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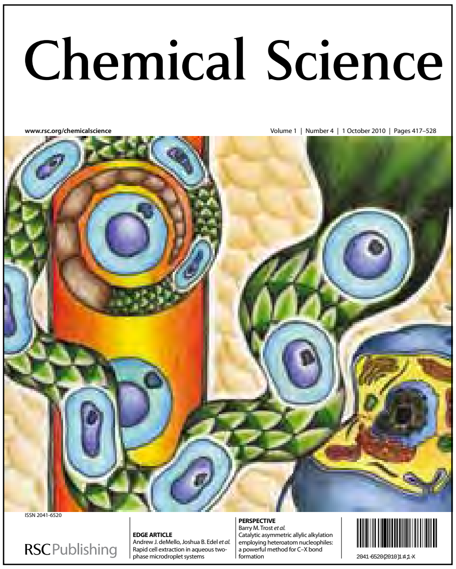

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A Bowl-Shaped Molecule for Organic Field-Effect Transistors: Crystal Engineering and Charge Transport Switching by Oxygen Doping

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A corannulene-based derivatives was facilely developed with a bowl-shaped structure. Highly ordered cofacial convex–concave stacking was realized through tuning the molecular dipoles, which is favorable to charge transport. Organic field-effect transistors were fabricated, providing opportunities for a broad class of corannulene derivatives and buckybowl aromatics for application in future organic electronic devices.

To acquire high-performance organic semiconductors, the development of planar polycyclic aromatics has always been the central issue.[1] In contrast, aromatics with curved, especially bowl-shaped conjugated backbones are less studied, which may be attributed to the synthetic challenge of constructing curved structures with large tension as well as their unpredictable packing in crystals. However, several organic semiconductors with curved conjugated skeleton, such as fullerene derivatives, hexabenzocoronene and diperylene bisimide, exhibited outstanding performance in organic field-effect transistors (OFETs) and solar cells.[2] Compared with traditional planar polycyclic aromatics, molecules with a bowl-shaped configuration may adopt a desired columnar crystal packing due to the shape-matching of curvature. Such a configuration-effect may provide new opportunities for exploiting extraordinary optoelectronic materials.

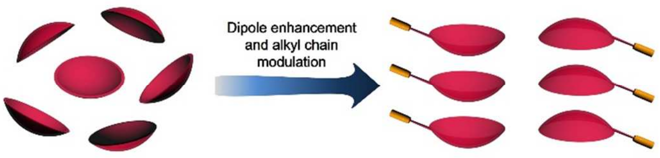
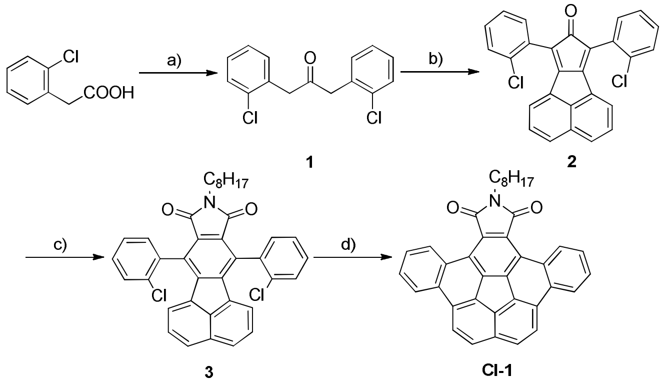


Figure 1. Stratergies to engineer crystal packing of bowl-shaped aromatics.

