Electronic transport properties of selected carbon π-bowls with different size, curvature and solid state packing

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Abstract
First-principles calculations combined with the Boltzmann transport theory are used to investigate the electronic transport properties of four members of the extended family of indenocorannulene molecular crystals. The results for the electrical conductivity suggest that all indenocorannulene derivatives should exhibit transport characteristics significantly improved compared to the parent corannulene. In particular, the transport properties of 1,2,4-triindenocorannulene crystal are found to be comparable for electron doping and likely surpass for hole doping the values achievable in sumanene, assuming the same carrier lifetimes. The findings point to a large sensitivity of the charge-carrier conductivity to the size as well as stacking direction of the carbon-rich π-bowls and indicate that this class of corannulene derivatives can provide new structural motifs that can be further tuned to achieve high-performance materials for organic electronic devices.

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1. Introduction

Bowl-shaped polyaromatic hydrocarbons (PAHs) have emerged in recent years as promising new materials for important technological applications: batteries, optoelectronic devices, photoactive switches and chemical sensors. These curved polyarenes (often called π-bowls) are excellent electron acceptors, comparable to planar PAHs [1,2] and fullerenes [3,4], and could serve as key anode components in rechargeable Li-ion batteries. Corannulene, the smallest non-planar fragment of C_{60} fullerene [5,6], was shown to exhibit high degree of lithium intercalation upon step-wise reduction [7–10] and corannulene-based anode materials have demonstrated a high reversible lithium capacity, almost twice as high as that of fully lithiated graphite [11,12]. The family of π-bowls also provides a natural platform for designing new organic materials with applications in light emitting-diodes [13–16], field-effect transistors [17–19], or photovoltaic cells [20]. While organic semiconductors may still not compete with their inorganic counterparts in terms of charge-carrier mobility or power efficiency performance, they do have the advantage of being low-cost, flexible, easily processable in solution, and compatible with many substrates [21,22].

First-principles calculations could provide unique design insights upon which a wide array of materials properties could be improved beyond the current state-of-the-art. Due to the complexity and size of organic molecular crystals, most theoretical studies up to date have only addressed the energetics of the interaction between isolated molecular bowls with various metal cations [23–28] or the energetics of small assemblies such as corannulene dimers [29–32] or π-bowl-fullerene binary systems [33–35]. Only recently, several studies have explored the optical and vibrational properties of corannulene-based crystals [14,16,36,37]. To the best of our knowledge, no theoretical insights into the electronic transport properties of crystalline bowl-shaped polyarenes have yet been provided.

In the recent years, the family of π-bowls has greatly expanded [38] and besides the smallest members, corannulene (C_{20}H_{10}) and sumanene (C_{21}H_{12}) [39,40], it now includes bowls as large as pentadendencorannulene (C_{60}H_{20}) [41] and a short capped carbon nanotube (C_{60}H_{10}) [42]. The in-depth structural analysis of π-bowls by Filatov et al. [43] has revealed that variation in the curvature and size of the molecular building blocks leads to very different crystal packing. In particular, π–π bowl interactions between molecules of the indenocorannulene family with strong dipole moments promote a one-dimensional (1D) columnar stacking which, in turn, should favor an efficient channel for charge transport. Experimental studies on sumanene [44] and corannulene derivatives [17–20,45] have indeed found strong anisotropy in the electronic transport properties with high charge-carrier mobilities along the π-bowl stacking direction. Given the lack of studies on the transport properties of large indenocorannulene bowls in the crystalline state, it is
important and timely to carry out a careful theoretical investigation in order to understand their potential as active materials in organic electronic devices.

In this work, we report the first systematic theoretical investigation of the electronic transport properties of a series of X-ray crystallographically characterized bowl-shaped PAH crystals from the indenocorannulene family [43] vs. those of the parent corannulene which lacks columnar π-stacking in the solid state [46,47] and sumanene which exhibits an efficient π-stacking in the crystalline state [48]. Specifically, first-principles band structure calculations coupled with the Boltzmann transport formalism are used to characterize the electronic transport properties of sumanene (C_{21}H_{12}), corannulene (C_{32}H_{16}), and four indenocorannulene crystals, namely monoindenocorannulene (mono-IC, C_{30}H_{12}), diindenocorannulene (ortho-di-IC and para-di-IC, C_{32}H_{14}), and triindenocorannulene (1,2,4-tri-IC, C_{34}H_{16}). The molecular building blocks are shown in Fig. 1. Comparison of the transport coefficients of the four indenocorannulene crystals with those of the parent corannulene and well-known sumanene allows us to identify the most promising candidates for experimental conductivity studies.

