Graphical Abstract

Corannulene derivatives for organic electronics: from molecular engineering to applications

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This review focuses on the recent progress in the functionalization of corannulenes and their applications in organic electronics.

Review

Corannulene derivatives for organic electronics: from molecular engineering to applications

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ABSTRACT

This paper intends to provide an overview for using corannulene derivatives in organic electronics such as organic field-effect transistors (OFETs), organic solar cells (OSCs), and organic light-emitting diodes (OLEDs). We highlight the rational design strategies, tuning molecular orbital energy levels and arrangement in single crystals of corannulenes. The topological structure and properties of corannulene make it a unique candidate for organic electronics.

1. Introduction

Corannulene, a bowl-shape fragment of C₆₀, was first synthesized in 1966 [1]; owing to the efforts of Siegel *et al.*, it can be produced in kilogram scale now [2]. Over the past several decades, chemists have been fascinated by its unique topological structure, and endeavor to its functionalization and properties [3-6]. These derivatives have been applied in the fields of supramolecular chemistry [7-10], liquid crystals [11,12], chiroptical activity [7,13,14], bottom-up synthesis of carbon nanotubes [15], radicals [16-20] and lithium-ion cells [21]. Although its semiconducting properties are also interesting and have attracted considerable attention on the synthesis and basic characterization, the device performance based on corannulene derivatives has not been demonstrated until recently [22-27].

Unlike planar polycyclic aromatic hydrocarbons (PAHs), corannulene has a dipole moment as high as 2.1 Debye, resulting from the different electron densities on its concave and convex surfaces [28,29]. The dipole moment, the size of the bowl surface and bowl depth will significantly influence their packing in single crystals [5,26]. For corannulene, CH... π interactions instead of π - π interactions [30] dominate in single crystal, thus prohibiting intermolecular charge carrier transport. Molecular orbital energy decides the injection barrier of hole or electron to electrode. Pristine corannulene exhibits high electron affinity (-2.65 eV) and low ionization potential (-6.30 eV) [24,31]. Both values are far from the work functions of common metal electrodes (Au: 5.2 eV, Ag: 4.2 eV, Al: 4.2 eV) [32], indicating high injection barrier for both holes and electrons. Hence, modulating the packing and molecular orbital energy of corannulene derivatives are critical for their applications in organic electronics. Fortunately, the rich chemistry of corannulene allows such on-demand rational design of different corannulene molecules. We and Pei *et al.* have developed a series of corannulene derivatives and used them as p-channel [22], n-channel [23] and ambipolar materials [26]. In addition, we also used corannulene derivatives as non-fullerene acceptors in organic solar cells [24]. In this review, we intend to provide an overview of the past, present of and future of the application of corannulene derivatives in organic electronics. We first summarize the functionalization to extend the π -conjugated framework of corannulene or incorporation of heteroatom on the backbone of corannulene from 2007-2016 (for those before 2007, see reviews [3-5,33,34]), then present the applications and device characterization of corannulene derivatives in organic electronics, and finally we evaluate the prospective of using corannulenes in organic electronics and outlines the trends for their future development.

2. Extended π -conjugated or nitrogen-doped corannulene derivatives

Extension of π -surface of the π -conjugated molecules both increases their intermolecular π - π interactions and effectively modulates their molecular optical and electrochemical properties [35,36]. As aforementioned, the dominating presence of CH... π interactions in pristine corannulene single crystals will prohibit intermolecular charge carrier transport [30]. To improve corannulene derivatives' intermolecular π - π interactions (electronic couplings) in the solid state, increasing the corannulene π -conjugated surface is effective