Corannulene ($C_{20}H_{10}$), a partial segment of fullerene, has attracted much attention due to its nonplanar conjugated buckybowl structure.[3] A few studies relevant to discotic liquid crystals based on its strong intermolecular π-π interaction and pentagonal dendrimers through versatile modification on its periphery have been reported.[4] Remarkably, the electron densities of corannulene on its concave and convex faces are different from one another, leading to a significant dipole moment as high as 2.1 Debye.[5] Such a high dipole moment endows corannulene with the potential to form one-dimensional (1D) columnar convex-concave stacking, resulting in a channel for efficient charge transport through the large π-π overlap between molecules. Therefore, the straightforward application of corannulene in optoelectronic devices and systematical assessment of corannulene derivatives are quite attractive while have not been explored yet. Many corannulene derivatives showed low solubility and unsatisfying yield, limiting their applications in organic electronics. Moreover, the solid state of corannulene is typically dominated by C—H⋯π interactions while there is no aromatic bowl stacking based on π-π interaction.[6] To acquire high performance OFETs, rational structure design and efficient derivatization of corannulene are desired. A powerful method to facilitate 1D columnar convex-concave stacking of corannulene is introducing functional groups with strong dipole orientation onto corannulene (Figure 1).[7] On the other hand, the introduction of flexible alkyl chains to large conjugated systems has been reported to not only significantly increase the solubility of the systems which facilitates solution processed OFETs, but also effectively influence their crystal packings.[8]

Herein, we develop an imide-fused corannulene derivative, *N*-octyldibenzo[*d,m*]-1,2-corannulimide (**CI-1**), as the active material for the application in OFETs. The efficient and general synthetic strategy provides an opportunity to functionalize corannulene with other aromatics or alkyl chains. The fused imide group affords additional intermolecular dipole-dipole interactions. Meanwhile, the alkyl chain on the imide group guarantees sufficient solubility and provides additional intermolecular interactions.[8] These derivations on corannulene promote a higher degree of ordering in the solid state. A 1D columnar convex-concave stacking of **CI-1** is readily achieved in the single crystal microwires (MWs). Moreover, the imide group also acts as an electron deficient group to lower the LUMO level for better electron transport. Solution processed OFETs based on these MWs exhibited good performance with an electron mobility of 0.02 cm^2 V^{-1} s^{-1} under vacuum. Moreover, under ambient condition, a hole mobility up to 0.05 cm^2 V^{-1} s^{-1} is observed due to oxygen doping. Thus, both hole transport and electron transport were realized in **CI-1**. As far as we know, this is the first example of applying corannulene-based, even buckybowl-based compounds in OFETs.



Scheme 1. Synthetic route to **CI-1**. Reagents and conditions: a) DCC, DMAP, DCM, RT, 12 h, 84%; b) acenaphthoquinone, KOH, EtOH, reflux, 15 min, 97%; c) 1-octyl-pyrrole-2,5-dione, nitrobenzene, 180 ^{o}C, 12 h, 75%; d) Pd(PCy$_3$)$_2$Cl$_2$, DBU, DMF, 160 ^{o}C, 36 h, 82%.

Scheme 1 illustrates the synthetic route to the imide-fused corannulene derivative **CI-1**. A condensation reaction of commercially available 2-chlorobenzeneacetic acid in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) afforded bisbenzyl ketone **1** in 84% yield. After a condensation between compound **1** and acenaphthoquinone, cyclopentadienone **2** was obtained in 97% yield. A Diels-Alder reaction of compound **2** with 1-octyl-pyrrole-2,5-dione provided imide-fused fluoranthene **3** in 75% yield. Finally, a cyclodehydrohalogenation of **3** catalyzed by Pd(PCy$_3$)$_2$Cl$_2$ with excess DBU produced **CI-1** in 82% yield.[9] The overall yield from 2-chlorobenzeneacetic acid to **CI-1** is around 50%, ensuring the following device investigation. The structure of **CI-1** has two phenyl rings fused onto corannulene core to extend the π-conjugated area for better intermolecular π-π stacking and to tune electronic properties. The introduction of alkyl chains provides opportunities to achieve solution-processed OFETs, which has distinctive features of low cost and large flexibility. **CI-1** was fully characterized by ^{1}H and ^{13}C NMR and ESI-HRMS (see the Supporting Information). Note that **CI-1** exhibited excellent chemical and thermal stability, facilitating its practical application in electronic devices.