![Fig. 1. Molecular building block of the crystal structures. (A color version of this figure can be viewed online.)](image)

**2. Computational method**

The calculations are performed within the local density approximation (LDA) [49] to density functional theory and norm-conserving pseudopotentials [50] using the QUANTUM-ESPRESSO package [51]. The valence electronic wave functions are expanded in a plane-wave basis set with a kinetic energy cutoff of 60 Ry. We use at least 2000/(number of atoms in unit cell) k-points distributed on a Monkhorst–Pack mesh [52] for ionic relaxations and a much denser mesh of at least 35,000/(number of atoms in unit cell) for transport properties calculations. We employ the experimental lattice parameters for all crystal structures [43,46,48] and relax the atomic positions until the force on each atom is smaller than 0.01 eV/Å. We checked and found that for the 1,2,4-tri-IC system the effect of full structural relaxation on the electronic band structure is negligible.

The conventional unit cells of three-dimensional (3D) crystal structures of sumanene, corannulene, mono-IC, ortho-di-IC, para-di-IC, and 1,2,4-tri-IC are shown in Figs. 2 and 3 and the experimental X-ray crystallographic parameters are listed in Table 1. Sumanene crystallizes in the trigonal R3c space group with N = 6 molecules in the unit cell stacked along the c-axis [Figs. 2(a) and 3(a)]. Corannulene crystallizes in the monoclinic P2_1/c space group with N = 8 molecules in the unit cell [Figs. 2(b) and 3(b)] without any preferential stacking orientation of the C_{20}H_{10} bowls. Mono-IC crystallizes in the monoclinic space group P2_1/n [Figs. 2(c) and 3(c)]. There are N = 4 tortoise-shaped inequivalent molecules in the unit cell and they are stacked along the a-axis. Ortho-di-IC crystallizes in the orthorhombic space group Pnma and there are N = 4 inequivalent molecules in the unit cell. The molecular bows are stacked along the c-axis [Figs. 2(d) and 3(d)]. Para-di-IC crystallizes in the polar orthorhombic space group Cmc2_1. There are N = 4 molecules in the unit cell with a preferential stacking orientation along the c-axis [Figs. 2(e) and 3(e)]. We note that the primitive unit cell of para-di-IC has only N = 2 inequivalent molecules and all electronic and transport properties in this work are calculated for the primitive unit cell.] 1,2,4-tri-IC crystallizes in the polar orthorhombic space group Pmn2_1 with N = 2 non-planar herringbone inequivalent molecules in the unit cell [Figs. 2(f) and 3(f)]. The molecules are stacked along the c-axis. More details about the crystal structures will be given in the next section in connection with the transport properties.

Electronic transport coefficients are computed with the BoltzTraP code [53] that solves the semi-classical Boltzmann transport equations (BTEs) in the constant relaxation-time and rigid band approximations [54]. The known difficulties of describing the finite lifetime of charge carriers due to various scattering mechanisms, have led to adopting the constant relaxation-time approximation in many theoretical studies [54–57]. This approximation is based on the assumption that the relaxation-time does not vary significantly in energy over the Brillouin zone, i.e. $\tau_{\text{L}} \approx \tau$. Moreover, within this approach, the Seebeck coefficient S, is independent of $\tau$ and can be calculated on an absolute scale. Despite its simplicity, the method has been shown to work rather well even for systems with substantially anisotropic conduction [58] and it is also the scheme adopted in this work.