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[5,33]. Lash *et al.* prepared corannulenoporphyrins **2-1** (Fig. 1) from nitrocorannulene in five steps [37]. Corannulenoporphyrins **2-1** exhibited significantly red-shifted absorption with onset absorption wavelength at about 680 nm. Later, Osuka *et al.* fused porphyrins into dibenzo[*a,g*]corannulene in just two steps by coupling porphyrins at different positions with dibenzo[*a,g*]corannulene, and then oxidatively fusing to give 5- or 6-membered rings linked dibenzo[*a,g*]corannulene-porphyrin **2-2** and **2-3**[38]. The HOMO level of **2-2b** is 5.14 eV and that of **2-3b** is 5.28 eV, both match the work function of gold (5.2 eV), indicating their potential applications as p-channel materials. Wu *et al.* used the straightforward palladium-catalyzed cyclization to construct the highly curved bulkybowls **2-4** and **2-5** [39,40]. Both compounds showed 2D columnar stacking with large π -orbitals overlap, thus facilitating the intermolecular charge carrier transport. Siegel *et al.* fused graphene fragment into corannulene with the key step of activation of a C(Ar)-F bond to give compound **2-6** [41]. Because of the steric hindrance, a *meso* pair of 5-helicenes existed in single crystals. And calculation revealed that the HOMOs mainly localized on graphenic region and the LUMOs on corannulene core, confirming that curvature changed the orbital levels and bandgap compared to a planar graphenic form [42,43]. Scott *et al.* proved that highly distorted conjugated molecules, with curvatures surpassing that of C₆₀, can be synthesized by solution phase synthetic approach instead of extreme conditions like high-temperature flash vacuum pyrolysis method [39]. They synthesized a series of multiindenocorannulenes (compound **2-7** to **2-13**) and investigated their optical properties, providing the basic ideas to extend corannulene π -system by Pd-catalyzed coupling reactions.

In 2012, Scott *et al.* developed an elegant “dynamic covalent” [44-46] approach to 1,3,5,7,9-pentakis(Bpin)corannulene after 96 hours through Ir-catalyzed C-H polyborylations [47]. The polyborylated corannulene is an important building block for a series of π -conjugated extended corannulene derivatives. Later, Siegel *et al.* optimized the procedures using microwave-assisted method to decrease the reaction time from 96 h to 4 h compared with the routine bench-top preparation [48]. The polyborylations of corannulene provide the multi positions for coupling reactions. 1,3,5,7,9-Pentakis(Bpin)corannulene coupled with 2-bromo-1,3-dichlorobenzene followed by flash vacuum pyrolysis to give isomerically pure [5,5]nanotube **2-14**[47]. Itami, Scott *et al.* also used 1,3,5,7,9-pentakis(Bpin)corannulene as a starting material to synthesize the defect nonplanar nanographene compound **2-15** with odd-membered rings [49,50].

Doping of heteroatoms into conjugated systems is an efficient method to alter their intrinsic properties such as orbital energy and optical properties [51-53], and thus to influence their semiconducting properties. It has been proved that nitrogen-doping can significantly increase the mobilities of conjugated molecules [54,55]. Several theoretical calculations on nitrogen-doped corannulenes have been reported [56,57] and revealed that the substitution of carbon atoms with nitrogen atoms in corannulene lowered the HOMO-LUMO gap. Nevertheless, it is a big challenge to incorporate nitrogen atoms into corannulene due to the synthetic difficulties, albeit several attempts [58]. Recently, Ito *et al.* reported the first nitrogen-doped corannulene named 8-*tert*-butyl-6b²-azapentabenzob[*bc,ef,hi,kl,no*]corannulene (**2-16**). Compound **2-16** adopted columnar stacking in single crystal with a π - π distance of 3.69 Å. And it showed a higher fluorescence quantum yield than that of corannulene (quantum yield is 0.24 for **2-16** and 0.07 for pristine corannulene) [59].

Fig. 1. π -surface extended corannulene derivatives.

3. Influence of energy levels and packing modes to mobility of corannulene derivatives

Electron-deficient groups such as imide, fluorine, trifluoromethyl and cyano groups are often introduced into molecular backbones not only to lower their LUMO levels, but also to form additional interactions such as F...H interactions sometimes, which may facilitate the charge carrier transport. Strauss, Lentz, Diederich et al. have developed a series of electron-withdrawing groups substituted corannulenes [60-65]. Those who interested in corannulenes bearing electron-deficient groups can refer to an elegant review by Lentz *et al.* in 2014 [6].