The influence of the imide unit on the energy level of **CI-1** was evaluated by the cyclic voltammetry measurement performed in solution. **CI-1** exhibited two reversible reduction waves with onset reduction potentials of -0.99 V and -1.51 V, indicating its LUMO level of -3.40 eV, much lower than that of corannulene,[10] while its HOMO level basically remains unchanged. Therefore, the introduction of electron-deficient imide group may facilitate the stable electron transport of **CI-1**. Density functional theory (DFT) calculations were carried out at the B3LYP/6-311+G(d,p) level to further investigate the electronic structure of **CI-1**, in which the octyl group was replaced by a methyl group for simplicity. The optimized geometry of **CI-1** displays a bowl-shaped π-skeleton. As shown in Figure S4, the LUMO of **CI-1** mainly delocalized on the imide and acenaphthylene parts, whereas its HOMO delocalized over the entire conjugated skeleton except the imide part. The DFT calculations demonstrate a good electron delocalization on the nonplanar bowl structure of **CI-1**.

The intermolecular packing mode of **CI-1** was further identified by the X-ray crystallographic analysis of its single crystals. The single crystals of **CI-1** are successfully grown through vapor diffusion of methanol into a toluene solution in a sealed chamber. As shown in Figure 2, in the single crystals, **CI-1** adopts a buckybowl structure with a bowl depth of 0.65 Å, shallower than that of corannulene, which may be attributed to the two fused benzene on the corannulene core. The molecular dipole of **CI-1** was calculated by DFT calculations and the dipole moment was calculated to be 2.92 Dedye, much larger than that of the unsubstituted corannulene. Moreover, due to the additional dipole caused by the imide group, which is perpendicular to the bowl-depth direction, the direction of the whole molecular dipole is no longer along the convex-concave direction as that in corannulene. As a result, the crystal packing of **CI-1** was more ordered. Interestingly, a columnar packing was observed, with stacks of molecules oriented along the *a* axis. The π-π stacking distance is 3.39 Å, which is the smallest π-π distance in comparison with other columnar π-stacking corannulene derivatives.[4d,7a,11] The molecules displayed cofacial stacking with an alternating head-to-tail orientation of the molecular dipoles induced by the imide group. In the same column, the molecules with the same dipole orientation (A and A, B and B) were strictly parallel, whereas the adjacent molecules of A and B with different dipole orientations were slightly tilted by 6.5^{o} with each other. The bowl direction of **CI-1** within columns is same, whereas adjacent columns have an opposite direction. Within the convex-concave stacks no pitch or roll angle is found, resulting in no transverse shifting. The unique intrinsic dipole–dipole interaction of the corannulene core, combined with the dipole caused by the imide group, contribute to the close π-π stacking and dominate the crystal growth of **CI-1**, providing a highly ordered packing mode[12].

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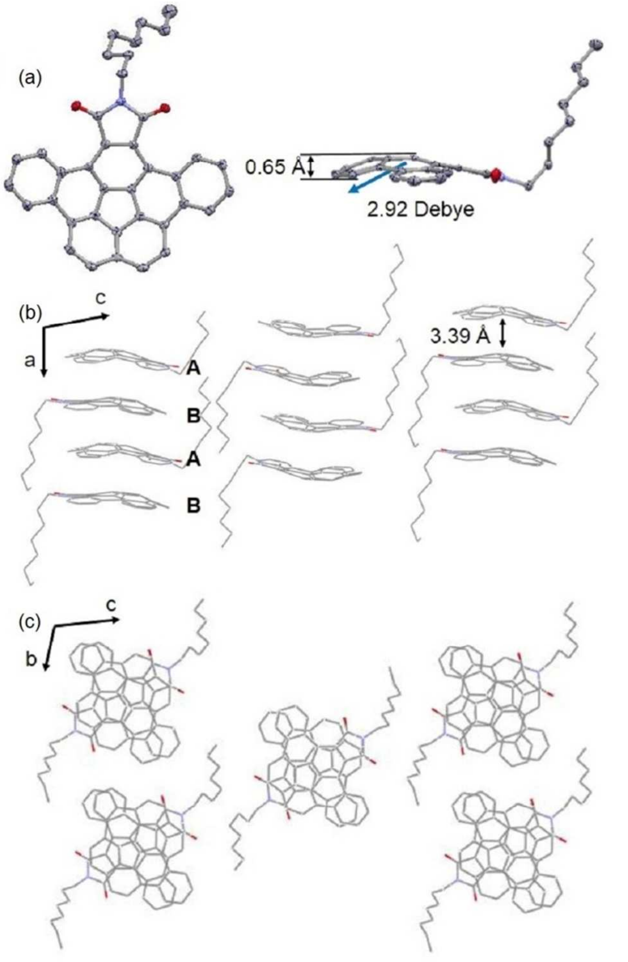

