

# Charge-transport properties of prototype molecular materials for organic electronics based on graphene nanoribbons†

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The semiconducting properties of molecular material prototypes for graphene nanoribbons are rationalized by quantum-chemical calculations. The present contribution focuses on the hole transport properties of circum(oligo)acenes and compares the intrinsic efficiency of these materials for charge transport in the hopping regime with respect to the (oligo)acenes parent compounds. The results at the molecular scale predict significantly higher mobilities in circum(oligo)acenes mainly due to lower electron–phonon coupling. The importance of non-covalent intermolecular interactions is also highlighted; the description of the dimeric nanostructures expected in thin films devices needs the inclusion of dispersion forces.

## 1. Introduction

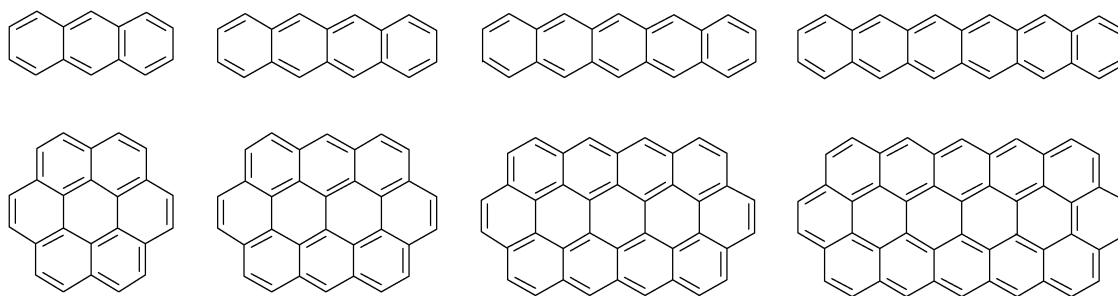
Graphene, defined as an extended planar sheet of bonded carbon atoms in a honeycomb crystal lattice, is considered today the basic structural element of all other graphitic materials including graphite, carbon nanotubes, and fullerenes, as well as the 2D infinite limit of finite size polycyclic aromatic hydrocarbons (PAHs).<sup>1</sup> Graphene was first isolated in 2004 from mechanical exfoliation of graphite crystals<sup>2–4</sup> but now soluble and finite fragments of graphene have been recently prepared through chemical modification of graphite.<sup>5</sup> A large array of technologically relevant yet potential applications are envisioned, which includes gas electrode sensors,<sup>6</sup> ultracapacitors for storage energy purposes,<sup>7</sup> and field-effect components of integrated circuits as memories<sup>8</sup> or transistors,<sup>9</sup> among others.<sup>10</sup> Of particular importance are finite graphene-based nanostructures called graphene nanoribbons (GNRs), which can be viewed as quasi-1D stripes of graphene thoroughly investigated in recent years to elucidate their semiconducting and magnetic properties.<sup>11–13</sup> We remark that computational studies might largely pave the way towards new GNRs-based applications, as it is indeed the case, due to the scarcity of experimental information about GNRs at this stage. A common key parameter for organic-based applications in devices is the charge carrier mobility.<sup>14</sup> In this sense, graphene has also a remarkably high hole and electron (ambipolar) mobility at room temperature, with reported values exceeding by few orders of magnitude the previous values found for the state-of-the-art PAHs materials as (oligo)acenes and their derivatives.<sup>15</sup> GNRs are expected to reach the graphene limit of zero band gap (extremely large mobilities) for sufficiently large widths. Despite the increasing and realistic optimism about graphene-based electronics, some fundamental aspects have not been fully covered yet, which prompted us to study

the conducting properties of nanometre-sized graphene-based materials in the hopping regime; *i.e.* when electron–phonon interactions are comparable to electronic interactions, as commonly found in organic molecular crystals at room temperature. Particularly, the impact of using GNRs in thin-film nanoelectronics or organic field-effect transistors,<sup>16,17</sup> besides improvements in device fabrication processes, is believed to depend not only on the intrinsic charge carrier mobilities of the organic materials but also on the relative positions of the interacting molecules, which is intimately related to the supramolecular ordering of the samples.

We would like thus to address these issues and explore a new direction for GNRs by comparing 1D oligomers of increasing size, (oligo)acenes, with narrow GNRs of moderate size, circum(oligo)acenes: see Fig. 1. The latter systems, also called circumarenes, contain a circularly fused benzannulated ring and, at the infinite limit, they should converge to a zigzag-edged GNR. Although common names exist for some of the molecules studied here (the two smallest oligomers of circum(oligo)acenes are sometimes called coronene and ovalene, respectively) we prefer to keep the generic form throughout this article. We have chosen to deal with this set of engineered PAHs for the main following reasons: (i) they pose both a rigid backbone and an energy gap of moderate size rapidly converging with the size of the molecule,<sup>18</sup> which is expected to provide intrinsically large carrier mobilities; (ii) their molecular packing in thin films might drastically differ from the classical herringbone structure found for the corresponding (oligo)acenes, which is already reflected in a smaller value for the shortest cell axis,<sup>19</sup> and thus might provide more efficient pathways for charge transport; and (iii) concomitantly with these relevant features, we note that, to the best of our knowledge, the synthesis of circumanthracene<sup>21</sup> as well as other versatile related molecules<sup>20</sup> has been successfully reported in the literature. Hence, we would like to study these low-dimensional carbon structures, which are placed at an intermediate point between two extremes, (oligo)acenes and GNRs, as promising candidates for new emerging technologies.