Lentz *et al.* first investigated the mobilities of corannulene derivatives by electrodeless microwave conductivity measurement [61]. They found that the mobility of columnar packed trifluoromethylated corannulene was significantly larger than that of corannulene ($\Sigma\mu > 0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for trifluoromethylated and $\Sigma\mu > 5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for corannulene). Their results emphasized the significant influence of packing on charge carrier mobility, although they did not report the applications of corannulene derivatives in OFET devices.

We and Pei *et al.* applied corannulene derivatives in OFETs devices, and the results revealed that both packing in the solid state and energy levels of corannulene derivatives lead to different charge carrier transporting properties [22,23,26]. Pei *et al.* used imide-fused corannulene derivative **3-5** as the active layer in OFETs [26]. The synthesis is shown in Scheme 1. **3-3** was synthesized from commercial available **3-1** by two condensations. **3-5** was obtained from **3-3** by D-A reaction and Pd-catalyzed intramolecular coupling. After introducing imide group to corannulene, the molecular dipole moment has been significantly changed up to 2.92 Debye and the LUMO level was lowered to 3.40 eV. By tuning the molecular dipole moment and choosing proper alkyl chain, **3-5** showed 1-D convex-concave columnar packing in the single crystal (Fig. 2a). The distance between π -stacking molecules is 3.39 Å. **3-5** in good solvent will assemble along π -stacking direction into single-crystal microwires (Fig. 2b, 2c) when poor solvent is added. Intriguingly, OFETs devices based on these microwires showed ambipolar transporting properties with an electron mobility of $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a hole mobility of less than $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in vacuum (Fig. 2d). Because of the doping of oxygen [66], it showed p-channel transporting property with a hole mobility of $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Fig. 2e) in air. It is the first time that the corannulene derivative is used in organic field-effect transistors.

Scheme 1. Synthesis of **3-5**.

Fig. 2. (a) Single-crystal structure and packing of **3-5**. (b) Transmission electron microscopy (TEM) image and (c) selective-area electron diffraction (SAED) pattern of **3-5** microwires. (d) Transfer characteristics of **3-5** microwire in vacuum and (e) under ambient conditions. Reprinted with permission from ref. 24. Copyright 2014, Royal Society of Chemistry.

Later, we developed pure p- or n-channel materials based on corannulene by introducing multi electron rich or electron deficient groups to conjugated backbones. To achieve pure hole injection, four electron-rich thiophenes were first fused into π system of corannulene by Stille coupling and then Scholl reaction to give two isomeric thiophene-fused dibenzo[*a,g*]corannulenes **3-8** and **3-10** (Scheme 2) [22]. Two benzene rings and four thiophene rings were introduced to conjugated system of corannulene. The larger effective conjugated length of isomer **3-8** and **3-10** led to red-shift absorption compared to that of corannulene. The HOMO levels and optical band gaps were determined to be -5.59 eV/-5.65 eV and 2.76 eV/2.87 eV for isomer **3-8/3-10**, respectively. The HOMO levels are more closed to the work function of Au (5.2 eV) than LUMO levels, indicating these two compounds may show p-channel transporting properties. We succeeded in obtaining the single crystal of isomer **3-8**, unlike **3-5**, isomer **3-8** exhibited layered packing fashion with two types of packing mode (Fig. 3a). The unique packing mode provided more charge carrier transport channels through different π - π interactions. OFET devices based on micro-ribbons or microwires of isomer **3-8** and **3-10** were fabricated. Isomer **3-8** displayed a hole mobility of up to $0.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a threshold voltage of -38 V and a current on/off ratio of 10^3 in air (Fig. 3b), which represented the highest hole mobility based on corannulene. Compared with isomer **3-8**, isomer **3-10** didn't show any field-effect properties although many microwires have been tested. The reasons remain unclear due to the lack of single crystal data. Nevertheless, the multi carrier transporting channels in the single crystal of compound **3-8** facilitated the improvement of mobility.

Scheme 2. Synthetic routes of compounds **3-8** and **3-10**.