**3. Results and discussions**

![Fig. 4.](image)

Fig. 4 shows the calculated electronic band structure and the density of states (DOSs) for the six π-bowl systems. The calculated band gaps are 2.80 eV for sumanene, 2.68 eV for corannulene, 1.97 eV for mono-IC, 1.87 eV for ortho-di-IC, 1.73 eV for para-di-IC, and 1.50 eV for 1,2,4-tri-IC. It can be noticed that in going from corannulene to 1,2,4-tri-IC crystals, the energy band gap decreases monotonically with the increase in the number of indeno-group substituents and the size of the bowl. As expected for traditional DFT, the calculated energy band gaps are underestimated by approximately 2 eV with respect to experimental values, but in good agreement with other theoretical studies at the same level of theory [16]. However, we should note that the exact magnitude of the band gap is not a critical parameter in this work and the transport coefficients are not affected as long as the size of the band gap is large enough compared to the temperatures considered. At room temperature, mostly carriers in a small energy window (approximately 0.1 eV) below the valence band maximum (VBM) and above the conduction band minimum (CBM) contribute to the charge-transport properties. In all cases, except corannulene, a large dispersion is observed at VBM and CBM along the crystallographic direction corresponding to the preferential π-stacking of the bowl-shaped molecules. Negligible band dispersions are found along the directions perpendicular to stacking, reflecting the molecular nature of the solid. From Fig. 4, we extract the bandwidth of the highest valence band (lowest
The conduction band along the high-symmetry direction corresponding to the π-stacking of molecules. The bandwidth values are: 0.19 (0.16) eV along the $\Gamma - A$ direction for sumanene, 0.25 (0.30) eV along the $Y - H$ direction and 0.28 (0.29) eV along the $\Gamma - X$ direction for mono-IC, 0.28 (0.07) eV along the $\Gamma - Z$ direction for ortho-di-IC, 0.15 (0.08) eV along the $\Gamma - Z$ direction for para-di-IC, and 0.47 (0.34) eV along the $\Gamma - Z$ direction for 1,2,4-tri-IC. Therefore, the band structure calculations suggest that all corannulene derivatives will exhibit anisotropic charge-transport properties similarly to what was found experimentally in the case of sumanene.

The calculated electrical conductivity $\sigma$ at 300 K for the set of systems under consideration is shown in Figs. 5 and 6. Since there are no available experimental data on the transport properties of indenocorannulene derivatives, we computed the electrical conductivity for a range of charge carrier concentrations. To simulate electron and hole doping, the position of the chemical potential is shifted up and down relative to the bottom of the conduction band and the top of the valence band, respectively. For sumanene, the electrical conductivity is found to be highly anisotropic with a dominant contribution along the $z$-axis which coincides with the
molecules stacking direction (Fig. 3a). The estimated anisotropic ratio varies from 10 to 15 for the electron-doped system for carrier concentrations in the $10^{18}$ to $10^{21} \text{ cm}^{-3}$ range. These values are in very good agreement with the experimental finding of a 9.2 anisotropic ratio for the electron mobility reported by Amaya et al. [44]. In comparison, for corannulene, the electrical conductivity is almost isotropic and an order of magnitude lower than that of sumanene. This behavior is consistent with the lack of any bowl-to-bowl stacking arrangement in the crystal structure of corannulene (Fig. 3b).

The situation changes considerably in the case of indenocorannulene derivatives. The attachment of one or more indeno-groups to the corannulene core leads to the formation of one-dimensional columnar π-stacking of the bowls in a concave-to-convex fashion in their solid state structures (Fig. 3c–f). As a result, for mono-IC, para-di-IC, and 1,2,4-tri-IC crystals, the largest contribution to $\sigma/\tau$ is found along the stacking direction and only negligible contributions along the other two directions. Despite these similarities, however, there are noticeable differences in the magnitude of the electrical conductivity due to the unique packing features that each individual crystal structure shows with respect to the orientation of the indeno-groups and the directions of the convex bowl surfaces.

1,2,4-tri-IC, having three indeno-groups, has the largest surface area and the most effective packing with all bowls oriented in the same direction in all stacks as shown in Fig. 3f. As one would expect, 1,2,4-tri-IC indeed exhibits the best performance among the corannulene derivatives investigated here and its electrical conductivity reaches $1.4 \times 10^{4} \Omega \text{ m fs}^{-1}$ and $1.1 \times 10^{4} \Omega \text{ m fs}^{-1}$ for hole and electron doping, respectively, at a carrier concentration of $10^{21} \text{ cm}^{-3}$. The larger conductivity values obtained under hole doping are consistent with both a larger DOS and a more disperse band at the top of the highest valence band compared to the bottom of the lowest conduction band. These results suggest that 1,2,4-tri-IC crystals are expected to show a high anisotropic mobility comparable to (or even exceeding) that of sumanene.

