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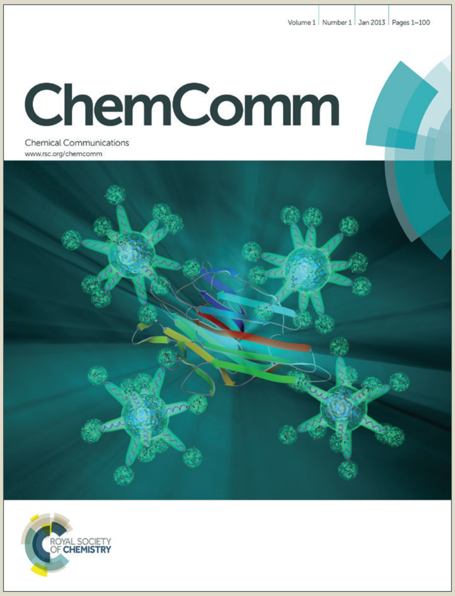

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Thiophene-fused bowl-shaped polycyclic aromatics with a dibenzo[a,g]corannulene core for organic field-effect transistors

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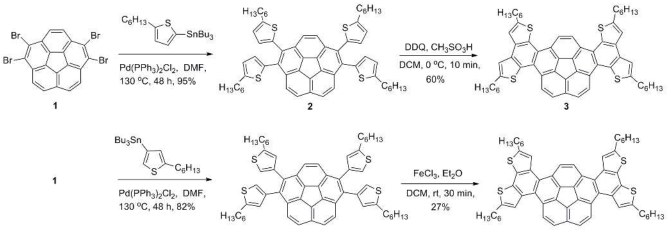
For the first time, electron-rich thiophene units were fused into the skeleton of corannulene to extend π-surfaces and tune arrangement in single crystal. Two isomeric butterfly-like thiophene-fused dibenzo[a,g]corannulenes (3 and 5) were synthesized. Isomer 3 showed p-type transport properties, with hole mobility of 0.06 cm^{2}V^{-1}s^{-1}.

Polycyclic aromatic hydrocarbons (PAHs) or heteroatom annulated polycyclic aromatics have been used extensively in organic electronics due to their strong π-network, which can facilitate charge carrier transport.[1-6] Structures with non-planar aromatic units are much less studied than flat PAHs in organic electronics due to their difficult synthesis and unpredictable packing modes. Nonetheless, non-planar structures with proper modifications, may achieve comparable device performance to those of flat PAHs.[7-10] Corannulene is a fragment of C_{60}, which can be applied in liquid crystals,[11,12] synthesis of carbon nanotubes (CNTs),[13,14] molecular tweezers,[15-17] dendrimers,[12] polymers,[18] but few in organic electronics.[19-21]

One factor that hinders further application of corannulene in organic electronics is the unpredictable packing in crystals. Corannulene itself only shows CH···π interaction between molecules, without any aromatic face-to-face stacking in single crystal.[22] Nonetheless, the packing mode of corannulene can be changed to columnar packing through, for example, fusing the electron-deficient imide unit.[19,23-25] Recently, more considerable efforts have been devoted to the application of corannulene derivatives in organic electronics. The introduction of electron-deficient groups such as trifluoromethyl,[26,27] annulated C_4F_8[28] and imide[19,23] into corannulene core tend to lower the LUMO level and enhance the electron-accepting ability. The OFET devices of corannulene derivatives show interesting charge transport properties, with hole mobility of 0.05 cm^{2}v^{-1}s^{-1} and electron mobility of 0.02 cm^{2}v^{-1}s^{-1}.[19] We also incorporated corannulene in donor-acceptor polymer and realized its application in OFETs.[29]

Although periphery modification mentioned above can drive corannulenes to form columnar packing, charge carriers may hop along the 1-D stacked column with few inter-columnar transport, thus limiting the mobility of the device.[30] Hence, more arrangements and more charge transport pathways are desired for the design of corannulene-based materials for OFETs. Annulation of heterocycles such as thiophene into PAHs both improve their electronic properties and the dimensionality of carrier transporting.[6] Fusing thiophenes into aromatic compounds is also a way to avoid sterically induced twist resulting from proximal aromatic rings.[31] The strategy of coupling thiophenes to aromatic cores followed by oxidative cyclization has proven to be a convenient way to extend π-systems.[31-41] Here, we applied such a strategy to corannulene to give two isomeric structures (**3** and **5,** Scheme 1), which significantly extends the π area. The single crystal of isomer **3** shows significant π interactions and two types of π-π overlap which may be beneficial to charge transport. OFETs based on micro-ribbons or wires of **3** and **5** were fabricated. Isomer **3** shows p-type transport properties, with hole mobility of 0.06 cm^{2}V^{-1}s^{-1}, which is the highest of the corannulene derivatives studied to date,[19] and a competitive device performance for thiophene-fused PAHs.[31,33-38]



Scheme 1. Synthetic route of isomer **3** and **5**.