Fig. 3. a) Single-crystal packing of **3-8**. b) Transfer characteristics of **3-8** micro-ribbon tested under ambient conditions. c) SEM device image of **3-8**. Copyright 2014, Royal Society of Chemistry.

As described before, corannulene has a high LUMO level (-2.65 eV), exhibiting high barrier for injection of electron to electrode. Taking both energy levels and arrangement in single crystals into consideration, we introduced imide and cyano groups into corannulene (Scheme 3) to lower its LUMO level and also tune its arrangement in single crystals, thus achieving n-channel transporting properties [23]. Surprisingly, because of the introduction of cyano groups into imide-fused corannulene, not only convex-concave columnar packing was achieved in single crystals, but also electronic couplings between columns were realized, leading to 2D columnar stacking (Fig 4a). The smallest π - π distances were 3.31 Å and 3.28 Å for **3-13a** and **3-13b**, and even smaller than those of high-performance air-stable compounds such as dicyanated and fluorinated PDI [67]. The dense packing in single crystals prohibits the penetration of water and oxygen into bulk phase [67,68]. The LUMO levels were also lowered to ~3.6 eV for two compounds. The dense packing and low LUMO work synergistically to achieve n-channel transporting properties even in air with an electron mobility of $0.07 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **3-13a** and $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **3-13b** based on their single-crystal microwires (Fig. 4).

Scheme 3. Synthetic routes of compounds **3-13a** and **3-13b**.

Fig. 4. Single-crystal packing of **3-13a** (a) and **3-13b** (b). Pathways 1 and 2 are two main charge carrier transporting pathways. t corresponds to electronic couplings. d_1 corresponds to the closest π - π distance and d_2 corresponds to the $-\text{CN}\dots\pi$ distance. Transfer and output characteristics of **3-13a** (c) and **3-13b** (d). (e) Device architecture. (f) Device SEM image. Copyright 2015, Royal Society of Chemistry.

4. Imide-fused corannulene as acceptor units in donor-acceptor polymer

Donor-Acceptor (D-A) conjugated polymers usually have large planar conjugated units, strong π - π interactions, readily tunable frontier orbital energy levels [69,70]. These features endow them with high carrier mobilities and broad absorption spectra and thereby significantly improved device performances of polymer FETs and photovoltaics [54,71,72]. Bowl-shaped molecules such as corannulene have seldom been incorporated into conjugated polymers [73-75]. We designed the imide-fused corannulene derivative **4-5** (Scheme 4) [25]. The alkyl chains can be easily introduced to imide N position and also the two halogens in 4- and 9-positions provide the coupling polymerization sites. Compound **4-5** copolymerized with 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, giving polymer **4-6** with the number average molecular weights of 40.5 kDa and polydispersity index of 3.5. Calculation based on three repeated units of **4-6** showed LUMO localized on electron-deficient imide-fused corannulene and HOMO delocalized along the polymer chain just like typical D-A copolymers [76]. HOMO/LUMO levels and optical band gap of **4-6** were determined to be -5.42/-3.31 eV and 1.98 eV. The semiconducting properties of **4-6** were also investigated. **4-6** showed ambipolar transporting properties with a hole mobility of $0.025 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an electron mobility of $7.45 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Fig. 5). Because the bowl-shaped structure of corannulene can accommodate PCBM through ball-socket interactions [10,75,77], corannulene-based conjugated polymers may also act as promising donors in organic solar cells. This work paved the way to introduce corannulene into conjugated polymers and significantly extended the applications of corannulene.

Scheme 4. Synthetic route of **4-6**.

Fig. 5. a) Transfer and b) output characteristics of **4-6**. Copyright 2014, Royal Society of Chemistry.