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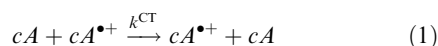
† Electronic supplementary information (ESI) available: Absolute energies and XYZ coordinates of the stationary states found. See DOI: 10.1039/b821748c



**Fig. 1** Chemical structures of (oligo)acenes (top), anthracene, tetracene, pentacene, and hexacene (from left to right) and corresponding circum(oligo)acenes (bottom), circumbenzene (cB), circumnaphthalene (cN), circumanthracene (cA), and circumtetracene (cT). The hydrogen atoms and corresponding C–H bonds have been omitted for clarity.

## 2. Modelling charge transport in conjugated materials

The interplay between electronic and vibronic interactions promotes charge-transfer (CT) at room temperature in organic molecular semiconductors. The widely applied idealized mechanism known as Marcus theory,<sup>22,23</sup> describes CT as a self-exchange hole-transfer chemical reaction between the circum(oligo)acenes (cA) molecules:



where the non-adiabatic transfer rate,  $k^{CT}$ , is used to semi-quantitatively rationalize these properties. According to the weak-coupling regime, the rate critically depends on two parameters that can be extracted from quantum-mechanical calculations:<sup>24–26</sup> the intramolecular coupling, or reorganization energy ( $\lambda$ ), and the electronic coupling between adjacent molecules, or transfer integral ( $t$ ). The form of the rate is thus approximated as:

$$k^{CT} = \frac{\sqrt{\pi}}{\hbar} t^2 \frac{1}{\sqrt{\lambda k_B \Theta}} e^{-\lambda/4k_B \Theta}, \quad (2)$$

where  $\Theta$  denotes temperature and  $\hbar$  and  $k_B$  are fundamental constants. Eqn (2) correctly predicts high transfer rates whenever large values of the transfer integral  $t$  are accompanied by low values of the reorganization energy  $\lambda$ . The detailed edge structures of the molecules is not expected to play a significant role. Admittedly, we are facing (*vide infra*) the limit of validity of the hopping model.<sup>27</sup> This transport regime assumes that the charge is completely localized on an individual molecule the time needed to allow the reorganization of the nuclei in order to accommodate the new state. Then, in a second step, which is normally driven by an externally applied electric field, the charge carriers jump along sufficiently ordered crystal structures from one molecule to the closest one. However, owing to the transfer integrals found for the stacking motifs, partial delocalization of the charge on neighboring molecules could be also expected, which would need more sophisticated theories.<sup>28,29</sup> Note also that we are mainly interested in this work in the relative transport capabilities of circum(oligo)acenes compared to (oligo)acenes.

The strategy to compute the internal reorganization energy uses the so-called four-point method<sup>30,31</sup> which involves: (i) the separate optimization of the geometry of the isolated neutral ( $E_{cA}$ ) and charged molecules ( $E_{cA^+}$ ); and (ii) the single-point calculations of the neutral molecule at the cation geometry ( $E_{cA//cA^+}$ ) and of the charged molecule at the neutral geometry ( $E_{cA^+//cA}$ ). From these values, the reorganization energy is directly calculated as:

$$\lambda = (E_{cA^+//cA} - E_{cA^+}) + (E_{cA//cA^+} - E_{cA}). \quad (3)$$

Note that the contribution to  $\lambda$  from the reorganization of the surrounding medium after arrival of the charge (the so-called external contribution to the reorganization energy<sup>32</sup>) has recently been calculated, and found to be of little significance for closely related molecules<sup>33</sup> and will thus be thereby neglected.

Furthermore, the mobilities not only depend on the intrinsic electronic properties of the materials but also on the dimeric interactions between neighboring molecules.<sup>34</sup> We remark that in these devices the bulk transport is largely assisted by the solid-state packing of the molecules as well as by a proper arrangement of the molecules on the electrode surface to facilitate charge injection. The transfer integral accounts for the former intermolecular interactions, which are of a very local nature.<sup>35,36</sup> We choose a cofacially stacked dimeric nanostructure to approximate the expected thin-films packing: the pair of molecules are thus separated by 3.5 Å. Note that the experimental interplanar distance of graphite is known to be 3.35 Å. Moreover, recent and highly accurate computational studies of the structure and intermolecular interactions of coronene ( $\equiv$  circumbenzene) dimers led to an optimized distance ranging from 3.3–3.6 Å.<sup>37,38</sup> Note also that many aromatic molecules form stacks with distances between parallel molecular planes with a rather limited range of values and that for circumacenes a close-to-cofacial packing is expected even for large aggregates,<sup>39</sup> which indicates substantial electronic coupling between the  $\pi$ -stacked fragments. The transfer integral is thus calculated here by the method known as “energy splitting in dimer”<sup>40</sup> to obtain a simple yet reliable<sup>41,42</sup> estimate of the electronic coupling for cofacial dimers:

$$t = \frac{\varepsilon_{\text{HOMO}} - \varepsilon_{(\text{H}-1)\text{OMO}}}{2}, \quad (4)$$

where  $\varepsilon_{\text{HOMO}}$  and  $\varepsilon_{(\text{H}-1)\text{HOMO}}$  are the highest occupied molecular orbital (HOMO) and the (H-1)OMO orbital energies of the dimer. The influence of thermal disorder will not be considered.<sup>43</sup>

### 3. Technical details

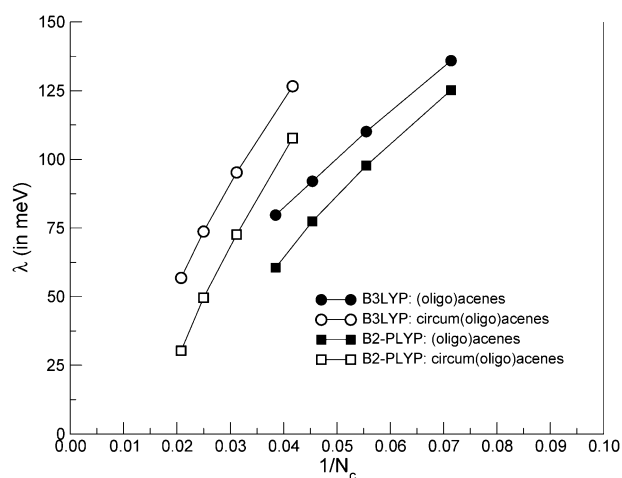
The way to estimate both orbital ( $\varepsilon$ ) and total ( $E_{\text{cA}}$ -based) energies is by applying density functional theory (DFT) at its highest level of accuracy; *i.e.* with global hybrids (B3LYP<sup>44,45</sup>) and double-hybrids (B2-PLYP<sup>46,47</sup>) exchange–correlation functionals. Note that wavefunction-based methods including high-order correlation effects, CCSD(T), are too costly for systems as large as the dimers treated here. However, the combination of density functionals with exact expressions taken from *ab initio* theories reduces the computational cost to a formal scaling of  $O(N^4)$  (B3LYP) and  $O(N^5)$  (B2-PLYP), where  $N$  is the number of basis functions. Next, the cc-pCVDZ basis sets was selected for two main reasons: (i) it is expected to provide nearly converged results at the B3LYP level, what might be interesting to check the performance of less costly basis sets such as 6-31G\*; and (ii) the basis set dependence of the B2-PLYP might presumably be larger and thus core–core and core–valence correlation effects also need to be included. Accordingly with this choice of this basis set, the core electrons were thus also correlated in all calculations. Note that these are very time-consuming calculations; for example, for the circumtetracene dimer, this basis set involves 1908 contracted and 3900 primitive Gaussian functions. Very dense and not-pruned grids were used for accurate numerical quadrature. The resolution-of-the-identity (RI) approximation<sup>48</sup> was used when possible. All the calculations were done with the ORCA package<sup>49</sup> using analytical gradients<sup>50</sup> to fully optimize the geometries of the isolated systems, from which the corresponding dimers are built.

### 4. Behavior of circum(oligo)acenes as potential candidates for organic electronics

Table 1 gathers the results for both key parameters, intramolecular and electronic coupling, see eqn (3) and eqn (4), respectively, at all levels of theory employed (B3LYP and

**Table 1** Computational estimates of reorganization energies ( $\lambda$ , in meV), transfer integrals ( $t$ , in meV), and charge-transfer rates ( $k^{\text{CT}}$ , in  $\text{s}^{-1}$ ) in circum(oligo)acenes as calculated by B3LYP and B2-PLYP methods with the cc-pCVDZ basis set

| Method  |                   | $\lambda$ | $t$ | $10^{-15} k^{\text{CT}}$ |
|---------|-------------------|-----------|-----|--------------------------|
| B3LYP   | circumbenzene     | 127       | 346 | 1.65                     |
|         | circumnaphthalene | 95        | 313 | 2.11                     |
|         | circumanthracene  | 74        | 340 | 3.50                     |
|         | circumtetracene   | 57        | 340 | 4.70                     |
| B2-PLYP | circumbenzene     | 108       | 399 | 2.85                     |
|         | circumnaphthalene | 73        | 363 | 4.05                     |
|         | circumanthracene  | 50        | 394 | 7.22                     |
|         | circumtetracene   | 30        | 395 | 11.2                     |



**Fig. 2** Evolution of the reorganization energy on the inverse of the number of carbon atoms ( $N_{\text{C}}$ ) in (oligo)acenes and corresponding circum(oligo)acenes.