The synthesis of **3** and **5** is shown in Scheme 1. Tetrabromocorannulene[42] reacted with 2-(tributylstannyl)-5-hexylthiophene and 3-(tributylstannyl)-5-hexylthiophene through Stille coupling reaction with a high yield of 95% and 85% to give compound **2** and **4**. Compound **2** underwent Scholl reaction using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as oxidant[43,44] and was purified by column chromatography followed by being recrystallized from CH_2Cl_2/MeOH to afford **3** as a yellow solid. $FeCl_3$-mediated oxidative cyclization of compound **4** gave **5**. Isomers **3** and **5** both showed great thermal stability with a decomposition temperature at 447 ^{o}C and 451 ^{o}C (Figure S1), respectively.

The normalized UV-vis absorption of **3**, **5** and corannulene in diluted solution (10^{-5} M in $CHCl_3$) is shown in Figure 1. Isomers **3** and **5** both showed three main absorption peaks, but **3** shows a slight bathochromic shift compared to **5** due to longer "effective conjugation length" of **3** versus that of **5**. Fusion of the thiophene units to dibenzo[a,g]corannulene core in **3** extends the conjugation length by two double bonds, however, in **5** the conjugation length is only extended by the lone pairs of the sulphur atoms.[34,45,46] The phenomenon can also be observed in tetrathienoanthracene.[34] Due to the extension of π-system, the absorption of **3** and **5** shows a significant bathochromic shift compared to that of corannulene. Cyclic voltammetry (CV) of **3** and **5** were performed in THF with $n\text{-}Bu_4NPF_6$ as supporting electrolyte. The HOMO of **3** and **5** were estimated to be -5.59 eV and -5.65 eV with Fc^+/Fc as an external reference. DFT calculation revealed that the LUMOs of **3** and **5** (Figure 1. c), d)) mainly localized on corannulene core and the HOMO distributed across the molecules. The highly delocalized conjugated systems may improve their intermolecular couplings and facilitate charge transport. All optical, calculated and electrochemical data were summarized in Table 1.

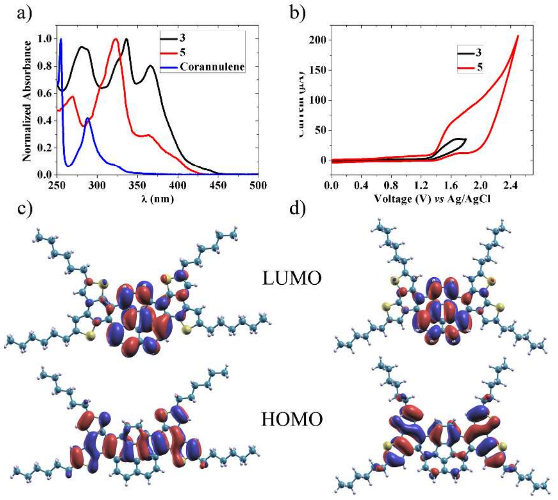


Figure 1. a) Normalized absorption spectra of **3** and **5** in $CHCl_3$(1×10^{-5} M). b) Cyclic voltammetry of **3** and **5** in THF. Calculated molecular orbitals of **3** and **5**. c), d) LUMO and HOMO of **3** and **5**.

Table 1 Summary of optical, calculated, and electrochemical data, in eV.

Compound	Expt HOMO (GW-HOMO)	IP_{cal}	$E°_{red,calc}$	E_g^{opt}
3	-5.59 (-5.90)	5.16	-2.24	2.76
5	-5.65 (-5.50)	5.15	-2.33	2.87

Isomer **3** shows strong aggregation tendency due to the π interactions, as confirmed by concentration-dependent ^{1}H NMR spectra[7,47] (Figure S2). The aromatic protons are shifted upfield with increase in concentration. However, the aromatic protons of **5** do not shift upfield with significant increase in concentration (Figure S2).

To understand supramolecular organization and to confirm our design strategy, the crystal structures of structure **3** were determined by single crystal X-ray diffraction. Single crystals of **3** were obtained from slow evaporation in $CHCl_3$/hexane solution. The results revealed that the molecules are arranged in a layered fashion and two types of` π-π packing modes exist in single crystals of **3**, as shown in Figure 2. The layered packing is an ideal arrangement for high-performance materials.[48] The π-π distance between A and B (mode 1) is 3.70 Å, which is longer than that between B and A (mode 2) of 3.48 Å. Mode 1 packing is mainly the overlap of thiophene moieties. The multi-packing modes may increase charge transport pathways and thus enhance charge carrier mobility. Unlike other π-stacking corannulene derivatives with the same bowl direction along π-stacking direction,[19,22-24] the bowl direction of two stacking molecules is opposite to each other in our case. The nearest S···S distance is 3.96 Å, which is slightly higher than double the van-der Waals radius of sulfur (3.68 Å[49]). Nonetheless, because of the introducing of thiophenes, the strong π-π interaction formed between molecules of **3** which may facilitate its charge transport. The bowl-depth of **3** was estimated to be 0.69 Å (calcd., 0.80 Å), somewhat lower than that of corannulene without functionalization, 0.87 Å (calcd., 0.92 Å). The extension of π-system forces **3** to be more planar. Unfortunately, we failed to obtain the single crystal of isomer **5**. But considering that the sulfur atoms in the isomer **5** are more exposed than in isomer **3**, it is reasonable to infer that isomer **5** may expect more intermolecular S···S interactions than in the isomer **3**[34], but the real arrangement of isomer **5** remains unclear. The calculated bowl depth of **5** is 0.88 Å, which is in between that of **3** and corannulene.

