼3.50 Å. The concave-convex overlap mainly lay on corannulene moieties (Figure 3d). The dimers stacked on top of each other by the overlap of the edge of 4−3 to corannulene core of 4−4 to form columnar motifs. Their strong intermolecular π−π interactions were also suggested by concentration-dependent 1H NMR, in which upfield shifted aromatic peaks were observed as the concentration increased (Figure S6).32,33 The bowl depths of 4−3 and 4−4 were 0.78 and 0.62 Å, which were also smaller than those from optimized geometries (0.85 Å for 4−3 and 0.74 Å for 4−4). The pristine corannulene with a bowl-to-bowl inversion barrier of 10.2 kcal/mol undergoes bowl-to-bowl inversion at a rate of >2 × 105 s−1 at 25 °C in solution.34 The calculated bowl-to-bowl inversion barriers were 11.3 kcal/mole from 4−3 to 4−4 and 4.45 kcal/mole from 4−4 to 4−3, suggesting their rapid interconversion at room temperature in solution.35 Hence, 4−3 and 4−4 cannot be isolated from each other at room temperature.

To further understand differences of Portion 1 and Portion 2 in electronic couplings, the transfer integrals for their main electron- and hole-transport pathways were calculated at the PBE0/DZP level of theory (Table 2). The transfer integrals of pathways t1, t2, and t3 of Portion 1 were 119, 2.09, and −1.96 meV for holes and −2.59, 0.0111, and 8.95 meV for electrons. The transfer integrals of pathways t1, t2, t3, and t4 of Portion 2 were 171.1, −1.30, 16.1, and −0.0574 meV for holes and 131.9, 16.5, 5.48, and 2.28 meV for electrons. Thus, the effective charge-transport directions along a and b axes for Portion 1 and along a axis for Portion 2 were formed.

The reorganization energies, another important factor in determining charge carrier mobility, were also calculated at the PBE0/6-31G* level of theory. Compounds 4−1 and 4−2 both showed reorganization energies of 381.1 meV for electron transfer and 190.5 meV for hole transfer. Compound 4−3 exhibited reorganization energies of 405.0 meV for electron transfer and 215.3 meV for hole transfer, and those of compound 4−4 were 396.5 meV for electron transfer and 198.1 meV for hole transfer. The different reorganization energies among these stereoisomers result from their slight structural difference induced by orientation of Mes groups.

The hopping model, usually applied in the case where the intermolecular electronic coupling is much less than the molecular reorganization energy, was used to describe the charge transport of the two packing motifs. Combining the transfer integrals and the reorganization energies, the electron/hole mobility of Portion 1 was calculated to be 9.37 × 10−4/5.25 × 10−3 cm2 v−1 s−1 along a axis and 6.81 × 10−9/2.18 × 10−2 cm2 v−1 s−1 along b axis using the Marcus hopping model (calculation methods see SI).35−39 The theoretical hole mobility is comparable to that of thiophene-fused dibenzo[c]corannulene (μh = 0.06 cm2 v−1 s−1)12 and imide-fused dibenzo[a,g]corannulene (μh = 0.05 cm2 v−1 s−1)40 from organic field-effect transistor (OFET) measurements. The electron/hole mobility of Portion 2 was calculated to be 1.03 × 10−5/3.37 × 10−8 cm2 v−1 s−1 along a axis. Thus, Portion 1 favors hole transport, whereas Portion 2 favors electron transport.

In conclusion, the layered packing and the columnar packing were realized for the pairs of enantiomers and mesomers of imide-fused corannulene derivatives, respectively. These molecular models and their corresponding crystal packing motifs allow the detailed investigations of charge-transport properties through theoretical calculations. The experiments together with theoretical calculations demonstrate that the stereoisomerism of the conjugated compounds can significantly alter their packing patterns and thus charge-transport properties (e.g., charge carrier mobility and even charge-transport polarities). This work provides a new perspective to modulate charge-transport properties without changing the molecular backbones, which can be extended to more diverse conjugated skeletons.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.9b00441.

Experimental details, characterization data, NMR spectra, calculation details, and single-crystal data (PDF)

Accession Codes

CCDC 1827422 and 1827425 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: xcao@xmu.edu.cn.
*E-mail: yizhao@xmu.edu.cn.

ORCID

Xiao-Ye Wang: 0000-0003-3540-0277
Yi Zhao: 0000-0003-1711-4250
Xiaoyu Cao: 0000-0003-0219-1798

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the supports from the 973 Program (No. 2015CB856505), the NSFC (Nos. 217223204, 91427304, 21573181, and 91227111), the Top-Notch Young Talents Program of China and the Fundamental Research Funds for the Central Universities of China (No. 20720160050). We also thank Prof. Ting Lei, Prof. Jian Pei, Prof. Wei Zhang, and Prof. Yan-Dong Zhang for helpful discussions.

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