B2-PLYP). The reorganization energies obtained with the B2-PLYP double-hybrid functional are systematically lower than the B3LYP values, whereas the transfer integral follows the opposite trend, which is tightly related to the higher weight of the exact exchange term (53%) of the former functional with respect to B3LYP (20%).<sup>51</sup> We note in passing that the results with the smaller 6-31G\* are very close to the cc-pCVDZ values (within 1%) at the B3LYP level.<sup>52</sup> Fig. 2 shows how the reorganization energies evolve as a function of the total number of carbon atoms, which is known to follow an inversely proportional relation due to strong electron–phonon coupling.<sup>53,54</sup> A much more pronounced slope is observed for circum(oligo)acenes compared to (oligo)acenes.

We note that our results for (oligo)acenes, which are included mainly as a source of comparison, closely compares with previous results also at the DFT level.<sup>55,56</sup> Remarkably, the reorganization energies for the largest circum(oligo)acenes considered here, circumanthracene and circumtetracene, are one of the lowest reported to date. The corresponding charge-transfer rates are obtained by feeding the results of the calculations into the expression given by eqn (2) and are also shown in Table 1. The order of magnitude of the hole-transfer rates of circum(oligo)acenes lies in the  $10^{15}$ – $10^{16} \text{ s}^{-1}$  range. It should be mentioned that we neglect at this stage the packing disorder and the reaccommodation of the surrounding solid-state medium during the charge hopping, which might decrease these rates up to one order of magnitude.<sup>57</sup> Nonetheless, these charge transfer parameters are comparable to theoretical estimates for the best suited materials currently in use, such as rubrene,<sup>58,59</sup> titanil phthalocyanines<sup>60,61</sup> or tetrathiofulvalene derivatives,<sup>62,63</sup> obtained at a similar level of theory. Altogether, the lower reorganization energies concomitantly with comparable transfer integrals for idealized packing motifs, allow us to anticipate higher mobilities for circum(oligo)acenes compared to (oligo)acenes of related length.

Actually, the ratio of the corresponding room-temperature charge mobilities for the two materials, circum(oligo)acenes (cA) and (oligo)acenes (A), with the same intermolecular

distance used to build the dimer, are obtained according to Marcus theory from the following expression:<sup>64</sup>

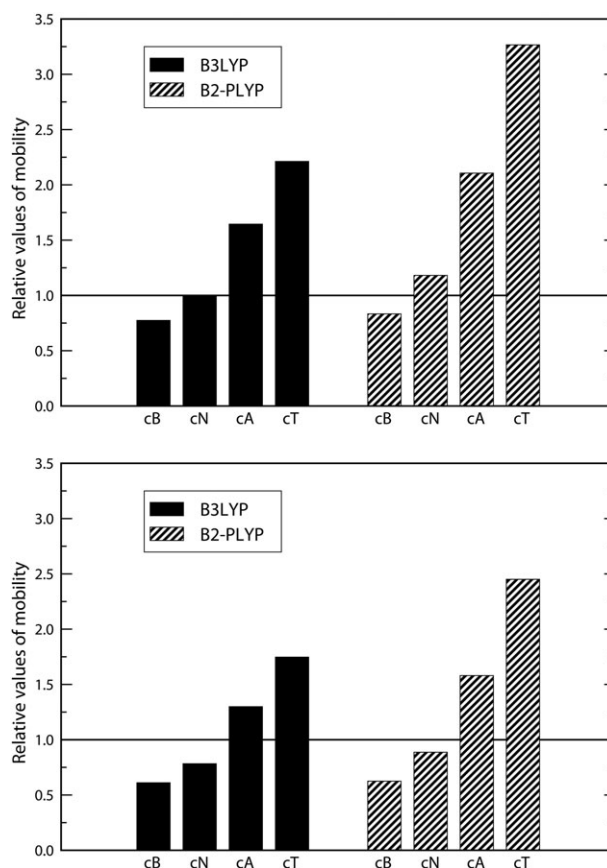
$$\frac{\mu_{cA}}{\mu_A} = \frac{k_{cA}^{CT}}{k_A^{CT}} = \frac{t_{cA}^2}{t_A^2} \sqrt{\frac{\lambda_A}{\lambda_{cA}}} e^{(\lambda_A - \lambda_{cA})/4k_B\Theta}, \quad (5)$$

which provides the tool needed for carrying out the direct comparison between the theoretical transfer rates and the expected mobilities. We feed the results of our calculations into the above expression to estimate first the corresponding ratios,