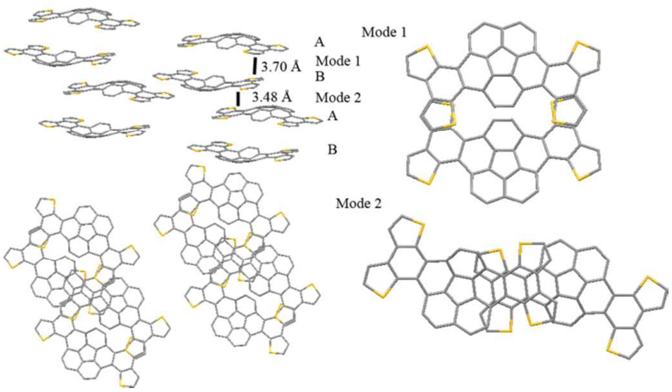


Figure 2. Single crystal of **3** and its packing mode (Alkyl chains were hided).

Because of π-π interactions, compounds **3** and **5** in favourable solvents may assemble into micro-wires or ribbons in the presence of unfavourable solvents. For example, an unfavourable solvent (MeOH) was added to a solution of **3** in dichloromethane with 10% (v/v) CS_2 to give single-crystal micro-ribbons of **3**. In contrast, **5** shows poor solubility in common solvents such as THF and chloroform, but shows little solubility in CS_2. In the presence of MeOH, **5** assembles into micro-wires that are about 2-5 μm in width and hundreds of micrometres in length (Figure S3). Bottom gate/top contact (BG/TC) device architecture was fabricated to evaluate the OFET performance of **3** and **5**. A suspension of micro-ribbons or wires in hexane was spin-coated onto a SiO_2/Si substrate with polystyrene-treatment and then annealed at 60 ^{o}C in a vacuum oven overnight. A polyethylene fibre was used as shadow mask,[50] and a layer of Au was deposited under high vacuum to be drain and source electrodes. The typical channel length was measured to be 10-15 μm by scanning electron microscope (SEM). All OFETs were tested in air. Isomer **3** showed p-type transporting property with a hole mobility of 0.06 $cm^2V^{-1}s^{-1}$, a threshold voltage of -38 V and a current on/off ratio of 10^3 (Figure 3). Unfortunately, **5** did not show any field-effect properties. We don't know the packing mode of isomer **5** due to the lack of single crystal. Many factors may influence the device performance based on single crystal mocro-wires or micro-ribbons such as packing mode, contacts between the micro-ribbons or wires and the dielectric.[30,50-52] Nonetheless, the highest mobility based on corannulene derivatives was achieved by the extension of π-system and the adjustment of arrangement.

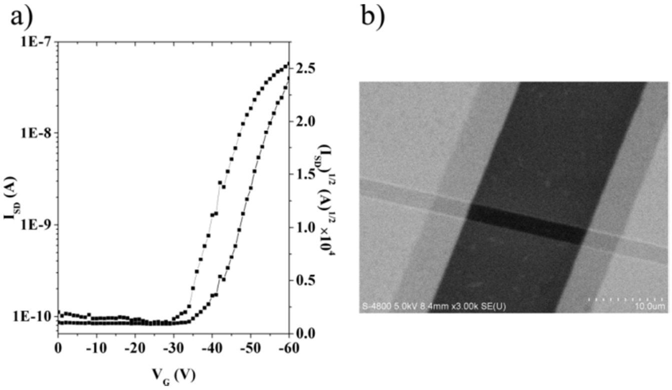


Figure 3. a) Transfer characteristics and c) SEM device image of **3**.

In summary, we have developed a convenient way to extend the π-conjugation area of corannulene and to tune its arrangement. Two isomeric structures (**3** and **5**) were synthesized. The introduction of thiophenes significantly improved the arrangement and charge transport properties of **3**. OFETs based on micro-ribbons of **3** showed a hole mobility of 0.06 $cm^2V^{-1}s^{-1}$. These preliminary results reveal that bowl-shape PAHs stemming from corannulene can provide new structural motifs for organic electronics.

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