5. Corannulenes as non-fullerene acceptors in organic solar cells

Fullerenes and their derivatives are star molecules in organic electronics especially in organic solar cells [78]. To our knowledge, their bowl-shaped fragments have never been used in organic solar cells. Compared with fullerenes, corannulene is much easier to be modified, thus more convenient to tune its derivatives' solubility, energy levels, absorption and charge carrier transporting properties. To lower corannulene's LUMO level and increase film forming ability, *n*-hexylphthalimide (**5-3**) and *n*-hexylnaphthalimide (**5-4**) were introduced to corannulene (Scheme 5) by Suzuki reactions [24]. The LUMO levels of resulting compounds **5-5** (**Cor-PI**) and **5-6** (**Cor-NI**) were significantly decreased to -3.10 eV and -3.24 eV. Blended with P3HT in bulk-heterojunction organic solar cells (BHJ-OSCs), **5-5** and **5-6** showed PCEs of 0.37% and 1.03%, V_{oc} of 0.83 V and 0.82 V (Fig. 6), respectively. The V_{oc} are 0.2 V higher than that of PCBM due to the higher LUMO levels of **5-5** and **5-6** [79]. The mobility, from the space charge limited current (SCLC) method, was $1.32 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **5-6**/P3HT blend film, which was much higher than that of **5-5** ($1.6 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and comparable to those of high-performance non-fullerene acceptors[80]. Note that further optimizations such as adding solvent additives, designing novel device structures, and incorporating different donors may increase the devices performances.

Scheme 5. Synthetic route of **5-5** and **5-6**.

Fig. 6. a) J - V curves and b) EQE curves of **5-5** (Cor-PI)/P3HT and **5-6** (Cor-NI)/P3HT blend films. Copyright 2014, Royal Society of Chemistry.

6. Corannulenes as light-emitting materials

Pristine corannulene exhibits a maximum emission peak at 423 nm and a fluorescence quantum yield (Φ_f) of 0.07 [27,59,81]. Siegel *et al.* found that multiethynyl corannulenes can display tunable emission, depending on the nature of substituent groups as well as the crystalline arrangement [82]. These results were supported by theoretical calculations by Baldrige *et al.* [83]. Multiethynyl corannulene derivative **6-1** (Fig. 7) even has a fluorescence quantum yield as high as 0.83, indicating its potential as light-emitting materials [82]. Diederich, Siegel *et al.* also synthesized a series of multi 4-(*N,N*-dimethylamino)phenylethynyl substituted corannulenes (compounds **6-2** to **6-5**). Emission peaks at 533 nm ($\Phi_f = 0.98$) for compound **6-2**, 538 nm ($\Phi_f = 0.93$) for compound **6-3**, 593 nm ($\Phi_f = 0.76$) for compound **6-4**, and 595 nm ($\Phi_f = 0.56$) for compound **6-5** were observed [63]. The fluorescence quantum yields were rather higher than that of pristine corannulene. Sutton *et al.* developed the corannulene-based blue emitters (compounds **6-6** and **6-7**) [81]. Compound **6-6** has red-shifted absorption and a higher fluorescence quantum yield than those of **6-7** ($\Phi_f = 0.60$ for **6-6**, $\Phi_f = 0.08$ for **6-7**), resulting from the longer effective conjugated length. Yamada *et al.* first applied corannulene derivatives to light-emitting active layers in their patent [27]. They fabricated a series of devices based on corannulene derivatives. Compound **6-8** exhibits the highest emission luminance of 2200 cd/m^2 , a power efficiency of 6.1 lm/W and a green electrogenerated luminescence peak at 515 nm. It is the first demonstration of using corannulene derivatives in OLED devices, although the performance is moderate [84,85]. Further optimizations could be focused on orbital energy tuning, balanced electron and hole mobilities, stabilities, film-forming properties and so on [86,87].

Fig. 7. Corannulene derivatives as light-emitting materials.

7. Conclusions and outlook

In this mini review, we summarized the recent advance in functionalization and applications of corannulene derivatives in organic electronics. The orbital energy and crystalline arrangement play important roles in their semiconducting properties. The basic results

show that corannulene derivatives can be novel materials for organic electronics, although the mobilities or PCEs are moderate. Note that limited applications of corannulene in organic electronics are reported up to date. To advance the applications of corannulenes in organic electronics, more efforts should be spared to enhance their mobilities, PCEs and luminous intensity, which require diversified structures, further device optimizations and an in-depth understanding of the structure-property relationships.

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