$$\frac{\mu_{\text{circumbenzene}}}{\mu_{\text{anthracene}}}, \frac{\mu_{\text{circumnaphthalene}}}{\mu_{\text{tetracene}}}, \frac{\mu_{\text{circumanthracene}}}{\mu_{\text{pentacene}}}, \text{ and } \frac{\mu_{\text{circumtetracene}}}{\mu_{\text{hexacene}}}, \quad (6)$$

which gives 1.1, 1.0, 1.3, and 1.5 (1.2, 1.2, 1.6, and 1.9) at the corresponding B3LYP (B2-PLYP) level. Note that in almost all cases the expected mobilities for circum(oligo)acenes are larger than those of (oligo)acenes. On the other hand, in order to qualitatively validate our approach, we remark the agreement between the predicted pentacene to tetracene mobility ratio (1.3 at both levels of theory) and the values found in experimental devices;<sup>15,65,66</sup> though it is well known how charge carrier mobilities are influenced by many factors including molecular packing and degree of order, impurities and crystal defects, and device configuration to name a few.<sup>14</sup> As a result, the measured mobilities can significantly vary as a function of these sample aspects.

It is worthwhile comparing now the mobility ratios of circum(oligo)acenes with respect to tetracene and pentacene; the latter oligomers are of the highest interest due to their high hole transfer mobilities in the crystalline state. We remind that our main goal here is to establish a connection between the molecular parameters (*i.e.*,  $\lambda$  and  $t$ ) described earlier and calculated for both circum(oligo)acenes and (oligo)acenes, and the related mobility ratios. Fig. 3 shows the corresponding  $\frac{\mu_{\text{circum(oligo)acenes}}}{\mu_{\text{tetracene}}}$  and  $\frac{\mu_{\text{circum(oligo)acenes}}}{\mu_{\text{pentacene}}}$  ratio, from which it is easy to infer a critical size for having higher mobilities than tetracene or pentacene if all the external conditions, including the sample quality, remain approximately the same. In this regard, the mobilities reported for pentacene thin films and crystals are usually in the range  $1\text{--}5\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  for an herringbone solid-state packing. However, the intrinsic mobility for the idealized dimeric structures of pentacene considered here is about an order of magnitude higher,  $128\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  for instance at the B3LYP level, which indicates that further effort could likely improve the hole mobilities of (oligo)acenes. Taking into account this extreme behavior, and considering that circum(oligo)acenes might stack differently, with or without further functionalization, we predict intrinsically reliable mobilities for circumanthracene and circumtetracene higher than  $200\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  with a possible upper limit of  $500\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ . We also note at both B3LYP and B2-PLYP levels, consistently with previous studies,<sup>18,67,68</sup> a relatively smooth decrease of the energy difference between the frontier orbitals, the HOMO–LUMO gap, which renders circum(oligo)acenes of large size, at least as large as the corresponding (oligo)acenes synthesized up to date, as



**Fig. 3** Relative values of mobility estimated for circum(oligo)acenes with respect to tetracene (top) and pentacene (bottom). The solid line is a guide to the eye.

potential synthetic targets useful in molecular electronics application.

## 5. Circum(oligo)acenes as prototypes for studying layered materials

As a further part of this study, we have tackled next the problem of how the different methods employed so far are able to accurately describe the interlayer interactions, aimed at approximating those found in graphite or stacked GNRs,<sup>37,69,70</sup> which are definitively expected to play a major role in the field of carbon nanostructures. The interaction (or association) energy of the circum(oligo)acenes dimers is defined as follows:

$$\Delta E = E_{\text{dimer}} - 2E_{\text{monomer}},$$

being  $E_{\text{dimer}}$  the total energy of the dimer at the fixed distance  $R = 3.5\text{ Å}$  between the center of mass of the monomers and  $E_{\text{monomer}}$  the energy of the single molecule. According to this definition, a bound dimer will have a negative interaction energy. We have studied the stability of the cofacial dimers of circumbenzene, circumnaphthalene and circumanthracene as models for larger GNRs-based systems; however, the conclusions are not expected to significantly vary as a function of the oligomer size. It is found in Table 2 that semi-local hybrid functionals (as B3LYP is) do not account for dispersion interactions<sup>71</sup> and thus wrongly predict that two monomers



**Table 2** Interaction energies of circum(oligo)acenes dimers (in kcal mol<sup>-1</sup>) as calculated by B3LYP and B2-PLYP methods with the cc-pCVDZ basis set

| Method    | Circum-benzene | Circum-naphthalene | Circum-anthracene |
|-----------|----------------|--------------------|-------------------|
| B3LYP     | 16.1           | 20.7               | 25.4              |
| B2-PLYP   | -0.3           | -2.5               | -5.0              |
| B3LYP-D   | -15.9          | -23.4              | -31.0             |
| B2-PLYP-D | -17.0          | -25.6              | -34.7             |