Figure 2. (a) ORTEP drawing of **CI-1** with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. (b) Crystal packing of **CI-1** viewed along the *b* axis. (c) Crystal packing of **CI-1** viewed along the *a* axis.

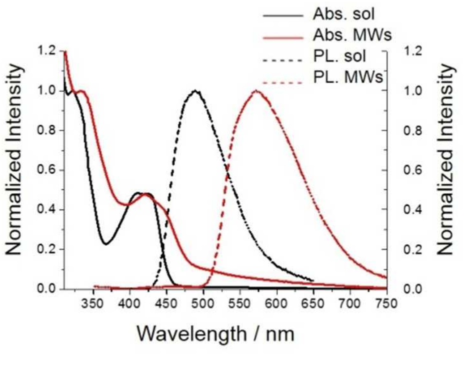

Figure 3. Absorption (solid line) and emission (dashed line) spectra of **CI-1** in CH_2Cl_2 (10^{-5} M) and of microwires. All emission spectra were collected under excitation at the absorption maxima of **CI-1**.

CI-1 is soluble in some common organic solvents, such as chloroform and THF, while they tend to aggregate via π-π stacking in the presence of unfavourable solvents. In this regard, single crystal MWs of **CI-1** are readily acquired by a phase transfer procedure of injecting methanol into the THF solution of **CI-1**. These microwires are hundreds of micrometers in length and display relatively high uniformity in width (1-2 µm). The absorption and emission spectra of these MWs are shown in Figure 3. The absorption features of **CI-1** in dilute solution showed two absorption bands, which peaked at 322 and 411 nm, respectively. Such absorption features onset was at 452 nm. In the case of MWs formed by **CI-1**, both absorption peaks red-shifted 11 nm, indicating an effective assembly of **CI-1** through π-π stacking in the MWs.[13] The emission features of **CI-1** displayed a similar bathochromic shift from dilute solution to the MWs.

In order to better understand the π-π stacking direction in these MWs, transmission electron microscope (TEM) and selective-area electron diffraction (SAED) were performed (as shown in Figure 4a and 4b). The diffraction patterns were indexed according to the single crystal data of **CI-1**, and the strong diffractions of (110), ($2\bar{2}1$), and ($1\bar{3}1$) were determined, indicating that the single crystal MWs were grown along the π-π stacking direction. As revealed by the calculated electronic couplings based on the crystal structure of **CI-1**, the adjacent molecules in the same column have large π-π stacking and exhibit large charge transfer integral, which is negligible between adjacent columns, regardless of the type of the charge carriers. In other words, the major charge-transport channel in the single crystal microwires is along the π-π stacking direction (see the Supporting Information), which is beneficial to the device fabrication.