Para-di-IC has the most loosely packed crystal structure of the four indenocorannulene family members and the π-bowls in the columns are significantly shifted with respect to one another. However, when viewed down the crystallographic $c$-axis, all bowls point in the same direction similarly to 1,2,4-tri-IC and a substantial overlap can still take place between the carbon π-surfaces of the molecules in the 1D stack (Fig. 3e). This latter aspect has an important impact on the electrical conductivity which turns out to be about one-half and one-third of that of 1,2,4-tri-IC for the hole- and electron-doped systems, respectively. The difference in conductivity between hole and electron doping can be traced back to the almost twice larger bandwidth along the π-stacking direction of the bowls at the top of the valence band compared to the bottom of the conduction band.

The crystal structure of mono-IC also displays a preferential stacking of the π-conjugated bowl cores along one crystallographic axis ($a$-axis) as shown in Fig. 3c. However, unlike the solid state

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Unit cell parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sumanene [48]</td>
<td>R3c</td>
<td>a (Å)</td>
</tr>
<tr>
<td>Corannulene [46]</td>
<td>P2$_1$/c</td>
<td>16.642</td>
</tr>
<tr>
<td>Mono-IC [41]</td>
<td>P2$_1$/n</td>
<td>13.156</td>
</tr>
<tr>
<td>Ortho-di-IC [41]</td>
<td>Pnma</td>
<td>3.871</td>
</tr>
<tr>
<td>Para-di-IC [41]</td>
<td>Cmc2$_1$</td>
<td>22.801</td>
</tr>
<tr>
<td>1,2,4-tri-IC [41]</td>
<td>Pmn2$_1$</td>
<td>17.238</td>
</tr>
</tbody>
</table>

Fig. 4. Electronic band structure and density of states for (a) sumanene, (b) corannulene, (c) mono-IC, (d) ortho-di-IC, (e) para-di-IC, and (f) 1,2,4-tri-IC. The zero of the energy in the figures is chosen as the middle of the calculated band gap that separates the bonding valence bands from the antibonding conduction bands. The density of states is in units of states/(eV atom). The labels and coordinates of the high-symmetry $k$-path points in the Brillouin zone were obtained from Ref. [59].
structures of 1,2,4-tri-IC and para-di-IC, the molecules are arranged such that each column has one neighbor with the same and one neighbor with the opposite direction of the bowls. In terms of charge transport properties, the electrical conductivity of mono-IC is predicted to be about one-quarter and three-quarters of that of 1,2,4-tri-IC for the hole- and electron-doped systems, roughly the opposite to what is found for para-di-IC.

Finally, the picture considerably changes when ortho-di-IC crystals are considered. Addition of two indeno-groups in the ortho-positions on the corannulene rim induces a clear alignment of the bowls along the c-axis (Fig. 3d), similar to mono-IC and 1,2,4-tri-IC. However, the solid-state packing of columns in the two directions perpendicular to stacking is completely unique to 1,2,4-tri-IC. For corannulene (dash, red), the electrical conductivity is averaged over the three crystallographic directions. The inset shows the electrical conductivity for ortho-di-IC along the stacking direction (dash dot, olive) and perpendicular to stacking along the length of the molecules (short dash dot, olive). (A color version of this figure can be viewed online.)

Based on the electrical conductivity results, it can be concluded that all four indenocorannulene derivatives show significantly improved transport properties compared to the parent corannulene. In particular, the molecular building motif of 1,2,4-tri-IC exhibits the largest \( \pi \)-conjugated surface and enough spatial overlap to result in a significant intermolecular coupling, and, thus, enhanced charge-carrier transport, along the \( \pi \)-stacking direction. In addition, 1,2,4-tri-IC could be considered a promising candidate for organic electronic devices since its performance should be comparable for electron doping and likely surpass for hole doping that of sumanene crystals, assuming the same carrier lifetimes and for carrier concentrations in the limits of \( 10^{18} – 10^{21} \text{ cm}^{-3} \).