are more stable than the perfect cofacial dimer, which is in agreement with previous studies on the coronene dimer.<sup>72</sup> Note that in the absence of experimental information about the way in which the molecules crystallize or self-assemble, and in order to study and design new  $\pi$ -conjugated charge-carrier materials, it is important to apply a robust theoretical method able to reliably predict the stability of selected nanostructures.<sup>73</sup> On the other hand, the more sophisticated B2-PLYP double-hybrid, which includes in its formulation a portion of correlation energy calculated by perturbation theory and thus reasonably accounts for a part of the dispersion energy,<sup>74,75</sup> is in principle able to assign a lower energy to the dimeric structure in all cases,  $|E_{\text{dimer}}| > 2|E_{\text{monomer}}|$ , although the value seems to be too low. A further degree of accuracy is accomplished by adding a van der Waals-type term, which scales as  $R^{-6}$  into the total energy of the system.<sup>76–78</sup> We thus adopt this approach here, which is termed in general DFT-D, and apply to the calculation of the interaction energy. Table 2 shows how the results are drastically altered for both methods predicting a considerable and effective attraction between circum(oligo)acenes or, at the infinite limit, between sheets of GNRs. Other empirical approaches used to correct the erroneous behavior of DFT functionals, as atom-centered effective potentials,<sup>39,79</sup> led to values for coronene in agreement with those reported here whereas previous values for circumnaphthalene and circumanthracene were not found in the literature.

Unfortunately, first-principles *ab initio* calculations are neither available nor feasible due to the large size of these systems for accurate treatments at the CCSD(T) or similar levels, and thus the B2-PLYP-D results can serve as benchmark purposes as recently being recognized due to its remarkable agreement with more costly methods.<sup>80,81</sup> Particularly striking are the large errors dropped by the commonly used B3LYP functional, between 1.4–1.5 kcal mol<sup>-1</sup> per atom, compared with the B2-PLYP-D values. We also note that these errors tend to accumulate, that is, they slightly increase with the size of the system, which might disqualify further applications of the B3LYP functional, without the -D correction, for carbon nanostructures and related systems. This behavior is rationalized by the fact that at the distance between the monomers, 3.5 Å, the interplay between inter-pair medium-range and long-range correlation effects, and the way in which each functional is able to accurately describe both effects, is expected to dominate the final accuracy of the calculations.<sup>82,83</sup>

## 6. Conclusions

Circum(oligo)acenes are considered as finite-sized prototype molecular systems for GNRs; consequently, they have been

systematically studied here as potential candidates to be used in efficient devices for organic electronics. We have thus described at the quantum-chemical level the key molecular parameters: reorganization energies and electronic couplings, entering into their associated intermolecular charge-transfer hole rates in the hopping regime. We have next estimated the mobilities for a cofacially ordered  $\pi$ -stacking of these molecules, considered as an idealized packing motif, and found that they are always higher than those of the corresponding (oligo)acenes of equivalent size due to a decrease of the electron-phonon coupling while maintaining substantial electronic coupling. This feature prompted us to study the mobilities of these systems with respect to tetracene and pentacene, which are two of the molecules widely used today as active materials for organic electronics. Interestingly, the results showed that the mobilities of circumanthracene and circumtetracene are intrinsically higher which, together with the fact that these molecules could present an ultra closely  $\pi$ -stacking structure, allows us to consider these molecular materials as very promising candidates for more efficient technologies at the nanoscale. We remark that these conclusions hold independently of the computational method employed, *i.e.* the hybrid B3LYP or the double-hybrid B2-PLYP density functional. However, if intermolecular interactions should be taken into account, as happens for instance when studying the stability of the dimeric structures representing the expected solid-state packing, the choice of the method is not a trivial issue. The non-covalent interactions are expected to dominate the relative orientations of the molecules and thus need to be accurately introduced, which is done here by a term accounting for the long-range decay of these forces concomitantly with an accurate exchange–correlation kernel for the medium-range regime.

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## References

- 1 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183.
- 2 K. S. Novoselov, A. K. Geim, S. V. Morozov and D. Jiang, *Science*, 2004, **306**, 666.
- 3 K. S. Novoselov, A. K. Geim, S. V. Morozov and D. Jiang, *Nature*, 2005, **438**, 197.
- 4 K. S. Novoselov, D. Jiang, T. J. Booth, V. V. Khotkevich, S. V. Morozov and A. K. Geim, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 10451.
- 5 S. Niyogi, E. Bekyarova, M. E. Itkis, J. L. McWilliams, M. A. Hamon and R. C. Haddon, *J. Am. Chem. Soc.*, 2006, **128**, 7720.
- 6 F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 652.
- 7 M. D. Stoller, S. Park, Y. Zhu, J. An and R. S. Ruoff, *Nano Lett.*, 2008, **8**, 3498.