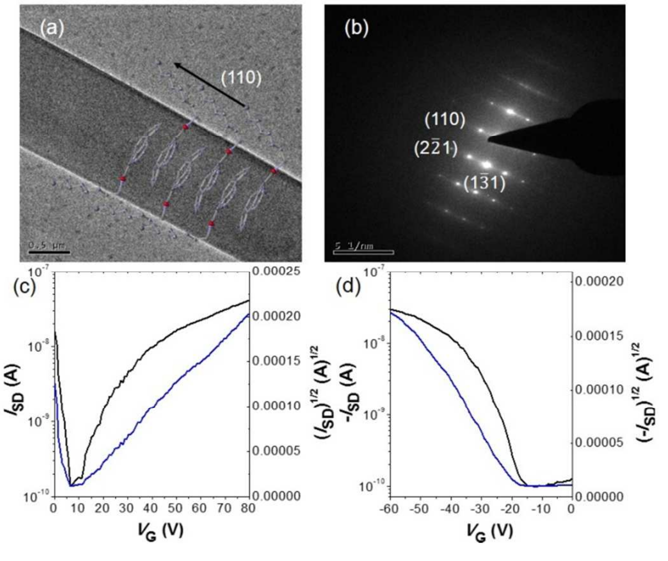

Figure 4. (a) TEM image and (b) SAED pattern of the microwires formed by **CI-1**. (c) Transfer characteristics of **CI-1** microwire device tested in vacuum. (d) Transfer characteristics of **CI-1** microwire device tested in air.

OFET devices based on the MWs of **CI-1** were fabricated and tested both under vacuum and under ambient condition. The microwires were directly dropped on the polystyrene-modified SiO_2/Si substrate. A polyethylene (PE) fiber with 20 µm diameter was mounted on the wafer as a shadow mask, and a layer of 40 nm Au was deposited onto the substrate by thermal evaporation. When the devices were tested under vacuum, the transfer curves showed an

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unconspicuous ambipolar behavior, and the electron mobility under vacuum was around 0.02 cm^{2} V^{-1} s^{-1}, with a threshold voltage of 30 V and a current on/off ratio over 10^{3}. This result is comparable to many traditional *n*-type molecules, such as PDI derivatives[14], implying the application potential of corannulene derivatives. At the same time, the hole mobility under vacuum was less than 0.01 cm^{2} V^{-1} s^{-1}. Surprisingly, when tested in the air, the devices displayed hole mobilities up to 0.05 cm^{2} V^{-1} s^{-1}, whereas the electron transfer character totally disappeared. This result might be attributed to the oxygen dopping within these microwires when the devices were tested under ambient condition.[15] The unexpected low electron mobility of the single microwires may be attribute to the oxygen and water trapping during the device fabrication, since most steps of the device fabrication, such as thermal annealing and shadow mask mounting, were carried out in the air. Recently, a series of results demonstrate that the length and branched site of alkyl chains of organic semiconductors have a significant influence on the charge transport properties of OTFTs through tuning the crystal packing and π-π distance.[16] As a consequence, the mobility of **CI-1** may be further improved through the optimization of the device fabrication process as well as tuning the alkyl chains.

Conclusions

In conclusion, we have facilely developed a curved corannulene derivative, **CI-1**. Due to its strong self-assembly behavior through π-π stacking and alkyl interaction, microcystal wires of **CI-1** are easily obtained through solution process. Highly ordered cofacial convex–concave stacking of **CI-1** is realized through tuning the molecular dipoles, which is favorable to the charge transport. We also use these microcrystal wires to fabricate the OFET devices, which is the first example of applying corannulene-based, even buckybowl-based compounds in OFET devices. Under vacuum, the molecule displays higher electron mobilities of 0.02 cm^{2} V^{-1} s^{-1} than hole mobilities. On the other hand, hole mobilities up to 0.05 cm^{2} V^{-1} s^{-1} are achieved in the air, while electron mobilities barely appear, indicating that both electron and hole transport can be realized in the corannulene derivative **CI-1**. Our work presents a bright future for the application of corannulene derivatives and buckybowl aromatics in organic electronics.

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Notes and References

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