We next evaluate the dependence of the Seebeck coefficient \( S \) as a function of the carrier concentration for hole and electron doping.
in all six systems at room temperature. Unlike the electrical conductivity which is strongly dependent on the transport direction, the Seebeck coefficient is almost isotropic. For hole doping, the calculated $S$ decreases logarithmically with increasing carrier concentration as the position of the chemical potential moves down into the valence band. From Fig. 7, we can see that the hole Seebeck coefficient of corannulene is the largest in magnitude, while that of para-d-IC is the smallest. This can be understood from the difference in the density of states between the two structures since the system with the most rapidly changing DOS (sharper distribution) is expected to have the largest Seebeck coefficient [60]. Indeed, in comparison to para-d-IC, corannulene exhibits a much sharper peak in the DOS near the top of the valence band. This is in accord with our earlier observation that in corannulene the energy bands are almost flat over the entire Brillouin zone closely resembling molecular-like states. The Seebeck coefficients for the other four systems fall in between those of corannulene and para-d-IC and the curves lie almost on top of each other. This reflects the close similarity in their DOS dependence near the VBM. Overall, the estimated values for $S$ are found to be in the same range with measured hole Seebeck coefficients in planar hydrocarbons near room temperature, namely, thin films of pentacene and single crystals of rubrene [61].

The situation is almost identical for the electron doped systems as shown in Fig. 8. The Seebeck coefficients follow a similar trend as for hole doping and the absolute value of $S$ increases logarithmically with decreasing carrier concentration. As before, there are no significant differences in $S$ among the six systems and, overall, the values for $S$ are only slightly smaller than those of the hole doped counterparts. The relatively large Seebeck coefficient and the presence of both flat and dispersed bands around the Fermi level indicate that some of these organic semiconductors could potentially serve as active materials in thermoelectric devices.

4. Conclusions

In this work, we explore the relationship between the solid-state packing and the charge-carrier transport properties in the extended family of indencorannulene molecular crystals. Using first-principles calculations coupled with the Boltzmann transport theory, we find that all four corannulene derivatives investigated here show significantly improved electrical conductivity compared to the parent corannulene. In particular, 1,2,4-tri-IC is identified as a promising active material for organic electronic devices exhibiting a pronounced anisotropy in the electrical conductivity along the stacking direction of the $\pi$-bowls similar to the well-known sumanene. The charge conductivity of 1,2,4-tri-IC is predicted to be comparable for electron doping and likely surpass for hole doping the values achievable in sumanene, assuming the same carrier lifetimes. Further modification of the corannulene derivatives through incorporation of functional groups as well as side chain engineering can lead to larger $\pi-\pi$ overlap and extended $\pi$-network which should be beneficial to the charge transport. Finally, the new class of carbon-rich bowl-shaped polyaromatic hydrocarbons should offer unique and yet unexplored opportunities in identifying organic superconductors with a high transition temperature since their structures constitute a direct link between zero-dimensional fullerenes and two-dimensional planar hydrocarbons, and that can bring novel synergistic qualities.

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References

[10] A.V. Zubula, S.N. Spisak, A.S. Filatov, M.A. Petrikhina, Pentadecacarbon, a molecular-like states. The Seebeck coefficients for the first-principles calculations coupled with the Boltzmann transport theory, we find that all four corannulene derivatives investigated here show significantly improved electrical conductivity compared to the parent corannulene. In particular, 1,2,4-tri-IC is identified as a promising active material for organic electronic devices exhibiting a pronounced anisotropy in the electrical conductivity along the stacking direction of the $\pi$-bowls similar to the well-known sumanene. The charge conductivity of 1,2,4-tri-IC is predicted to be comparable for electron doping and likely surpass for hole doping the values achievable in sumanene, assuming the same carrier lifetimes. Further modification of the corannulene derivatives through incorporation of functional groups as well as side chain engineering can lead to larger $\pi-\pi$ overlap and extended $\pi$-network which should be beneficial to the charge transport. Finally, the new class of carbon-rich bowl-shaped polyaromatic hydrocarbons should offer unique and yet unexplored opportunities in identifying organic superconductors with a high transition temperature since their structures constitute a direct link between zero-dimensional fullerenes and two-dimensional planar hydrocarbons, and that can bring novel synergistic qualities.

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