- 8 T. J. Echtermeyer, M. C. Lemme, M. Baus, B. N. Szafrank, A. K. Geim and H. Kurz, *IEEE Electron Device Lett.*, 2008, **29**, 952.
- 9 X. Wang, Y. Ouyang, X. Li, H. Wang, J. Guo and H. Dai, *Phys. Rev. Lett.*, 2008, **100**, 206803.
- 10 L. A. Ponomarenko, F. Schedin, M. I. Katsnelson, R. Yang, E. W. Hill, K. S. Novoselov and A. K. Geim, *Science*, 2008, **320**, 356.
- 11 V. Barone, O. Hod and G. E. Scuseria, *Nano Lett.*, 2006, **6**, 2748.
- 12 M. Y. Han, B. Özyilmaz, Y. Zhang and P. Kim, *Phys. Rev. Lett.*, 2007, **98**, 206805.
- 13 J. Fernández-Rossier and J. J. Palacios, *Phys. Rev. Lett.*, 2007, **99**, 177204.
- 14 V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J. L. Brédas, *Chem. Rev.*, 2007, **107**, 926.
- 15 J. E. Anthony, *Angew. Chem., Int. Ed.*, 2008, **47**, 452.
- 16 G. Horowitz, in *Organic Electronics Materials Manufacturing and Applications*, ed. H. Klauk, Wiley-VCH, Weinheim, 2006.
- 17 T. Mori, *J. Phys.: Condens. Matter*, 2008, **20**, 184010.
- 18 D.-e. Jiang and S. Dai, *Chem. Phys. Lett.*, 2008, **466**, 72.
- 19 A. Gavezotti and G. R. Desiraju, *Acta Crystallogr.*, 1988, **B44**, 427.
- 20 J. Wu, W. Pisula and K. Müllen, *Chem. Rev.*, 2007, **107**, 718.
- 21 R. D. Broene and F. Diederich, *Tetrah. Letters*, 1991, **32**, 5227.
- 22 R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265.
- 23 R. A. Marcus, *Rev. Mod. Phys.*, 1993, **65**, 599.
- 24 J. Cornil, D. Beljonne, J. P. Calbert and J. L. Brédas, *Adv. Mater.*, 2001, **13**, 1053.
- 25 J. L. Brédas, D. Beljonne, V. Coropceanu and J. Cornil, *Chem. Rev.*, 2004, **104**, 4971.
- 26 F. C. Grozema and L. D. A. Siebbeles, *Int. Rev. Phys. Chem.*, 2008, **27**, 87.
- 27 D. Cheung and A. Troisi, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5941.
- 28 A. Troisi, *Adv. Mater.*, 2007, **19**, 2000.
- 29 J.-D. Picon, M. N. Bussac and L. Zuppiroli, *Phys. Rev. B*, 2007, **75**, 235106.
- 30 Y. Berlin, G. R. Hutchinson, P. Rempala, M. A. Ratner and J. Michl, *J. Phys. Chem. A*, 2003, **107**, 3970.
- 31 K. M. Rosso and M. Dupuis, *Theor. Chem. Accounts*, 2006, **116**, 124.
- 32 E. Vladimirov, A. Ivanova and N. Rösch, *J. Chem. Phys.*, 2008, **129**, 194515.
- 33 J. E. Norton and J. L. Brédas, *J. Am. Chem. Soc.*, 2008, **130**, 12377.
- 34 W.-Q. Deng and W. A. Goddard III, *J. Phys. Chem. B*, 2004, **108**, 8614.
- 35 J. L. Brédas, J. P. Calbert, D. A. da Silva Filho and J. Cornil, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 5804.
- 36 J. Cornil, V. Lemaure, J.-P. Calbert and J. L. Brédas, *Adv. Mater.*, 2002, **14**, 726.
- 37 S. Grimme, C. Mück-Lichtenfeld and J. Antony, *J. Phys. Chem. C*, 2007, **111**, 11199.
- 38 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. C*, 2008, **112**, 4061.
- 39 M. Rapacioli, F. Calvo, F. Spiegelman, C. Joblin and D. J. Wales, *J. Phys. Chem. A*, 2005, **109**, 2487.
- 40 M. D. Newton, *Chem. Rev.*, 1991, **91**, 767.
- 41 E. F. Valeev, V. Coropceanu, D. A. da Silva Filho, S. Salman and J. L. Brédas, *J. Am. Chem. Soc.*, 2006, **128**, 9882.
- 42 F. Castet, P. Aurel, A. Fritsch, L. Ducasse, D. Liotard, M. Linares, J. Cornil and D. Beljonne, *Phys. Rev. B*, 2008, **77**, 115210.
- 43 A. Troisi and G. Orlandi, *J. Phys. Chem. A*, 2006, **110**, 4065.
- 44 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- 45 P. J. Stephens, F. J. Devlin, C. F. Chabrowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
- 46 S. Grimme, *J. Chem. Phys.*, 2006, **124**, 034108.
- 47 T. Schwabe and S. Grimme, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4398.
- 48 K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283.
- 49 F. Neese, *ORCA—an ab initio density functional and semiempirical program package, Version 2.5.20*, University of Bonn, Germany, 2006.
- 50 F. Neese, T. Schwabe and S. Grimme, *J. Chem. Phys.*, 2007, **126**, 124115.
- 51 J. C. Sancho-García and A. J. Pérez-Jiménez, *J. Phys. Chem. A*, 2008, **112**, 10325.
- 52 J. C. Sancho-García, *Chem. Phys.*, 2007, **331**, 321.
- 53 A. Devos and M. Lannoo, *Phys. Rev. B*, 1998, **58**, 8236.
- 54 T. Kato and T. Yamabe, *Chem. Phys. Lett.*, 2005, **403**, 113.
- 55 V. Coropceanu, J. M. André, M. Malagoli and J. L. Brédas, *Theor. Chem. Account*, 2003, **110**, 59.
- 56 M. Malagoli, V. Coropceanu, D. A. da Silva Filho and J. L. Brédas, *J. Chem. Phys.*, 2004, **120**, 7490.
- 57 Y. Olivier, V. Lemaure, J. L. Brédas and J. Cornil, *J. Phys. Chem. A*, 2006, **110**, 6356.
- 58 D. A. da Silva Filho, E.-G. Kim and J. L. Brédas, *Adv. Mater.*, 2005, **17**, 1072.
- 59 J. C. Sancho-García and A. J. Pérez-Jiménez, *J. Chem. Phys.*, 2008, **129**, 024103.
- 60 L. Li, Q. Tang, H. Li, X. Yang, W. Hu, Y. Song, Z. Shuai, W. Xu, Y. Liu and D. Zhu, *Adv. Mater.*, 2007, **19**, 2613.
- 61 J. E. Norton and J. L. Brédas, *J. Chem. Phys.*, 2008, **128**, 034701.
- 62 M. Mas-Torrent, P. Hadley, S. T. Bromley, X. Ribas, J. Tarrés, M. Mas, E. Molins, J. Veciana and C. Rovira, *J. Am. Chem. Soc.*, 2004, **126**, 8546.
- 63 S. T. Bromley, F. Illas and M. Mas-Torrent, *Phys. Chem. Chem. Phys.*, 2008, **10**, 121.
- 64 V. Lemaure, D. A. da Silva Filho, V. Coropceanu, M. Lehmann, Y. Geerts, J. Piris, M. G. Debije, A. M. van de Craats, K. Senthikumar, L. D. A. Siebbeles, J. M. Warman, J. L. Brédas and J. Cornil, *J. Am. Chem. Soc.*, 2004, **126**, 3271.
- 65 J. R. Weinberg-Wolf, L. E. McNeil, S. Liu and C. Kloc, *J. Phys.: Condens. Matter*, 2007, **19**, 276204.
- 66 X. Chi, D. Li, H. Zhang, Y. Chen, V. García, C. García and T. Siegrist, *Org. Electron.*, 2008, **9**, 234.
- 67 D.-e. Jiang, B. G. Sumpter and S. Dai, *J. Chem. Phys.*, 2007, **127**, 124703.
- 68 D.-e. Jiang and S. Dai, *J. Phys. Chem.*, 2008, **112**, 332.
- 69 L. Zhechkov, T. Heine, S. Patchkovskii, G. Seifert and H. A. Duarte, *J. Chem. Theory Comput.*, 2005, **1**, 841.
- 70 B. Civalieri, D. S. Middlemiss, R. Orlando, C. C. Wilson and P. Ugliengo, *Chem. Phys. Lett.*, 2008, **451**, 287.
- 71 S. Grimme, J. Antony, T. Schwabe and C. Mück-Lichtenfeld, *Org. Biomol. Chem.*, 2007, **5**, 741.
- 72 O. I. Obolensky, V. V. Semenikhina, A. V. Solov'yov and W. Greiner, *Int. J. Quantum Chem.*, 2006, **107**, 1335.
- 73 B. Civalieri, C. M. Zicovich-Wilson, L. Valenzano and P. Ugliengo, *CrystEngComm*, 2008, **10**, 405.
- 74 J. Černý and P. Hobza, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5291.
- 75 S. M. Cybulski and M. L. Lytle, *J. Chem. Phys.*, 2007, **127**, 141102.
- 76 Q. Wu and W. Yang, *J. Chem. Phys.*, 2002, **116**, 515.
- 77 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787.
- 78 P. Jurečka, J. Černý, P. Hobza and D. R. Salahub, *J. Comput. Chem.*, 2007, **28**, 555.
- 79 I. D. Mackie and G. A. DiLabio, *J. Phys. Chem. C*, 2008, **112**, 10968.
- 80 T. Schwabe and S. Grimme, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3397.
- 81 S. Grimme, M. Steinmetz and M. Korth, *J. Org. Chem.*, 2007, **72**, 2118.
- 82 S. Grimme, *Angew. Chem., Int. Ed.*, 2006, **45**, 4460.
- 83 P. R. Schreiner, *Angew. Chem., Int. Ed.*, 2007, **46**, 4217.